Chem. Rev. **2003,** *103,* 4307−4365 **4307**

Lewis Acids: From Conventional Homogeneous to Green Homogeneous and Heterogeneous Catalysis

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Received March 28, 2003

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1. Introduction

1.1. Scope and Organization of the Review

Acid-catalyzed reactions are by far the most numerous and best-studied reaction type,[1−5] in which organic functional groups undergo an array of different transformations with nucleophilic reagents in the presence of acids as catalysts. The aim of this review is to show the logic of the evolution of Lewis

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10.1021/cr030680z CCC: $44.00

Avelino Corma Canos was born in Moncófar, Spain, in 1951. He studied chemistry at the Universidad de Valencia (1967–1973) and received his Ph.D. at the Universidad Complutense de Madrid in 1976. He has been director of the Instituto de Tecnología Química (UPV–CSIC) at the Universidad Politécnica de Valencia since 1990. His current research field is zeolites as catalysts, covering aspects of synthesis, characterization, and reactivity in acid–base and redox catalysis. Avelino Corma has coauthored a large number of scientific papers and patents, and six of his discoveries have been commercialized. He has been awarded the Dupont Award on New Materials (1995), the Spanish National Award "Leonardo Torres Quevedo" on Science and Technology (1995), Iberdrola Award in Chemistry, (1998) F. Ciapetta award of the North American Catalyst Society (1998), "Rey Jaime I" Award on New Technologies (2000), The European Award in Catalysis François Gault (2002), and the Eugene J. Houdry Award of the North American Catalysis Society (2003).

Hermenegildo (Herme) García was born in Canals, Spain, in June 1957 and studied chemistry at the Faculty of Science of the Universidad de Valencia (Spain), where he graduated in 1979 with Honors. He did his Ph.D. on preparative organic photochemistry under the guidance of Prof. Miguel A. Miranda and was awarded also with Honors by the Universidad de Valencia in 1983. He then moved to the Technical University of Valencia, where he initiated his career in 1983 first as Assistant Professor, becoming finally Full Professor in 1996. In 1991, he was appointed member of the Institute of Chemical Technology, a joint center depending on the Spanish National Research Council (CSIC) and the Technical University of Valencia, that was founded at this year. He did a postdoctoral stay at the Chemistry Department of the University of Reading (U.K.) with Prof. Andrew Gilbert in 1987, and later three successive sabbatical leaves in 1992–1993 (1 year), 1995 (6 months), and 2000 (3 months) at the University of Ottawa, joining the Laser Flash Photolysis group leaded by Prof. J. C. (Tito) Scaiano. He has coauthored over 200 papers, most of them dealing with the application of zeolites as hosts of organic guests and as solid catalysts. He holds three international patents. His main current interests are in supramolecular photochemistry and photocatalysis, development of photoactive nanoscopic materials, and heterogeneous catalysis.

acid catalysts from the homogeneous liquid phase to solid acids. This shift was initiated in the petrochemical industry long before the principles of green or sustainable chemistry were stated, but it is now evident that this replacement will continue with renewed impetus, reaching most of the processes for the production of fine chemicals.

It is out of the scope of this review to cover comprehensively all the organic reactions that have ever been reported in the presence of Lewis acids or the use of homogeneous Lewis acids in organic synthesis.[2] Instead, the focus of this review is to show the current state of the transition from environmentally nontolerable, homogeneous Lewis acids toward solid Lewis acids. We will also comment in detail on those current industrial processes requiring Lewis acid catalysis in the petrochemical industry for the production of fuels or bulk chemicals and the industry of base chemicals.

The review has been organized starting with the definition of Lewis acid and the softness—hardness concepts (section 2), followed by a section addressing the need to characterize Brönsted/Lewis and softness—hardness character of a catalyst, particularly solid acids. The next section gives an overview of the organic reaction types that have been traditionally conducted under homogeneous Lewis acids (section 3). No attempt has been made to be exhaustive in exemplifying all reaction types. Green Lewis acid reactions performed in the homogeneous liquid phase, in which the medium rather than the catalyst has been adapted to convert the reaction in a more environmentally tolerable process, is discussed (section 4). In these cases, the Lewis acid catalysts are generally the same as those used with organic solvents. The next logical step is toward supporting the Lewis acid catalyst on "inert" carriers of large surface area, to make the system heterogeneous and the catalyst recoverable and reusable. After the general characterization techniques applicable to solid acids are described (section 5), heterogeneous acid catalysts based on supporting conventional Lewis acids and their reactions are described in section 6. The general problems to be addressed for these supported catalysts are their instability and leaching of the active sites under operation conditions. Discussion about supported catalysts leads to the description of truly solid acids (section 7).

The last part of this review (section 8) is devoted to comments on the current technology in existing petrochemical processes and those for the production of bulk and base chemicals that employ Lewis acids as catalyst. There, the evolution from highly active and corrosive $AlCl_3$ to the present solid acids is emphasized. Finally, prospects for the evolution of acid-catalyzed industrial processes, motivated by changes in the nature of the feedstocks and the need to comply with the "green chemistry" principles, are discussed in section 9.

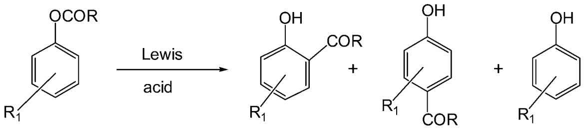
This review covers the chemical literature up to the year 2002. Although most of the examples have been selected from recent reports, seminal and important contributions to this area have also been conveniently credited. Given the importance of industrial applications in this review, patent literature has also been sufficiently covered.

1.2. Need for Green Lewis Acids

In a green process carried out in a batch reactor or a continuously stirred tank reactor (CSTR), the catalyst must be separated from the reaction mixture and recycled a certain number of times. This results not only in a more cost-effective processes derived from a higher productivity of the catalysts, measured as kilograms of products per kilogram of catalyst, but also, even more importantly, in a considerable waste reduction, measured as kilograms of wastes per kilogram of desired product. Thus, recycling of the catalyst helps to develop an environmentally sustainable chemistry.[6]

The need for green chemistry in Lewis acid-catalyzed reactions derives from the fact that the usual procedure in conventional Lewis acid-catalyzed reactions requires, after completion of the reaction and before isolation of the reaction mixture, an additional step to destroy the acid−base adduct between the catalyst and products. This step normally leads to the complete decomposition of the Lewis catalyst, making its reuse impossible and, moreover, producing undesired wastes, normally inorganic salts dissolved in wastewaters. Since reaction products are frequently stronger bases than reactants, many Lewis acid-catalyzed reactions require more than catalytic amounts of catalyst and very commonly stoichiometric proportions. An example of the above operational procedure is the Fries rearrangement of aryl esters to form hydroxyaryl ketones (Scheme 1).[7,8]

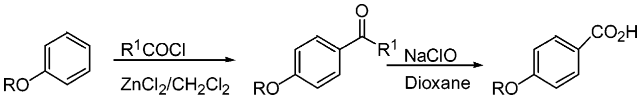
Scheme 1



Thus, even though the reactions are misleadingly termed as catalytic, it is common practice to employ greater than stoichiometric equivalents of Lewis acid. Therefore, it follows that the percentage of catalyst-derived byproducts and wastes is considerable in most of the processes, particularly in those of fine chemistry in which the lower production volumes had not made extensive catalytic research and development projects necessary in the past. It is then possible to say that Lewis acid-catalyzed reactions are among the less environmentally friendly industrial processes, there being a real and urgent necessity to develop heterogeneous solid Lewis acid catalysts for this reaction type.[9,10] The use of solid acids facilitates catalyst recovery, operation in continuous reactors, reactivation, and reuse. At the same time, processes based on solid catalysts do not require the use of special solvents, in addition to the common organic solvents, to manipulate reagents and products.

A paradigmatic example that can serve to illustrate the use of Lewis acids in an environmentally unfriendly way is the preparation of alkoxyphenyl ketones (Scheme 2). These compounds are useful synthetic intermediates for the preparation of agrochemicals and pharmaceuticals. They can be obtained by Friedel−Crafts acylation of phenyl ethers with acyl chlorides in the presence of Lewis acids such as $ZnCl_2$ in CH_2Cl_2 at room temperature.[11] These phenyl ketones can be in turn converted into aromatic carboxylic acids via lateral chain oxidation with NaClO in dioxane.[11] The combined whole process, i.e., acylation and oxidation, to obtain aryl carboxylic acids produces a considerable amount of inorganic byproducts and requires the use of halogenated organic solvents and stoichiometric amounts of oxidants and catalysts. Clearly this process is very unsatisfactory from the point of view of green chemistry, and new processes based on the use of solid acids and catalytic oxidations are needed to replace the sequence based on stoichiometric reagents.

Scheme 2



2. Lewis Acidity

2.1. The Concept

According to Lewis,[12] an acid is an electron pair acceptor. This definition is more general than that given by Brönsted, according to which an acid is a molecule that is able to give protons. Indeed, a proton is a particular case of an electron pair acceptor. However in aqueous solution, protons exist as H_3O^+ and related hydrated species, and taking into account the above definition, H_3O^+ and other Brönsted acids could not be considered as Lewis acids. This, however, was discussed by Lewis considering the kinetics of the acid neutralization process. Thus, he named acids and bases which react having zero activation energy as primary acids and bases, while those possessing measurable activation energy were termed secondary acids and bases. The second group is divided into molecules which need activation energy before their primary acidic or basic properties appear, and those other molecules for which the breaking of one of more bonds during neutralization is required. Taking all this into account, the definition of Lewis covers practically all acid−base processes, whereas the definition of Brönsted represents a particular type.

In 1963, Pearson[13] introduced the concept of hard and soft acid and bases (HSAB) in order to explain affinities between acids and bases that do not depend on electronegativity or other related macroscopic properties.[13,14] Pearson formulated one thermodynamic rule saying that hard acids prefer to associate with hard bases, and soft acids prefer to associate with soft bases, and a kinetic rule from which hard acids react readily with hard bases and soft acids react readily with soft bases. Hard acids are defined as small-sized, highly positively charged, and not easily polarizable electron acceptors, while in soft ones the acceptor atom is large, possesses a small positive charge, and has some valence electrons which can be easily removed.[13,15,16]

Although the HSAB theory is qualitative, there have been proposals to define a hardness−softness quantitative scale associated with physical properties. In this way, Fukui's function is related, by density functional theory,[17] to Fukui's frontier density[18] and can be interpreted as a local softness.[19] Two other approaches have been based on quantum mechanical principles using perturbation molecular orbital theory[20] and density functional theory.[17] This approach discusses the softness–hardness as defined from the charge and frontier orbital control. The larger the difference between the energy of the highest occupied molecular orbital (HOMO) of the donor atom and the lowest unoccupied molecular orbital (LUMO) of the acceptor atom, the larger the charge control is and hard–hard interactions are favored. On the other hand, when the above energy difference is small, soft–soft interactions become preferred and the interaction is frontier orbital controlled.

The softness character (determined by the relative frontier orbitals' energy) of potential isolated Lewis acids and bases has been calculated,[17,20] as well as the hardness–softness of acid sites in solids and, more specifically, zeolites.[21–23]

2.2. Test Reactions To Address the Brönsted/Lewis Nature and Softness–Hardness of the Catalysts

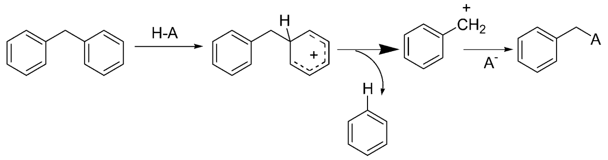
Comprehensive tables listing typical homogeneous hard and soft Lewis acids can be found in the literature.[14,24] Compared to the considerable amount of studies dealing with hardness–softness in homogeneous catalysis, it is surprising that the concept of HSAB has only been occasionally discussed for solid acids. Obviously, the problem arises from the existence in the solid of a distribution of sites which may contain simultaneously Brönsted and Lewis sites, making it considerably more difficult to address the hardness–softness issue in solids. This is the reason for the paucity of studies dealing with hardness–softness of solid acids.

Exclusive Brönsted-catalyzed reactions have probably not been demonstrated beyond any doubt. Therefore, it can be said that, in principle, each acid-catalyzed reaction can be conducted using a Lewis acid as catalyst, although with different activity and selectivity. The activity and selectivity also change depending on the nature of the Lewis acid. One point of special concern when addressing the Brönsted/Lewis nature of the acid sites is the fact that Brönsted acid sites can be generated from Lewis acid sites through hydrolysis in the presence of water (eq 1). Thus, to be meaningful, these tests should be conducted in the absence of moisture in the reaction medium, including solvent, catalyst, and feed.

$$\square\mathrm{LA} + \mathrm{H_2O} \rightarrow \underset{\text{(adduct)}}{\mathrm{H_2O^{+\delta}\text{- - -}LA^{-\delta}}} \rightarrow \underset{\text{(hydrolysis)}}{\mathrm{H^+ + LA(OH)^-}} \tag{1}$$

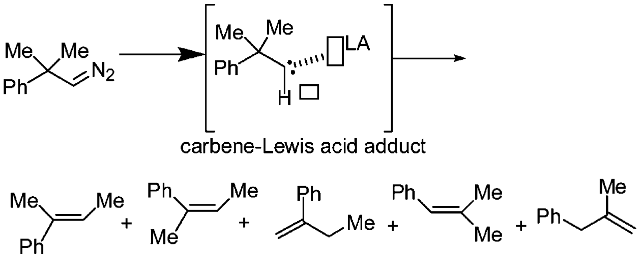
One simple approach to discuss the Brönsted/Lewis nature of a solid would involve, however, developing test reactions in which the product distribution would depend on the nature of the sites present in the solid. In this regard, the search for a specific Brönsted- or Lewis-catalyzed reaction in the liquid phase has long been pursued.[25] For instance, it is generally accepted that Friedel–Crafts reactions require Lewis acidity when using alkyl halides, but Brönsted acidity when the alkylating reagent is an alcohol.[26,27] Unfortunately, because of the strong acidity requirements of Friedel–Crafts reactions and the harsh reactions required, this process has not been so widely used as test a reaction as could be expected. With regard to Friedel–Crafts alkylations, it has been proposed that the protolytic C–C bond breaking of diphenylmethane to give toluene and benzene is a truly specific Brönsted reaction (Scheme 3).[25]

Scheme 3



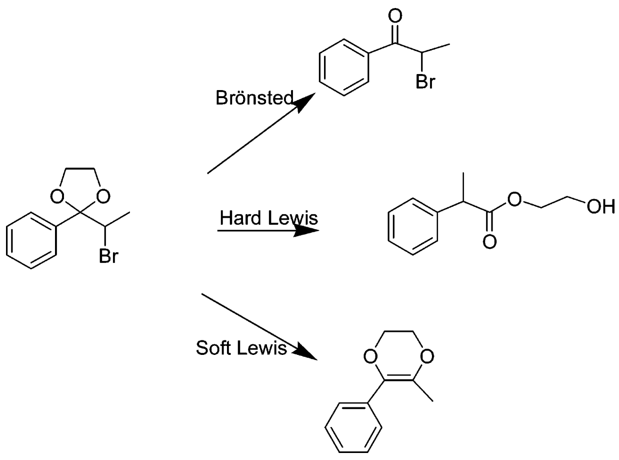
Another reaction that has been studied in the context of disclosing the acid nature, either Brönsted or Lewis, of homogeneous catalysts is the decomposition of 2-phenyl-2-methyl-1-diazopropane.[28] In the absence of any catalyst, this diazo compound has a half-life of 2 days at 69 °C in hexane, but Brönsted and Lewis acids catalyze the decomposition of the diazopropane.[28] Treatment of phenyl methyl diazopropane with 0.1 mol ‰ of BF_3 in hexane gave 95% olefins consisting of *trans*- and *cis*-2-phenyl-2-butene, 2-phenyl-1-butene, 1-phenyl-2-methylpropene, and 3-phenyl-2-methylpropene (Scheme 4). When BF_3 is used as catalyst, the decomposition occurs with a nearly indiscriminate migration of Ph and Me. This similar migration aptitude of Ph and Me rules out the intermediacy of a fully developed $Ph(CH_3)_2CH_2^+$ carbocation, for which a Ph/CH_3 migration aptitude of 6.7 was measured. The $Ph(CH_3)_2CH_2^+$ carbocation is the reaction intermediate for Brönsted acid-promoted decomposition. In the presence of BF_3 and other Lewis acids, a complex of these acids with the carbene, instead a fully developed carbocation, has been proposed as the actual rearranging species.[28] Thus, the product distribution can give an indication whether the catalyst behaves as pure Brönsted or pure Lewis, or exhibits an intermediate situation.

Scheme 4



Likewise, a liquid-phase reaction that has been proposed as a test is the 1,2-aryl rearrangement of cyclic acetals of α-bromo aryl ketones (Scheme 5). Brönsted acid sites in the presence of moisture lead to hydrolysis, giving rise to the corresponding α-

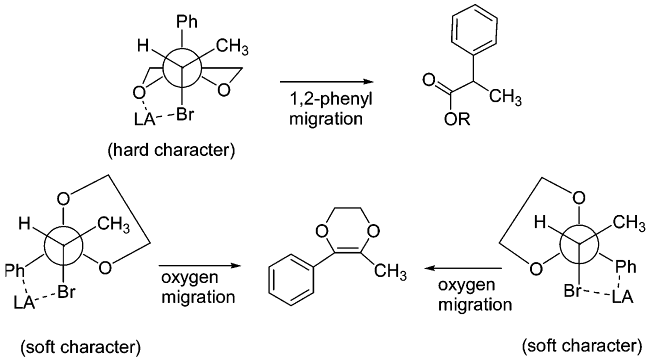
Scheme 5



bromo aryl ketone. On the other hand, Lewis acid sites promote dehalogenation, yielding either 2-hydroxyethyl α-arylpropanoate (hard Lewis sites) or 5-aryl-2,3-dehydro-1,4-dioxane (soft Lewis sites), arising from the 1,2-aryl or 1,2-oxy migration, respectively.[29]

On the basis of the reported XRD structure of related Lewis adducts of α-halo ketones, it has been proposed that the selectivity of the rearrangement derives from the preferred conformation of the cyclic acetals–Lewis acid adduct prior to the rearrangement. If the interaction with the Lewis acid occurs at the bromo atom and the π-system of the aryl ring (soft character), then the leaving group (Br) and the oxy group are antiperiplanar, and alkoxy migration occurs. On the other hand, if the Lewis acid sites interact with the bromo and the oxygen atom of the cyclic acetal (hard character), then the phenyl ring is the group that occupies the anti disposition with respect to the bromine, and 1,2-phenyl migration occurs (Scheme 6).

Scheme 6



In this way, it has been possible to order by softness–hardness a series of solid catalysts (Table 1), the outcome being that Zn^{2+}-exchanged zeolite NaY is softer (higher selectivity toward phenyl migration) than Zn^{2+}-exchanged zeolite HY and that Ag^{+}-exchanged zeolite is even softer. This order agrees with the order of electron density in framework oxygen atoms that is known to correlate with the basicity of the zeolites.[30−32]

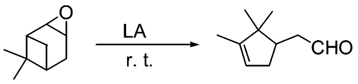
The rearrangement of α-pinene oxide to camphonelal (Scheme 7) has also been proposed as a test reaction for Lewis acids.[34]

Table 1. Results of the Reaction of the Cyclic Ethylene Acetal of α-Bromoacetophenone in Chlorobenzene at 130 °C for 20 h in the Presence of Solid Acid Catalysts[a]

		selectivity (%)		
catalyst	conversion (%)	ketone	α-phenyl-propionate	dehydro-dioxane
HY	100	91	0	0
ZnHY	98	66	8	2
ZnNaY	86	23	38	19
$ZnCl_2$	89	15	56	14
AgNaY	97	3	11	75
HgNaY	94	73	3	9
Hg_2Cl_2	6		71	28

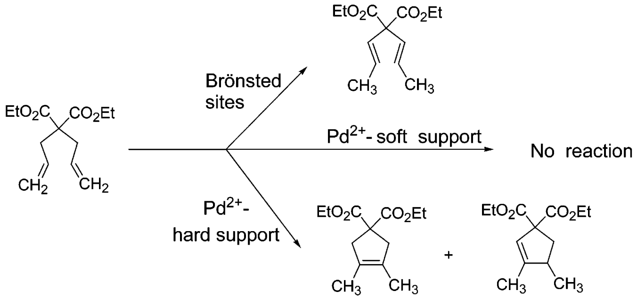
[a] Ketone, α-phenylpropionate, and dehydrodioxane correspond to acetal hydrolysis (Brönsted), 1,2-phenyl rearrangement (hard Lewis), and alkoxy rearrangement (soft Lewis), respectively, as indicated in Scheme 5. Data taken from ref 33.

Scheme 7



Palladium-catalyzed reactions are attracting much current interest due to the versatility in forming C–C and C–heteroatom bonds under conditions that are compatible with numerous functional groups.[35−46] In the homogeneous phase, the activity of the palladium complex largely depends on the nature of the ligands. The influence of the ligands has sometimes been rationalized as modifying the softness–hardness of the Pd atom; however, this concept has not yet been fully exploited in palladium-containing solids. A case in which the activity of the Pd^{2+} ion has been modulated by the softness–hardness of the support is the cyclization of diallylmalonates to form cyclopentenes (Scheme 8). In this case, the crucial step in the reaction mechanism is the electrophilic attack of electron-deficient palladium on the C=C bonds. It has been observed that adsorption of palladium salts on hard zeolites renders an active heterogeneous catalyst, while increasing the softness of the support produces a gradual loss of activity of the solids.[47]

Scheme 8



On the other hand, Brönsted acid sites give a different product distribution which arises from a C=C bond isomerization lacking cyclized products.

Clearly, given the paucity of reports in which attempts to characterize the hardness–softness of Lewis acid sites in solid acids have been made, it would be of much interest to know to what extent the softness–hardness nature of a Lewis site can be modulated by a support. In many cases, the Brönsted or Lewis nature of the sites is assumed without any measurement to provide evidence in support of the assumption. For instance, in many cases, Lewis acids develop Brönsted acid sites by interaction with the surface OH of the support.[34] If solid catalysts have to be developed to suit a particular transformation, it is obvious from liquid-phase reactivity that control of the support composition to modulate the distribution of Lewis acid sites would be necessary. In view of the importance of the softness–hardness concept, it can be anticipated that more effort is going to be devoted to the exhaustive characterization of the distribution of solid acids in the future. The use of soft–soft and hard–hard interactions, by means of a set of basic probes of different softness/hardness, to titrate the solid is also an alternative to test reactions that deserves deeper investigation.

3. Catalyzed Reactions Using Conventional Lewis Acids

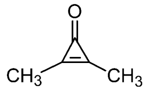
To put into context the recent efforts toward developing green Lewis acids, it is of interest to give an overview of some general reaction types that are commonly catalyzed by conventional Lewis acids. The Lewis acid–base interaction of some typical homogeneous Lewis acids and the structure of the adducts will be discussed separately before describing the reaction types.

In what follows, we will summarize briefly the features of some important Lewis acid-catalyzed reactions, emphasizing the diversity of the processes and the variety of functional groups that react in the presence of Lewis acids as well as those aspects relevant to the understanding of the developments in heterogeneous Lewis acid catalysts.

3.1. Conventional Homogeneous Lewis Acids and Structure of Lewis Acid–Base Adducts

The empty 2p orbital on the boron makes trivalent boron compounds act as Lewis acids. The acid strength of the boron atom is obviously a function of the nature of the groups covalently bonded to it. Electron-withdrawing groups are expected to enhance the Lewis acid strength and the hardness of the boron atom. Thus, BF_3 is a hard Lewis acid, while BH_3 is a soft one. In a challenge to this simple model, ab initio calculations of the optimized geometry of cyclopropenone and dimethylcyclopropenone adducts with borane and boron trifluoride have led researchers to propose that borane is a stronger Lewis acid than BF_3 and that dimethylcyclopropenone is stronger base than the parent cyclopropenone.[48]

cyclopropenone



dimethylcyclopropenone

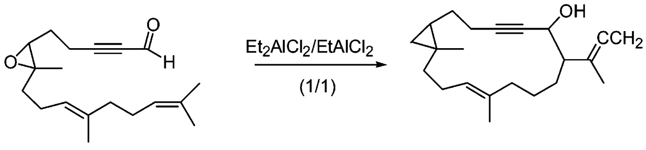
As in the previous example, an analogous violation of simple electronegativity rules is the reported stronger Lewis acidity of BCl_3 than BF_3 with respect to strong bases, in particular NH_3.[49] In contrast, BF_3 is a stronger acid than BCl_3 toward weaker bases such as CO.[50] This unexpected variation on the relative strength has been the subject of much discussion and debate. Among the numerous explanations that have been proposed, the most widely accepted is that stronger back electron donation from fluorine than from chlorine decreases the availability of the otherwise empty boron 2p orbital to accept an electron pair from a base.

Calculations of the optimized geometry for BF_3 and BCl_3 adducts with strong and weak bases provide, however, an alternative interpretation of the variation on the relative acid strength of boron Lewis acids as a function of the base strength.[50] For adducts with strong bases, the initial planarity of BX_3 is distorted and the B–X bond lengths increase. It takes more energy to lengthen the short, strong B–F bonds than the longer and weaker B–Cl bonds. For this reason, the adducts of BCl_3 would be more stable than those of BF_3, since the former boron species would more easily adopt the adduct geometry at a lower energy cost. In contrast, for the adducts with weak bases, BX_3 is barely distorted from planarity and, in these cases, BF_3 becomes a stronger acid than BCl_3.[50] Analogously, ab initio quantum chemical calculations and thermochemical studies in both gas and condensed phases have been used to show that SO_3 is a stronger Lewis acid than BF_3.[51] This higher acidity of SO_3 has been ascribed to the relative resonance energies of the Lewis acids and the Lewis adduct complex.[51]

Although they have not yet found practical application, boron heterofullerenes $C_{59}B$ and $C_{69}B$ and higher homologues have been shown to behave as strong Lewis acids.[52] In fact, these borofullerenes, prepared by arc evaporation of boron-doped graphite rods, are separated from the soot by using pyridine as solvent. XPS analysis reveals that, in these heterofullerenes, boron is in a higher oxidation state than in regular alkylboranes.[52] Since the preparation of heterofullerenes is an active area of research, a whole family of novel Lewis acids based on this concept is expected.[53]

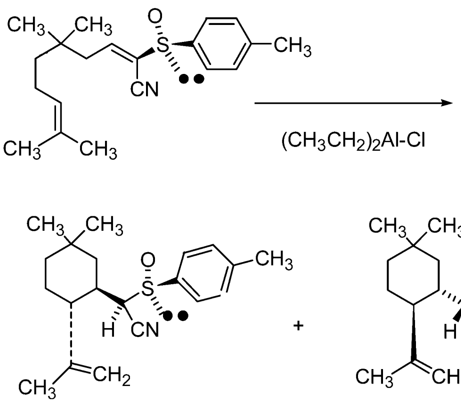
The use of alkylaluminum chlorides instead of aluminum trichloride is a way to control the softness/hardness of the metal site. Ethyl- and diethylaluminum chlorides have been used as catalyts for the ene cyclization of terminal methylpropenyl-substituted α,β-ynals (Scheme 9)[54] and for the intramolecular asymmetric ene reaction of chiral α-cyanovinylic sulfoxide (Scheme 10),[55] among other recent reactions.

Scheme 9



Tin is a metal of the fifth period having empty 5d orbitals. Compared to boron and aluminum Lewis acids, tin compounds, particularly organotin deriva-

Scheme 10

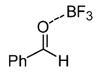


tives, are softer Lewis acids; therefore, different activity and selectivity may derive from this relative softness. Likewise, the acid strength of the tetrahedral titanium(IV) Lewis center obviously depends on the nature and electronegativity of the groups attached. Electron-withdrawing groups such as F or Cl increase the acid strength of titanium. In contrast, electron-donating groups such as alkoxy substituents reduce the acid strength of the titanium atom. Tuning of the acid strength on the titanium atom between tetrahalides and tetraalkoxy can be achieved in titanium mono-, di-, and trialkoxy halides. Besides electronic effects, the acidity of the Ti atom also depends on the steric hindrance to coordination.

The structure of many Lewis acids bound to carbonyl groups has been resolved by single-crystal X-ray diffraction and can be taken as archetypical of some other Lewis acid−base adducts. The structural variation can be, however, very large, and it can range from a linear up to an orthogonal C═O···Lewis acid conformation, the bulkiest substituent of the carbonyl group being generally the farthest possible from the Lewis acid. Besides the angle, the distance between the oxygen and the Lewis acid is also a parameter that may be used to characterize the strength of the interaction with the Lewis acid and the carbonyl group.

Two views of Lewis acid (LA)-carbonyl adducts and the two important angles defining the structure (O and Φ)

The structure of the benzaldehyde−BF_3 adduct has been determined by X-ray crystallography. BF_3 is complexed anti to the phenyl group.[56] The B−O−C−C fragment is essentially planar. The same study has shown that anti complexation also occurs in solution, as revealed by heteronuclear Overhauser effects.[56] MNDO calculations of the acetaldehyde−BF_3 adduct also predict anti complexation, the difference from the syn stereoisomer being 1.8 kcal mol^{-1}.[56] The calculations indicate a lowering of the LUMO energy and an increase in the positive charge at the carbonyl carbon atom upon complexation. These calculations and interpretations are relevant in the context of understanding the Lewis acid-mediated nucleophilic addition to aldehydes.



anti adduct

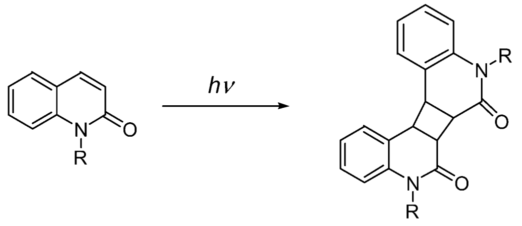
Measurements of the enthalpies of BF_3 addition to a series of 10 substituted cyclohexanones and cyclopentanones in CH_2Cl_2 solution indicate the exothermic formation of stable 1:1 adducts.[57] Addition of greater than stoichiometric amounts of BF_3 leads to a negligible additional caloric effect. While the 1:1 stoichiometry is overwhelmingly predominant, double or even triple coordination of Lewis acids to carbonyl groups has been observed, mainly for lanthanides, Li^+, and Hg(II) species, when very hard−hard ionic-like interactions prevail.[58,59] The quantitative data of the complexation reaction show that the acid−base enthalpy is particularly sensitive to the steric effects of substituents.[57] Gas-phase thermochemical measurements, supported by ab initio calculations, have revealed that simple aliphatic aldehydes and ketones, when complexed with BF_3, increase spectacularly the acidity of α-hydrogens and the electrophilicity of the C═O carbon.[60] In fact, this complexation transforms them into gas-phase superacids and superelectrophiles, with acidity enhancements of up to 50 kcal mol^{-1} and an increase in hydride affinity of up to 66 kcal mol^{-1}. In the condensed phase, changes of up to 24 pK_a units are estimated on the basis of the gas-phase measurements and the computed solvation energies.[60]

The relative acid strength of BF_3 can also be deduced from equilibrium constants. Thus, in contrast to what had been reported earlier, the reaction of BF_3 with $SnCl_3^-$ or $GeCl_3^-$ does not lead to the formation of the corresponding acid−base adduct. Instead, a Cl^- transfer occurs from a weak Lewis acid ($SnCl_2$ and $GeCl_2$) to a stronger Lewis acid, such as BF_3, according to the following equation:[61]

$$BF_3 + SnCl_3^- \rightleftharpoons BF_3Cl^- + SnCl_2$$

Coordination of Lewis acid with a photoactive basic molecule can be utilized to modify and control the photochemistry of this molecule by irradiating the Lewis acid−base adduct rather than the substrate. For instance, 2-quinolones form strong complexes with BF_3 through the amide oxygen. This complexation provokes a decrease in the energy of the oxygen nonbonding orbitals that leads to a change in the lowest singlet excited state from n,π* to π,π* upon complexation.[62] The shift in the nature of the excited state results in an increase in the singlet lifetime and in the spin multiplicity of the photochemical cycloaddition (Scheme 11) of 2-quinolones that varies from triplet (stepwise) in the absence of BF_3 to singlet (concerted) upon complexation.

Scheme 11

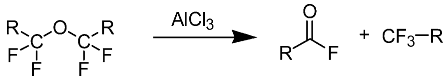


Analogously, quantitative photoisomerization of the *E* stereoisomer of cinnamides complexed with BF_3 to the *Z* isomer has been observed,[63] while irradiation of uncomplexed cinnamides gives rise to photostationary mixtures in which both *Z* and *E* isomers are present.[63]

3.2. Selected Reactions Catalyzed by Lewis Acids

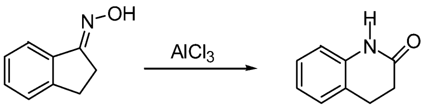
Lewis acids have been used as catalysts for an enormous variety of organic reactions, including electrophilic additions to C−C multiple bonds,[34,64−66] hydroborations,[67] and degradation of perfluorinated compounds (Scheme 12).[68]

Scheme 12



The Beckmann transposition of oximes to amides is typically carried out using Brönsted acids as catalysts, but it can also be effected with Lewis acids. In this way, the rearrangement of 1-indanone oxime has been performed using $AlCl_3$ (3 equiv) as catalyst in dichloromethane at −40 °C to yield 91% of the corresponding aromatic lactam (Scheme 13).[69] The use of other conventional acids such as polyphosphoric or sulfuric acid leads to much lower yields, around 20%.

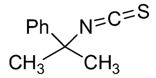
Scheme 13



3.2.1. Alkene Alkylation and Dimerization

Alkenes between ethylene and decene can be alkylated by alkanes ranging from butane to decanes from −18 to 38 °C in the presence of $AlCl_3$ or a strong Brönsted acid such as H_2SO_4, HSO_3F, or HF.[70] This is a reaction of huge economical importance for the production of high octane number gasolines, and the industrial processes will be commented on in the last part of this review (section 8.5). $AlCl_3$, in combination with Ni(0) phosphine, is an active catalyst for the dimerization of propylene at 0 °C.[71]

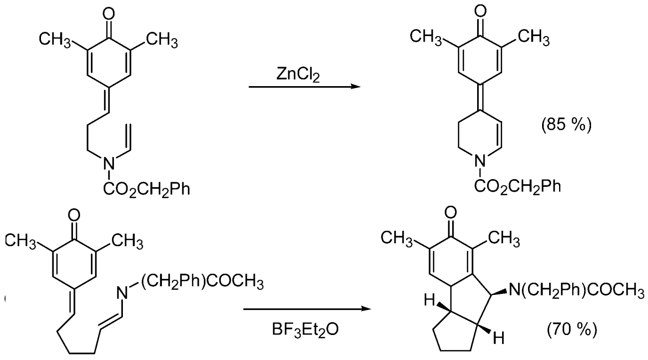
Alkenes can also dimerize and oligomerize in the presence of conventional Lewis acids or mixtures of organometallic compounds and Lewis acids. Isobutylene can be oligomerized using 2-isothiocyanato-2-phenylpropane as initiator in the presence of $SnCl_4$ or a mixture of $Al(CH_2CH_3)_2Cl/Al(CH_2CH_3)Cl_2$, the former having higher selectivity toward acyclic oligomers and lower polydispersity.[72]



2-isothiocyanato-2-phenylpropane

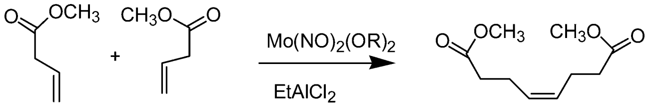
Cyclization of terminal enamides and encarbamates to form five- or six-membered rings using $ZnCl_2$ or BF_3 as Lewis catalyst has been reported (Scheme 14).[73]

Scheme 14



Alkene metathesis is a modern synthetic strategy to obtain selectively large macrocycles by cyclization of open precursors bearing many different reactive functionalities, the Grubbs reaction based on ruthenium imidazolidene complexes as catalysts being a powerful synthetic tool. Frequently, conventional Lewis acids are added to enhance the activity of organometallic compounds (Scheme 15).[74,75]

Scheme 15



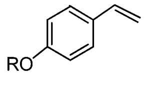
3.2.2. Alkene Polymerization

Lewis acids are widely used pure or in combination with organometallic compounds as catalysts for alkene polymerization.[76−78] Vinyl monomers such as acrylamide, methyl methacrylate, vinyl acetate, and styrene can graft into 1,2- and 1,4-polybutadiene in benzene at 60 °C through a radical mechanism initiated by azobis(isobutyronitrile).[79] The grafting efficiency increases upon addition of a small amount of $ZnCl_2$ or $AlCl_3$ up to an optimum value. Further addition can decrease the efficiency, and $ZnCl_2$ was found to be more active for this purpose.[79] This seems to be an interesting example of a Lewis-assisted radical reaction.

Lewis acids have been reported to produce the polymerization of electron-rich olefins through a cationic mechanism. Even living cationic polymerization, in which the polymer continuously grows upon addition of further quantities of monomer, can be initiated with $(1-100) \times 10^{-3}$ M concentrations of Lewis acids such as $SnCl_4$, BCl_3, $TiCl_4$, SbF_5, $ZnCl_2$, $FeCl_3$, etc.[80,81]

A good example of the influence of substitution on the titanium acid strength has been observed for the living cationic polymerization of styrene. Polymerization of styrene in CH_2Cl_2 has been achieved at temperatures between −40 and −78 °C by promoting the HCl−styrene adduct with $TiCl_3(O^iPr)$ as Lewis acid.[82] In contrast to the findings with $TiCl_3(O^iPr)$, a stronger Lewis acid such as $TiCl_4$ produced low-quality polystyrene, and weaker titanium(IV) Lewis acids such as $TiCl_2(O^iPr)_2$ did not induce the polymerization.[82] The cationic polymerization of β-pinene has been carried out with 1-phenylethyl chloride as initiator and a mixture of $TiCl_4$ and $Ti(O^iPr)_4$ as Lewis acids in CH_2Cl_2 at 40 °C.[83] Stronger $TiCl_4$ effected the polymerization instantaneously but gave polymers with a broad molecular weight distribution. The addition of $Ti(O^iPr)_4$, which alone does not have catalytic activity, retarded the polymerization and led to polymers with a narrower molecular weight distribution. An optimum $Ti(O^iPr)_4/TiCl_4$ ratio was 1:3.[83]

As commented earlier, the presence of water, even in trace quantities, is generally extremely detrimental in Lewis acid-catalyzed reactions, due to the hydrolysis of metal halide Lewis acid or to the strong coordination of water with the Lewis center. Thus, it is worth noting a process for the living cationic polymerization of *p*-hydroxystyrene using $BF_3{\cdot}Et_2O$ as Lewis acid catalyst that is performed in the presence of a large amount of water. The polymerization initiators are adducts of *p*-methoxystyrene and a series of protonic compounds.[84] In contrast to most living cationic polymerization, the presence of water produced polymers with an average molecular weight close to the calculated values by dividing the moles of monomer by the moles of initiator, indicating that ideally each initiator gives rise to a single polymer. With 4-methoxy-α-methylbenzyl alcohol as initiator, the average molecular weight of the polymers increased with monomer conversion with fairly narrow polydispersity. The living nature of the chains was confirmed by sequential monomer addition experiments. Apparently, the success of this controlled cationic polymerization of unprotected *p*-hydroxystyrene in large amounts of water is due to the stability of $BF_3{\cdot}Et_2O$ and to its tolerance to hydroxy groups of the monomer and water.[84] However, since living polymerization could also occur through the intermediacy of carbocations promoted by Brönsted acid sites, it would be of interest to demonstrate under the polymerization conditions that Lewis acids, and not adventitious Brönsted sites, are still the actual catalysts.



R=H p-hydroxystyrene
R=CH$_3$ p-methoxystyrene

A system containing a mixture of $Mo(NO)_2(RCO_2^-)$ and a Lewis acid has been reported to act as a catalyst for polymerization of monosubstituted acetylenes.[85] The catalytic ability strongly depends on the Lewis acid and the solvent. The mixture comprising $SnCl_4$ in benzene is almost completely selective in the polymerization of phenylacetylene, yielding 56% polymer at 60% monomer conversion.[85] The use of toluene for the same reaction or $TiCl_4$ as acid leads to the formation of cyclotrimers rather than polymers.

$$Ph{-}C{\equiv}C{-}H$$

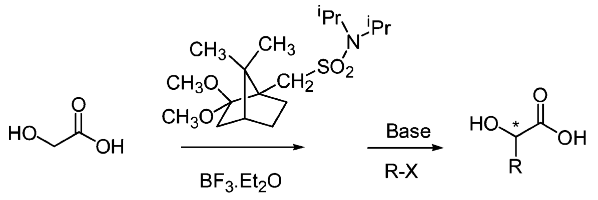
phenylacetylene

3.2.3. Formation and Hydrolysis of Acetals

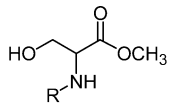
Acetalization of C=O by alcohols or glycols and hydrolysis of acetals reverting to the carbonylic compound is a typical reaction sequence that requires acid catalysis, acetals being stable products in basic media. The reversible acid-catalyzed formation and hydrolysis of acetals is the reason these derivatives are widely used in organic synthesis as carbonyl protecting groups.[27]

$BF_3{\cdot}Et_2O$ promotes acetalization of carbonylic compounds, formation of paraformaldehyde and copolymers with oxymethylene units, and transacetalization reactions.[86−89] Advantage of the reversible acetalization can be taken to induce asymmetry in the alcoholic moiety by using a chiral ketone as chiral auxiliary. Thus, for instance, the dimethyl acetal of (1*S*)-(+)-*N*,*N*-diisopropyl-10-camphorsulfonamide reacts, when $BF_3{\cdot}Et_2O$ is used as catalyst, with α-hydroxy acids to produce a chiral 1,3-dioxolate (Scheme 16). The enolates derived from these compounds undergo reactions with alkyl halides with a high level of diastereoselectivity. Subsequent hydrolysis gives mono- and disubstituted α-hydroxy acids with high enantiomeric excesses (Scheme 16).[90]

Scheme 16



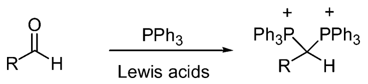
ZnCl$_2$ is also widely used as catalyst to form acetals and thioacetals from carbonylic compounds. Stereoselective glycosidic coupling of fully benzylated monosaccharides with *N*-benzoyloxycarbonyl and *N*-tosyl-L-serine methyl ester provides a new entry to 1,2-trans-linked glycopeptides.[91]



R: PhCH$_2$OCO-
R: CH3-C$_6$H$_4$-SO$_2$-
derivatized serine

By treatment of aldehydes and ketones with 1 equiv of triphenylphosphine and 1 equiv of $TiCl_4$ or some other Lewis acids, such as $NbCl_5$ and $TaCl_5$, the corresponding chlorides of the phosphonium acetals are formed as air- and moisture-sensitive solids (Scheme 17). NMR spectra of the reacting

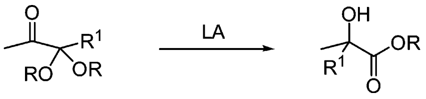
Scheme 17



solution indicate that these compounds exist in solution as a mixture of oligomers.[92]

α-Keto acetals rearrange in the presence of water and Lewis acid catalysts, in particular $SnCl_4$, to give high yields of α-hydroxy esters (Scheme 18).[93] This rearrangement fills the gap of a synthetic route in which, starting from a carboxylic ester, the corresponding α-hydroxy ester homologue with one more carbon is obtained. This sequence is particularly suited for aliphatic esters.[93]

Scheme 18



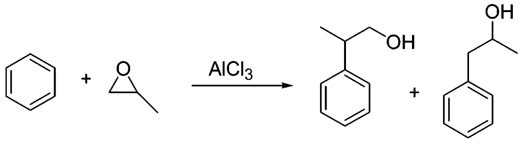
3.2.4. Friedel–Crafts Reactions

Friedel−Crafts is the reaction type for which $AlCl_3$ is most frequently used.[26,70,94−98] The conventional reaction mechanism, in which the role of the Lewis acid catalyst is limited to the generation of the electrophilic alkyl or acyl species without interaction with the aromatic compound, has been recently challenged. By means of high-level ab initio quantum chemical calculations on the $C_6H_6-BCl_3$ and $C_6H_6-AlCl_3$ adducts as model systems, it has been proposed that one benzene carbon becomes highly nucleophilic, thereby facilitating the attack of incipient, not-fully developed electrophiles.[99]

A factorial design and multivariate analysis to optimize the yield of Friedel−Crafts acylation of monosubstituted benzene with benzoyl chloride has revealed that the nature of the Lewis acid catalyst, the amount of Lewis acid, and the reaction temperature are the three major parameters controlling the reaction yield out of the five parameters investigated, which also included reaction time and aromatic compound-to-benzoyl chloride ratio.[100] $AlCl_3$ was the most active catalyst of the series studied, but the optimum yield could also be achieved with a very small amount of moderately active catalyst such as $ZnCl_2$ and $FeCl_3$ if the reaction is conducted at higher temperature.[100]

Besides alkyl halides,[27] chlorosilanes[101] and epoxides have also been employed as alkylating agents for the $AlCl_3$-catalyzed Friedel−Crafts alkylation.[102] Thus, propylene oxide (0.2 mol) reacts with benzene and alkyl derivatives (1.4 mol) using 0.2 equiv of $AlCl_3$ at 0 °C with or without addition of CS_2 as solvent.[102] Benzene gives 99% of 2-phenyl-1-propanol, and alkylbenzenes give also predominantly primary alcohols (Scheme 19). $SnCl_4$ was found to be more selective toward primary alcohols than $AlCl_3$.

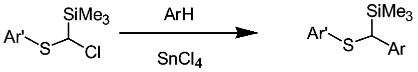
Scheme 19



Alkyl sulfonates in protic solvents form complexes with $TiCl_4$, $GaCl_3$, and $AlBr_3$. Alkyl halides may result from the process. These complexes of alkyl sulfonates and Lewis acids can react with benzene to give alkylbenzene.[103] The activity of the catalysts increases in the order of their acid strength.[103] Similarly, the $TiCl_4$−acetonitrile complex can promote the alkylation of aromatics by alkyl halides.[104]

Also, treatment of equimolar amounts of [arylthio(chloro)methyl]trimethylsilanes and electron-rich arenes with an equimolar amount of Lewis acid such as $SnCl_4$ or $TiCl_4$ gives the corresponding Friedel−Crafts alkylation product in high yields (Scheme 20).[105] Similar treatment of the chloro-substituted silane with 1-alkene gives ene-type products in moderate yields.[105]

Scheme 20

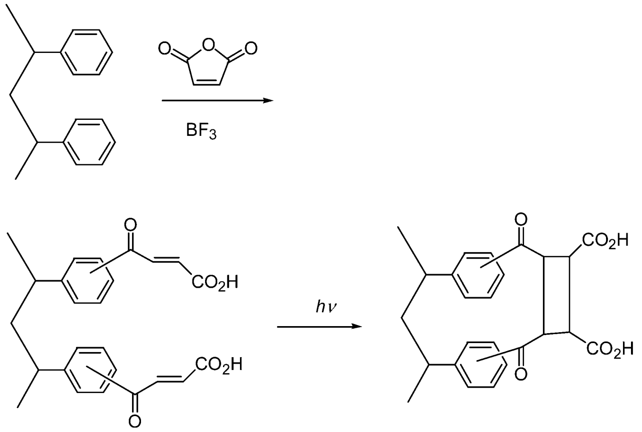


Friedel−Crafts reactions are generally irreversible. However, particularly when there are bulky *tert*-butyl groups, $AlCl_3$ can also be used to effect the dealkylation with loss of the lateral alkyl chain.[106,107]

It has been reported that hyperbranched aromatic polymers can be obtained by self-condensation of benzyl chloride and (chloromethyl)naphthalene in the presence of $AlCl_3$ or $ZnCl_2$.[108] Terephthaloyl dichloride can be copolymerized using $AlCl_3$ and LiCl mixtures through multiple Friedel−Crafts acylation processes with 1,4-diphenoxybenzene and diphenyl ether to form block polymers in which, by means of ^{13}C NMR spectroscopy, it has been demonstrated that diphenoxybenzene and diphenyl ether tend to segregate in different regions of the polymer.[109] Also, hyperbranched polyethylene and polyethylene-grafted polystyrene polymers have been synthesized at ambient temperature using as catalyst π-(methallyl)nickel bromide and an excess of $AlCl_3$.[110]

Polymers containing phenyl groups, such as polystyrene, can be functionalized through Lewis acid-catalyzed Friedel−Crafts acylation.[111] For instance, polystyrenes with different average molecular size can be derivatized by Friedel−Crafts acylation with maleic anhydride using Lewis acid catalysts in chloroform.[112] Modified polystyrenes having pendant $COCH{=}CHCO_2H$ groups can be easily cross-linked at 140−150 °C and by UV irradiation (Scheme 21).[112]

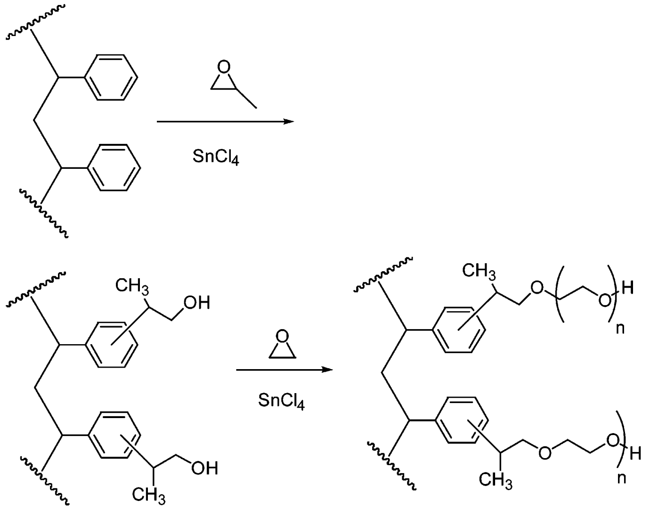
Scheme 21



This procedure serves to modify the solubility, swelling properties in organic solvents, and functionality of the initial polystyrenes.

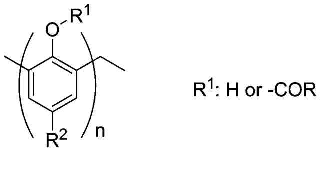
Friedel−Crafts alkylation of polystyrene resin with propylene oxide in the presence of $SnCl_4$ affords 1-methyl-2-hydroxyethyl polystyrene. Subsequent addition of ethylene oxide gives poly(ethylene glycol)-grafted polystyrene resins with high poly(ethylene glycol) content (60−80%) and excellent stability to highly acidic media (Scheme 22).[113]

Scheme 22



$ZnCl_2$ has also been frequently used as catalyst for Friedel−Crafts reactions.[114] Solutions of high-molecular-weight polystyrene (average MW 280 000) can be chloromethylated in a solution of dimethoxymethane using thionyl chloride and a Lewis acid such as $ZnCl_2$ or $SnCl_4$ in dichloromethane.[115] Chloromethylpolystyrenes are insoluble polymers of the Merrifield-type resins that are useful to effect organic syntheses in which the reagents are bound to the polymer beds. The choromethylation of polystyrene proceeds through the in situ generation of chloromethyl methyl ether, without the need to handle this highly toxic reagent.

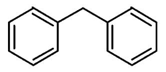
Fries rearrangement of aryl esters is a valid synthetic alternative to overcome the direct Friedel−Crafts acylation of phenols (Scheme 1).[7] Direct acylation of phenols is problematic and normally results in low acyl phenol yields due to the interaction of the phenolic hydroxyl group with the Lewis acid catalyst. Fries rearrangement of aryl esters also requires generally a stoichiometric amounts of a strong Lewis acid. As a recent example, the Fries rearrangement of various calix[*n*]arene esters (*n* = 4, 6, 8) in organic solvents (benzene, chlorobenzene, nitrobenzene, carbon disulfide) has been performed under the influence of various Lewis acid catalysts, including $AlCl_3$, $FeCl_3$, and $BF_3 \cdot Et_2O$.[116] The best conditions for the conversion of calix[*n*]arene esters to *p*-acyl calix[*n*]arenes are $AlCl_3$ as catalyst in CS_2 or benzene as solvent.[116]



calixarene

3.2.5. Other Electrophilic Aromatic Substitutions

Besides Friedel−Crafts reactions, $AlCl_3$ is also the preferred Lewis acid for other electrophilic aromatic substitutions. For instance, $AlCl_3$ has also been used as a chlorinating reagent in acidic conditions. A study has compared the liquid-phase chlorination of diphenylmethane to give 4,4′-dichlorodiphenylmethane at 60 °C and atmospheric pressure over a series of zeolites using sulfuryl chloride with the same reaction over $AlCl_3$.[117] A method for the preparation of brominated polystyrene consists of the reaction of BrCl in dichloroethane using $AlCl_3$ as catalyst.[118]

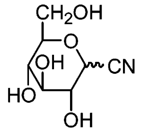


diphenylmethane

$AlCl_3$ can also be used to effect dehalogenation of aromatic compounds. Polychloroanilines and polychlorophenols undergo selective dechlorination at the 2- or 4-positions with respect to the amino or hydroxy group when the reaction is carried out in chlorobenzene containing HCl and $AlCl_3$ or another Lewis acid.[119] Very good yields (95%) of 3,5-dichloroanilines or phenols can be obtained.

Nitronium ion (NO_2^+) is an electrophilic species that intervenes as reaction intermediate in the nitration of aromatic compounds. A process for preparing isolable nitronium salts in high purity consists of treating an alkyl nitrate in nitromethane as solvent with a mixture of BF_3 and HF.[120] The reaction is carried out at temperatures between −20 and 15 °C, and $NO_2^+BF_4^-$ precipitates from the solution in higher than 90% purity.

Analogously to halogenations or nitrations, it is possible to introduce a cyano group using cyanotrimethylsilane as reagent and a Lewis acid such as $SnCl_4$ or $AlBr_3$ as catalyst.[121] In this way, hexapyranosyl cyanides can be prepared by reaction of glycals with trimethylsilyl cyanide in the presence of $SnCl_4$ or BF_3 as catalyst.[122]

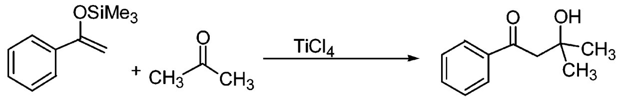


hexapyranosyl cyanide

3.2.6. Aldol and Related Reactions

A general method for the preparation of crossed aldols, known as the Mukaiyama aldol condensation, consists of the reaction of silyl enol ethers with aldehydes and ketones in the presence of Lewis acids. $TiCl_4$ is the preferred Lewis acid catalyst for the Mukaiyama reaction. For instance, the trimethylsilyl enol ether of acetophenone reacts with acetone in the presence of $TiCl_4$ to give 74% of 1-phenyl-3-methyl-3-hydroxy-1-butanone (Scheme 23).[123] There have been numerous reports describing the use of $TiCl_4$

Scheme 23

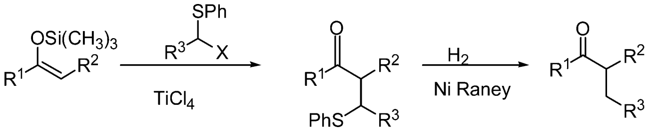


as Lewis acid catalyst for other reactions also involving organosilicon reagents.[123−127]

Silyl enol ethers are also convenient enolate derivatives to effect α-alkylation with higher yields and selectivity than the corresponding alkali metal enolates. *tert*-Butylation of ketones can be performed by treating their silyl enol ethers with a *tert*-butyl halide in the presence of $TiCl_4$.[128] Adamantyl halides are also suitable reagents to effect the α-alkylation of silyl enol ethers.[128] Unsymmetrical ketones react regiospecifically.[128]

Phenylthioalkylation of silyl enol ethers, followed by reductive sulfur removal with Raney nickel, has been reported as an indirect way to reliably effect α-alkylation to carbonyl compounds (Scheme 24).[129]

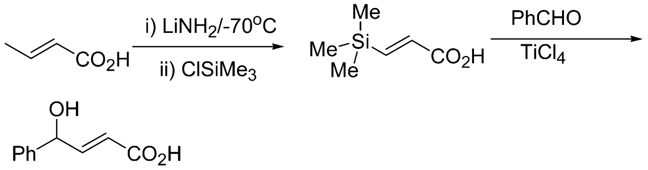
Scheme 24



Alternatively, sulfur can be removed via the sulfoxide. This procedure allows the regio- and stereocontrolled α-alkylidenation of carbonyl compounds. This reaction is applicable to aldehydes, ketones, esters, and lactones.[129]

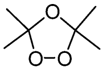
Metalation using lithium amide as base at −70 °C has been reported as a convenient procedure to introduce the trimethylsilyl group in the allylic position of crotonic or vinylacetic acids (Scheme 25).[130] The resulting trimethylsilyl compounds can react with benzaldehyde in the presence of $TiCl_4$ or even in the absence of any catalyst at higher temperature.[130]

Scheme 25



3.2.7. Heterocyclic Ring Aperture

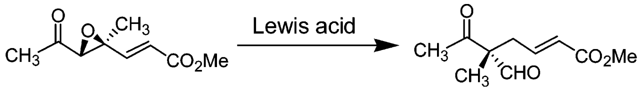
Small cyclic ethers, epoxides, oxetanes, and ozonides having an alkoxy group on the side chain rearrange in the presence of $BF_3{\cdot}Et_2O$ or $TiCl_4$ to give the ring-expanded cyclic ethers or addition products.[66,131−134] Analogously, *cis*- and *trans*-2,3-dimethyldioxirane react in the presence of $BF_3{\cdot}Et_2O$ or $SnCl_4$ in a stereoespecific manner with thiocarbonyl compounds to afford 4,5-dimethyl-1,3-oxathiolanes.[135]



ozonide

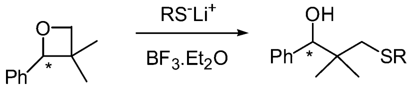
Functionalized chroman diols of potential biological activity can be obtained via Lewis acid rearrangement of aryloxyepoxy alcohols.[136] Stereoselective Lewis acid-catalyzed acyl migration of a chiral α,β-epoxy methyl ketone with an alkenyl substituent has been used for the construction of a chiral quaternary carbon center (Scheme 26).[137]

Scheme 26



Optically pure 2-aryl-3,3-dimethyloxetanes undergo ring opening with lithium thiolates, assisted by $BF_3{\cdot}Et_2O$, to give the corresponding β-substituted benzyl alcohol, in which substitution occurs at the less hindered carbon and the configuration of the asymmetric center remains unaffected (Scheme 27).[138]

Scheme 27



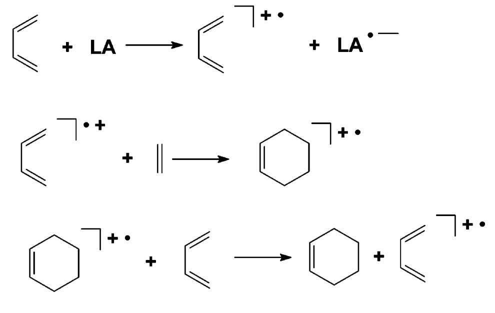
In contrast, hydrolysis or alcoholysis catalyzed by sulfuric acid occurs at the benzylic position with partial inversion of the configuration.[138]

3.2.8. Electrocyclic Reactions

Diels−Alder cycloadditions are the most powerful C−C bond-forming reaction to obtain complex six-membered rings. Uncatalyzed Diels−Alder cycloadditions are generally limited to electron-rich or cyclic dienes reacting with electron-deficient dienophiles or the opposite case (inverted electronic demand).[27] However, most commonly Diels−Alder reactions require Lewis acid catalysis when the reagents do not meet the electron density mismatch.

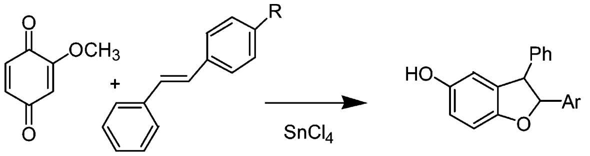
Concerning the mechanism in which Lewis acids can catalyze the Diels−Alder [4 + 2] cycloadditions, it has been frequently established that dienes, being electron-rich, undergo an electron abstraction by the Lewis acid (see reaction type below) to form the corresponding diene radical cation. This electrophilic species would be the actual reaction intermediate through a chain mechanism (Scheme 28). In support of this mechanism, many Diels−Alder reactions can also be promoted photochemically or by radical cations.[139−152]

Scheme 28



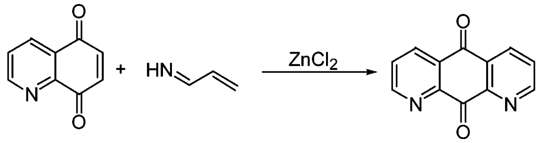
Numerous reports have also shown the activity and regio- and stereoselectivity of Lewis acids as catalysts for Diels–Alder cycloadditions.[153–158] $SnCl_4$ and $TiCl_4$ have been found to catalyze stereoselectively the reaction of unsymmetrically substituted stilbenes with 2-methoxy-1,4-benzoquinones to form *trans*-2,3-diaryl-2,3-dihydrobenzofuran-5-ols in good yield (Scheme 29).[159]

Scheme 29



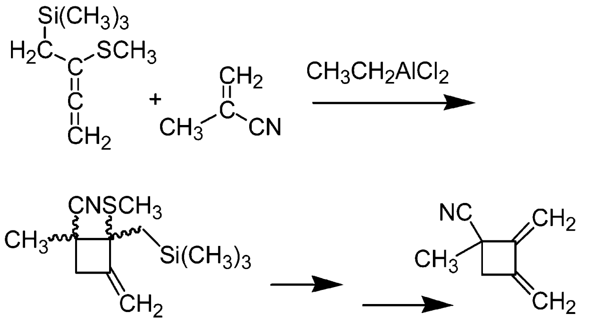
Lewis acids can also catalyze hetero-Diels–Alder reactions. For instance, 1-aza-1,3-butadiene reacts with quinoline-5,8-dione as an electron-deficient dienophile to form the corresponding 1,8-diazaanthraquinonone with complete regioselectivity (Scheme 30).[160]

Scheme 30



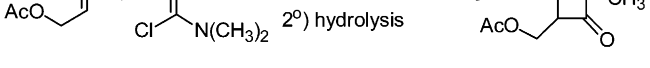
Examples of [2 + 2] cycloadditons catalyzed by Lewis acids have also been reported.[161] For instance, biacetyl reacts with isocyanates in the presence of $TiCl_4$ to form oxazolidinones.[157] Likewise, methylthio-substituted allenylmethylsilane undergoes [2 + 2] cycloaddition with alkenes, promoted by ethylaluminum dichloride, to afford the corresponding methylenecyclobutanes, which were readily converted into di-*exo*-methylenecyclobutanes by sequential oxidation of the methylthio to sulfone and 1,2-elimination (Scheme 31).[161]

Scheme 31



2,2-Dimethylcyclobutanones, useful as intermediates for the synthesis of 2,2-dimethylcyclopropanecarboxylic acids, can be prepared by [2 + 2] cycloaddition catalyzed by $ZnCl_2$ (Scheme 32).[162] Selective cyclotrimerization of phenylacetylene in chlorobenzene has been reported.[85]

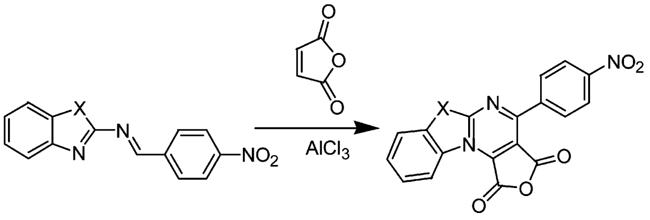
Scheme 32



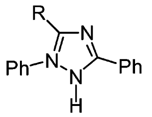
Cross-linked polystyrene resins containing pendant benzyl acrylate or chiral acrylates derived from (*R*)-1,3-butanediol react with 1,3-butadiene or 2,3-dimethyl-1,3-butadiene in the presence of $TiCl_4$, $TiCl_3(OiPr)$, or $TiCl_2(OiPr)_2$ to yield Diels–Alder adducts.[163] Ester hydrolysis gives racemic or optically active 3-cyclohexen-1-ylmethanol and 3,4-dimethyl-3-cyclohexen-1-ylmethanol. Compared to the same reactions carried out in solution, the enantiomeric excesses of polymer-bound Diels–Alder reactions were at least as high as those performed in solution.[163]

Likewise, 2-(*p*-nitrobenzylideneamino)benzoxazole, -benzothiazole, and -benimidazole having a –N=C=N=C– (heterodiene) react with electron-deficient dienophiles such as maleic anhydride in a normal Diels–Alder cycloaddition to give pyrimidines (Scheme 33).[164] These heterodienes can react equally well with electron-rich dienophiles such as styrene through an inverted electron-demand Diels–Alder reaction.[164] Both the *normal* and *inverted* polarity demand Diels–Alder reactions are accelerated by the presence of $AlCl_3$.

Scheme 33



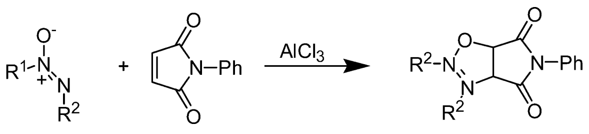
1,3-Dipolar cycloadditions can also be catalyzed by $AlCl_3$ and other Lewis acids. For instance, PhNHN=CClPh hydrazone reacts with R–C≡N in the presence of $AlCl_3$ to afford 1*H*-1,2,4-triazoles.[165]



Substituted 1,2,4-triazol

Azomethine *N*-oxides also react with *N*-phenylmaleimide in benzene at room temperature in the presence of $AlCl_3$ (Scheme 34).[166]

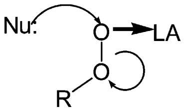
Scheme 34



3.2.9. Lewis Acid-Catalyzed Oxidations

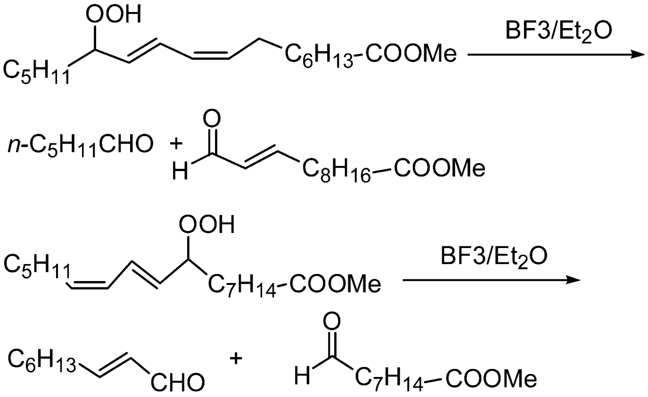
Lewis acids can catalyze oxidation reactions through three major reaction mechanisms. Recently we have reviewed Lewis acid-catalyzed oxidation reactions, particularly those using solid acids, the different reaction mechanisms, and their relevance in green chemistry.[167] The reader should go to that review for an in-depth coverage of this subject. One simple way in which Lewis acids can act as oxidation catalysts is by coordinating with a peroxy compound and enhancing dramatically the electrophilicity of these oxidizing reagents toward their reaction with weakly nucleophilic substrates, such as alkenes (Scheme 35).

Scheme 35



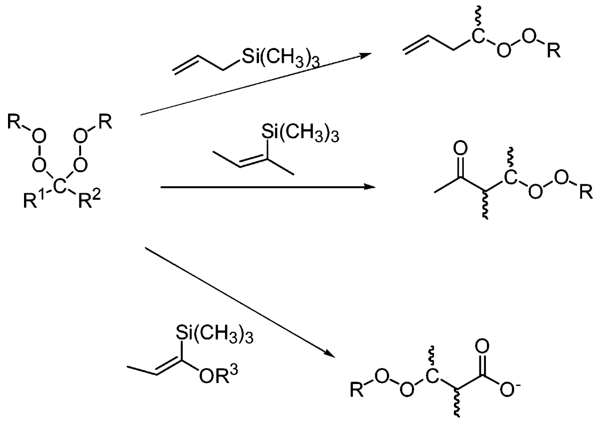
As a competitive reaction, the peroxy reagent can decompose due to the strong interaction with Lewis acids. Thus, $BF_3 \cdot Et_2O$ promotes the decomposition of isomeric methyl linoleate hydroperoxides into shorter chain aldehydes.[168] However, hexanal and 2-nonenal, which are the corresponding aldehydes derived respectively from 9,11- and 10,12-octadecadienoate, do not coincide with the complex volatile profile usually obtained by β-scission of oxyl radicals derived from homolysis of the hydroperoxide group (Scheme 36). Rather this product distribution resembles that of the reaction catalyzed by the plant enzyme hydroperoxide lyase.[168] This distinctive product distribution has been taken as evidence that the Lewis acid- or enzyme-catalyzed decomposition does not occur through the intermediacy of oxyl radicals.[168]

Scheme 36



The Lewis acid-mediated reaction of alkene nucleophiles with peroxyacetals and peroxyketals provides an effective route for the synthesis of homologated peroxides and hydroperoxides through the corresponding peroxycarbenium intermediate.[169] In the presence of $TiCl_4$ or $SnCl_4$, peroxyacetals and peroxyketals react with allyltrimethylsilane, silyl enol ethers, and silyl ketene acetals to afford homoallyl peroxides, 3-peroxyketones, and 3-peroxyalkanoates, respectively (Scheme 37).[169]

Scheme 37



Baeyer–Villiger oxidation of optically active 1-alkoxyalkyl ketones gives chiral 1-alkoxyalkyl carboxylates with high optical purity. These alkoxyalkyl carboxylates undergo alkylation with lithium dialkylcuprates, assisted by BF_3, to give stereospecifically alkylated products with a high degree of inversion of configuration.[170]

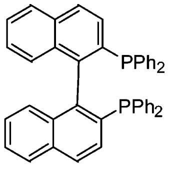
3.2.10. Lewis Acids as Single-Electron Acceptors

Lewis acids can accept a single electron from an electron-rich organic molecule of low oxidation potential to generate the corresponding radical cation.[171] When these radical cations are sufficiently long-lived on the medium, they can be characterized by conventional spectroscopy.[172–174] The fate of the electron gained by the Lewis acid is usually unknown, and it is believed to be delocalized through the Lewis acid.

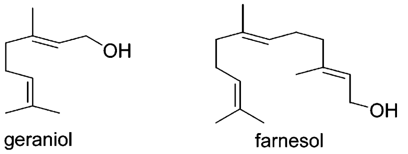
Polyaniline and other conjugated polymers exhibit a much enhanced conductivity upon positive or negative doping. A convenient procedure to produce positive doping is to use a Lewis acid as single-electron acceptor. The Lewis acid can exhibit dual behavior as an acid and as an oxidizing reagent. In the first instance, a Lewis acid is able to catalyze the formation of the conjugated polymer that grows until a certain threshold in oxidation potential of the growing conducting polymer is achieved. At this point the polymer can undergo single-electron abstraction from the polymer as donor to the Lewis acid as acceptor to form polarons. The nature of the Lewis acid may play an important role in the polymerization process and consequent doping. Thus, it has been reported that BF_3-doped polyaniline can exhibit a conductivity at room temperature of 20 S cm^{-1} that is over 10 000 times enhanced over that of the $SnCl_4$-doped polyaniline and even higher than that of protonated polyaniline.[175]

3.2.11. Enantioselective Lewis Acid-Catalyzed Reaction

Compared to analogous enantioselective hydrogenations and oxidations, catalytic enantioselective Lewis acid reactions are much less general. An obvious possibility to develop such enantioselective reactions is to develop chiral Lewis acids. $AlCl_3$ has been modified in a controlled way with chiral alcohols to form alkoxyaluminum chloro reagents that can be used to promote asymmetric reactions.[176] The monoalkoxyaluminum dichloride of menthol was particularly suited for this process.[176] $ZnCl_2$ can be used to prepare a chiral ruthenium phosphine complex derived from a 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ligand containing Zn metal.[177]



Also the combination of $SnCl_4$ with chiral 2,2′-dihydroxy-1,1′-binaphthyl has been found to effect the enantioselective cyclization of geraniol and farnesol.[178]



4. Green Lewis Acid Catalysis in the Liquid Phase

One strategy to transform a Lewis acid-catalyzed reaction into a green process consists of having a two-phase liquid system in which the Lewis acid remains dissolved in one of the solvents, while the products can be extracted by another immiscible liquid. The simplest approach of these liquid-phase methodologies uses the same Lewis acid as in the homogeneous phase. This is the case of reactions in supercritical fluids, and they will be discussed in first place. A further evolution of the biphasic liquid−liquid methodologies requires not only modifications in the medium and engineering of the process, but also synthetic efforts to alter the structure of conventional Lewis acid catalysts to adapt them to a particular solvent, at the same time making the modified Lewis acid insoluble in other solvents. Among the representative examples of the latter methodology, we will summarize the use of the so-called biphasic fluorous systems and the use of ionic liquids. These three methodologies to conduct Lewis acid-catalyzed reactions in the liquid phase have experienced growth at a breathtaking speed and have become separate disciplines in green chemistry by their own right. They offer new opportunities to replace conventional organic solvents in synthesis and industrial processses.[179−184]

Finally in this section we will include the recent efforts to conduct green Lewis acid catalysis in mixtures of organic solvent/water or even in pure aqueous media. In these cases, besides the solubility of organic reagents and products, the crucial issue is the stability of the Lewis acid catalyst in water.

4.1. Lewis Acid-Catalyzed Reactions in Supercritical Fluids

A *Chemical Reviews* thematic issue has been devoted exclusively to the properties and application of supercritical fluids, including their use as reaction media.[185] The reader is referred to that issue for fundamentals of supercritical fluids as well as an overview of the homogeneous[186] and heterogeneous[187] catalyzed reactions in supercritical fluids. Herein we will focus on their use as solvents for Lewis acid-catalyzed reactions. As implied in the term “supercritical fluid”, this state corresponds to a fluid at conditions above its critical point in temperature.[188] The temperature and pressures of the critical point for some common compounds are given in Table 2.

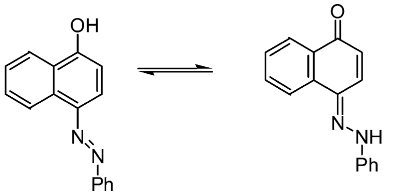
Table 2. Temperature and Pressure of the Critical Point for Some Compounds Commonly Used as Supercritical Fluids

compound	critical temperature (°C)	critical pressure (bar)
carbon dioxide	31	73.8
ethane	32.3	48.8
water	374.0	220.6

4.1.1. Supercritical CO_2

Supercritical carbon dioxide is an environmentally friendly solvent that has attracted much attention as an alternative to the use of less tolerable organic solvents.[188,189] For catalytic reactions in supercritical CO_2, the temperature and pressure play an important role by varying the viscosity, solubility, polarity, and other parameters that influence the ability of CO_2 to act as a solvent.[188] For instance, the azo-hydrazone tautomeric equilibrium of 4-(phenylazo)-1-naphthol has been studied to determine changes in polarity and hydrogen-bonding ability in supercritical fluids (Scheme 38).[190] While the less polar azo tautomer is predominant in compressed and liquid alkanes, in supercritical or liquid CO_2 the equilibrium shifts toward the more polar hydrazone, yielding similar amounts of the two tautomers. This shift was interpreted as due to the Lewis acidity and large quadrupole moment of CO_2.[190] Increases in the equilibrium constant as a function of the supercritical CO_2 pressure have been considered as indicating polarity increases.

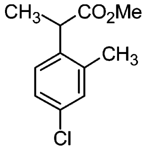
Scheme 38



Supercritical CO_2 is used widely in selective extractions and separations. The industrial production of decaffeinated coffee and the extraction of hops aroma are by far the most important.[188] A more recent example is the extraction of polycyclic aromatic hydrocarbons from polluted soils, heavily contaminated with brown coal tar, using supercritical carbon dioxide and solvent modifiers such as *n*-hexane, cyclohexane, toluene, methyl *tert*-butyl ether, etc.[191] Interestingly, the efficiency of the extraction of polycyclic aromatics from soils having a high content of humic acid increases considerably upon addition to the supercritical CO_2 Lewis acids.[192]

Supercritical fluids can also be used as mobile phases in supercritical fluid chromatography.[193,194] Chiral Ni(II) or Zn(II) complexes of 3-heptafluorobutanoyl-10-methylene-(1*R*)-camphorate anchored on dimethylsiloxane (Chirasil-nickel and Chirasil-zinc) have been reported that can act as enantioselective Lewis acids to effect the separation of enantiomers,[195] particularly for large-scale separations of configurationally labile, nonvolatile racemates such as that of methyl 2-(4-chloro-2-methylphenoxy)propanoate (mecoprop). Analogous complexes of 3-heptafluorobutanoyl-

10-methylene-(1*R*)-camphorate with lanthanides have been used as stationary phases in complexing gas chromatography.[196]



mecoprop

Catalytic reactions reported in supercritical carbon dioxide include Lewis acid-catalyzed aromatic alkylation and acylation, selective catalytic oxidation of olefins using transition metal catalysts, and phase-transfer oxidation catalysis.[189] Conventional $AlCl_3$ and other metal halides can be used as Lewis acids exactly as they are used in common organic solvents.

Hydrocracking of high-molecular-weight hydrocarbons into lower molecular weight compounds has also been performed in supercritical fluid using as homogeneous catalyst a system comprising a metal halide Lewis acid and a Brönsted acid.[197] The supercritical fluids consist of a C_2-C_{14} alkane dissolved in a fluid hydrocarbon. The process is especially useful when the hydrocarbon feedstock is deasphalted oil or mixed paraffins.

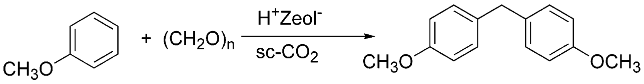
C_2-C_{12} paraffins isomerize with AlX_3 in CO_2 or HX as solvent above the critical temperature of the mixture of hydrocarbon and solvent and a pressure of 1000−5000 psig.[198] For instance, at 38% hexane conversion in the presence of $AlBr_3$, the isomerization−cracking ratio in supercritical CO_2 was 4, while in the liquid phase the ratio was 1.[198]

Besides aluminum halides, other solid acids have also been used as catalysts in supercritical fluids. Alkylation of isobutane and isopentane using a La^{3+}-exchanged zeolite Y as heterogeneous catalyst has been carried out under supercritical conditions of these hydrocarbons.[199] Compared to reactions in the gas or liquid phase, olefin alkylation in the supercritical phase enhances the activity of the zeolite Y catalyst and increases its lifetime. High-molecular-weight olefins are also formed under supercritical conditions through oligomerization by Lewis acids. However, while these byproducts strongly deactivate the catalyst in the liquid- or gas-phase reaction, the supercritical fluid is able to extract these high-molecular-weight olefins, removing them from the solid and extending the catalyst life.[199]

In an attempt to reduce coke formation, isobutane alkylation over sulfated zirconia and promoted sulfated zirconia was conducted under supercritical conditions.[200] It was observed that catalyst deactivation was considerably reduced at reaction conditions slightly above the critical point, particularly when Fe- or Mn-promoted sulfated zirconia was used as catalyst.[200]

Friedel−Crafts alkylations and acylations can be carried out using heterogeneous catalyst in a continuous-flow reactor containing a supercritical fluid.[201] The selectivity of the reaction can be varied by controlling the temperature, pressure, flow rates, catalyst, and the ratio between the aromatic compound and reagent. The first three parameters influence the density and properties of the fluid. Thus, anisole was added at 0.2 mL min^{-1} to propene at a flow rate of 420 mL min^{-1}, and the mixture was heated at 200 °C at 165 bar and circulated through an acidic sulfonic resin to yield 38% of cumene. Likewise, hydroxyalkylation of anisole with paraformaldehyde can be carried out in supercritical CO_2 using acidic large- and medium-pore zeolites as catalysts.[202] Compared to conventional hydrocarbon solvents, such as cyclohexane, not only is supercritical CO_2 a greeener solvent, but also the product yield in monodirectional zeolites is significantly higher, due to the more favorable diffusion of reagents, intermediates, and products in CO_2.[202] Hydroxyalkylation of aromatics with carbonylic compounds (Scheme 39) is a reaction of economical importance for the synthesis of bis(aminophenyl)methane and bisphenol A, which are commodities for the preparation of polyurethanes, polycarbonates, and epoxy resins.[203]

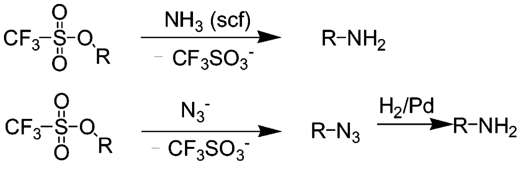
Scheme 39



Polysaccharides can be esterified or etherified in supercritical CO_2.[204] The process achieves a high degree of OH derivatization without the need for repeated reactions or the use of organic solvents. Unreacted reagents and byproducts are easily separated since the polysaccharide is insoluble in the supercritical fluid. Aliphatic polyketones are produced in the reaction of CO and C_2-C_{20} olefins in the presence of palladium complex as polymerization catalyst in a supercritical solution or suspension of CO_2.[205]

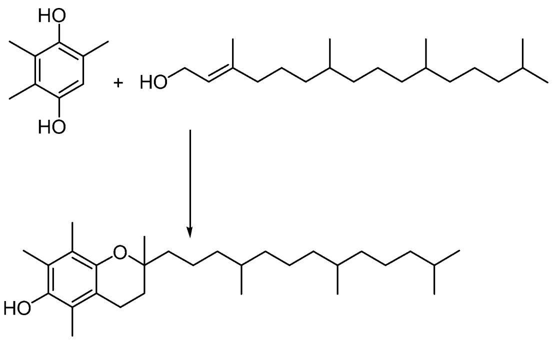
Supercritical fluids are being used increasingly in the synthesis of pharmaceutical compounds and intermediates.[206] Supercritical ammonia has been used in the ammonolysis of esters to amides and of mesylates to amines. In the latter case, amines are formed in high yield (>95%) in anhydrous supercritical ammonia, this representing an interesting alternative to the conventional azide substitution/hydrogenation synthetic sequence normally followed to introduce the amino functionality (Scheme 40). The synthesis of d,l-α-tocopherol in supercritical CO_2 or N_2O can also be accomplished by condensation of trimethylhydroquinone with isophytol in the presence of Brönsted or Lewis acids.[206] This represents a greener alternative to existing process employing $AlCl_3$ (Scheme 41).

Scheme 40



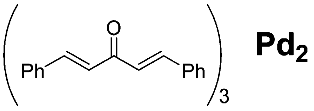
scf: supercritical state

Scheme 41



α-tocopherol

A new palladium-catalyzed addition of phenols to alkynoates to form coumarins has been reported.[207] In contrast to the acid-catalyzed aromatic alkylation that generally requires stoichiometric, if not excess, amounts of typical Lewis acids, the palladium process is truly catalytic from the catalyst point of view. The reaction is carried out in formic acid as solvent and uses palladium acetate or, better, tris(benzylideneacetone)dipalladium as catalyst, being applicable to propynoate, butynoate, and phenylpropynoate ethyl esters.[207]

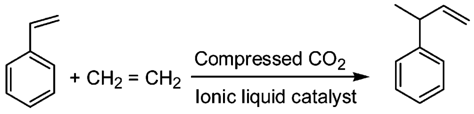


tris(benzylideneacetone)
dipalladium

Heck coupling of iodobenzene and methyl acrylate has been catalyzed by Pd(0) nanoparticles in supercritical CO_2.[208] Solubilization of the Pd(0) metal particles in supercritical CO_2 was accomplished using a perfluoropolyether-functionalized poly(propylene imine) dendrimer.[208]

Innovative biphasic systems in which supercritical CO_2 containing reactants flows through a stationary ionic liquid phase containing the catalyst have been recently developed.[209] This biphasic system allows designing a continuous-flow reactor to carry out homogeneous catalysis. The methodology combines the advantages of supercritical fluids and ionic liquids and is based on the properties of nonpolar, gaslike CO_2 with those of polar, nonvolatile ionic liquids. The hydroformylation of alkenes[210] and the hydrovinylation of styrene[211] (Scheme 42) are two processes reported so far by using this novel system.

Scheme 42



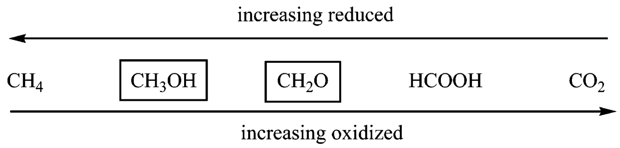
For this type of supercritical CO_2/ionic liquid systems, a recent in situ IR spectroscopic study of CO_2 dissolved in ionic liquids at high pressure (supercritical state) has demonstrated that the counteranion of the melt interacts with dissolved CO_2.[212] This could lead to fine-tuning of the properties of ionic liquids and supercritical fluids as media to perform catalytic reactions, but applications in catalysis of the effect of pressure on the activity in this interesting combination are still to be seen.

4.1.2. CO_2 Fixation

Related to the use of supercritical CO_2 as a medium for green chemistry, a subject of emerging interest is CO_2 fixation, i.e., those reactions in which atmospheric CO_2 is used as feedstock. Excess carbon dioxide in the atmosphere is responsible in part for the greenhouse effect that produces global warming and climatic changes. This excess of CO_2 emission comes from the massive combustion of fossil fuels. The setting up of artificial mechanisms and processes to help the natural photosynthetic CO_2 fixation to deal with the excess of CO_2 emissions has been seriously considered, and the reduction of the percentage of atmospheric CO_2 by artificial means has been proposed as one of the targets of environmental chemistry.[6] Fixation of CO_2 occurs naturally in the photosynthesis process of green plants, algae, and bacteria, but it has been calculated that there has been an unbalance in the last 50 years as a consequence of human activity, emission being higher than the natural capacity of CO_2 fixation by 3500×10^6 tons year^{-1}.

The above considerations serve to explain the interest in promoting the industrial use of CO_2 as a C_1 feedstock (Scheme 43). In principle, bulk chemicals such as formaldehyde and methanol could be obtained by reduction of CO_2. Unfortunately, the stability of CO_2 makes this molecule extremely unreactive. Chemical fixation of CO_2 can be done under supercritical conditions by using simultaneously as a medium and reactant.

Scheme 43

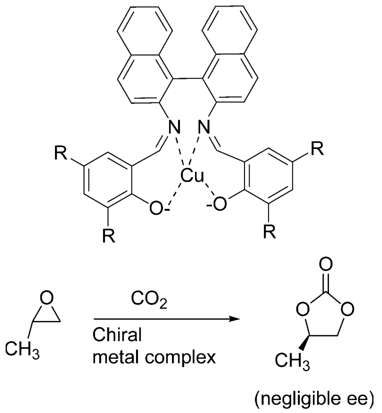


C_1 feedstocks ordered based on the C oxidation state
Those currently more important from the industrial point
of view have been highlighted

Olah and co-workers have studied the carboxylation of benzene to benzoic acids at moderate temperatures (up to 80 °C) using $AlCl_3$ as catalyst.[213] The reaction occurs with excellent yield, and the product is essentially free from diaryl ketones. This carboxylation is accelerated and the yields increased by the co-addition of Al metal. Unfortunately, the reaction is stoichiometric from the point of view of $AlCl_3$, and it would be worth trying it with strong solid Lewis acids. Theoretical calculations suggest that the reaction mechanism does not involve the activation of benzene by $AlCl_3$ species, but rather a $CO_2{-}AlCl_3$ complex that would exhibit superelectrophilic behavior.[213]

Transition metal Schiff base complexes are Lewis acid catalysts for the chemical fixation of CO_2 by reacting CO_2 with terminal epoxides, rendering cyclic carbonates with almost complete chemical yield.[214,215] Among the metal ions studied are Cr(III), Zn(II), Co(II), and Cu(II). Organic bases are used as cocatalysts of this CO_2 insertion.[214] Although this reaction can, in principle, produce chiral products, attempts to effect the asymmetric version of this catalytic reaction, starting from propylene oxide and using chiral Cu(II) salen complexes of 2,2′-diamino-1,1′-binaphthyl or chiral Co(II)salen complexes, gives only low to moderate enantiomeric excesses of the corresponding cyclic carbonate of propylene glycol (Scheme 44).[214,216]

Scheme 44



As mentioned earlier, supercritical CO_2 forms a single phase with ionic liquids, and the latter medium has also been used for the addition of CO_2 to epoxides to form cyclic carbonates using zinc iodide as catalyst.[217] Cyclic carbonates can even be formed without catalyst using room-temperature ionic liquid *N*-ethyl-*N*′-octylimidazolium tetrafluoroborate as cosolvent.

It is well known that CO_2 reacts with alkali metal ion hydroxides to form the corresponding carbonates. Other strong bases behave similarly. The carbonation of hydroxide ions can also take place in certain metallic complexes in which hydroxide is a ligand of the transition metal.[218,219] This carbonation of hydroxide ligands can be reversible for certain complexes. However, this ability has not yet been exploited to develop a catalytic cycle for the fixation of CO_2.

Methylamines can be synthesized from CO_2, H_2, and NH_3 using palladium supported on alumina. Selectivities higher than 80% were achieved using a fixed-bed reactor, dimethyl- and trimethylamines being present in minor amounts, together with lesser quantitites of CO and methane.[220] *N*,*N*-Dimethylformamide and *N*,*N*-diethylformamide can be synthesized by reacting supercritical CO_2, H_2, and the corresponding secondary *N*,*N*-dialkylamines in the presence of metallic complexes of Ru, Ir, Rh, Pt, or Pd.[221] Baiker and co-workers have developed a series of heterogeneous catalysts by incorporating these complexes into silica gel.[222]

Photocatalytic CO_2 reduction with water to form methanol is a process that in a certain way mimics the natural photosynthetic process. The energy of the light harvested by the photocatalyst is transformed into chemical energy during the reduction of CO_2. There is no doubt that this process will have a large impact, provided that solar light is used. Anpo and co-workers have made a significant contribution in this field.[223−225] Other photo processes of less industrial relevance than the photochemical reduction of CO_2 by water include the addition of CO_2 to carbonylic compounds such as benzophenone. However, this process is still very inefficient since, in addition to using poly-*p*-phenylene as photocatalyst, triethylamine is required as an electron donor. The presence of quaternary ammonium salts increases the yield of diphenylglycolic acid by stabilizing the diphenylcarbinol anion intermediate.[226−229]

4.1.3. Supercritical Water

Another supercritical fluid that is also attracting a growing interest as a medium for organic reactions is supercritical water. Compared to CO_2, water has the disadvantage of the high pressure (22.1 MPa) and temperature (374.2 °C) required to reach the supercritical state, as well as the corrosion of the reactors due to the higher concentration of H^+ and OH^- ions in the water supercritical state. Conditions are particularly corrosive when chlorinated organic compounds are used as reagents due to the partial formation of HCl and metal chlorides by reaction with the reactor walls.[230]

On the positive side, many important physicochemical parameters characteristic of liquid water, such as density (that can be decreased to nearly 0 g cm^{-3}), formation of intermolecular hydrogen bonds (that can almost disappear in the supercritical state), dielectric constant, and the ionic product, can be adjusted over a wide range simply by varying the pressure and the temperature in the supercritical state. In particular, the increase of the ionic product of water increases the concentrations of H^+ and OH^- due to self-ionization without addition of any extrinsic acid or base. Therefore, water in its supercritical state can promote Brönsted acid- and base-catalyzed reactions that would not occur in liquid water. This is the reason the majority of the reactions in supercritical water do not require the addition of any Lewis acids as catalysts.[231] The same applies for base-catalyzed reactions.[232,233]

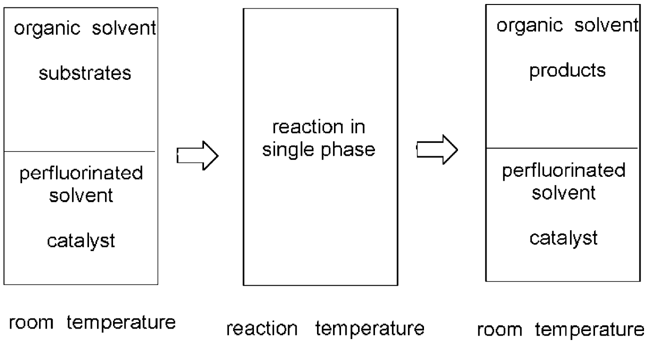
Among the classes of reactions for which supercritical water is particularly suitable as reaction medium, the most important are hydrolysis,[234,235] hydrations/dehydrations,[236−240] pinacol[241,242] and Beckmann rearrangements,[231,242,243] Diels−Alder cycloadditions,[244] Friedel−Crafts phenol alkylation,[245] and more surprinsingly oxidations[246−248] and degradation of organics.[249−251] Compounds such as ammonia,[252] phenols,[253−257] anilines,[258,259] pyridines,[260,261] chlorinated aromatics,[262−266] dibenzothiophenes,[267] and carboxylic acids[251,268] can be degraded in supercritical water. The last reaction type has led researchers to consider supercritical water for the treatment of wastewater streams.[246,251,269,270] In this case, the addition of some solid as oxidation catalyst, very frequently containing noble metals, can increase the overall efficiency of the process.

Hydration of propylene to the Markovnikov 2-propanol product can be carried out in sub- and supercritical water in the presence of alumina or molybdena supported on alumina as catalyst;[271] the latter catalyst exhibits higher activity. It has been observed that the hydration rate depends on the ionic product of water, and this has led to the conclusion that H^+, most probably on the solid surface, also cooperates in the catalysis. Cyclohexanol dehydration in supercritical water has been found to require the presence of added acid or bases, while cyclohexene hydration can be effected with PtO_2 and a Brönsted acid.[272]

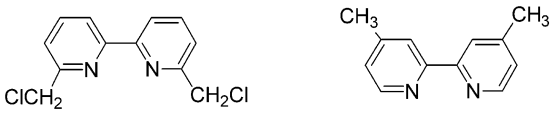
4.2. Lewis Acid-Catalyzed Reactions in Biphasic Fluorous Systems

A recent *Tetrahedron* symposium in print has been devoted to showing the state-of-the-art in fluorous systems and to exemplifying the various possible applications including synthesis of fluorous ligands, reagents, catalysts, and solvents as well as different catalytic reactions carried out in fluorous media and fluorous supramolecular polymer and materials chemistry.[273] Following a parallelism with the word “aqueous”, the adjective “fluorous”, initially coined by Horváth and Rabai,[274−278] has been defined as referring to highly fluorinated saturated organic molecules or molecular fragments.[274−277,279−285] Herein, we will focus on the application of biphasic fluorous systems to conduct Lewis acid-catalyzed reactions. Scheme 45 summarizes the successive steps in a catalytic reaction based on a fluorous system.

Scheme 45

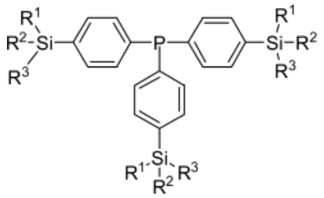


Besides the temperature-dependent miscibility of the two solvents, the key point of this strategy lies in the fact that the catalyst has to be very soluble in the perfluorinated solvent, while the products not. The exclusive solubility of the catalyst in the fluorous phase normally requires an adequate functionalization.[281,286] Some examples of how common ligands are modified to increase their solubility in biphasic fluorous phase are worth comment to give an idea of the advantages and limitations of this methodology. Given the commercial availability of the required perfluorinated alcohols or carboxylic acids, fluorous tags are normally perfluorinated alkyl or ether chains linked to the non-fluorous moiety through an ether or ester group. Fluorous soluble bipyridines bearing two perfluoroalkylated side chains in the 6,6′- or 4,4′-positions have been prepared via etherification of 6,6′-bis(chloromethyl)-2,2′-bipyridine or C-alkylation of 4,4′-dimethyl-2,2′-bipyridine.[287] These fluorinated ligands form in situ ruthenium complexes that are efficient for the Lewis acid-catalyzed epoxidation of *tert*-stilbene with IO_4^-.[287]



2,2'-bipyridines

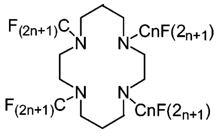
Likewise, triphenylphosphine, which is a common ligand for palladium and other late transition metals, can be functionalized using *p*-perfluoroalkylsilyl substituents.[288,289] This approach permits the attachment of 3−9 perfluoro tails per P atom.[288] Perfluorinated binol ligands have also been widely used in the asymmetric version of fluorous biphase systems.[290]



R^1, R^2, R^3: CH_3 or $-CH_2CH_2C_nF_{2n+1}$

fluorinated triarylphosphines

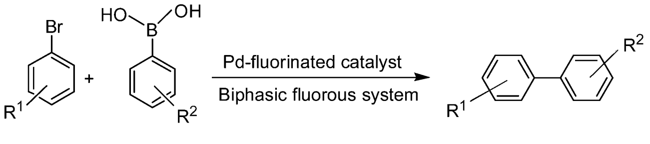
Commercially available tetraazacyclotetradecane (cyclam) can be functionalized through the N-atoms to introduce a perfluoroalkyl chain. Complexes of this fluorinated macrocycle with transition metal ions are soluble in fluorocarbons, and they can act as Lewis acids. These complexes have been used for the oxidative functionalization of hydrocarbons under typical fluorous biphase conditions.[291]



fluorinated cyclam

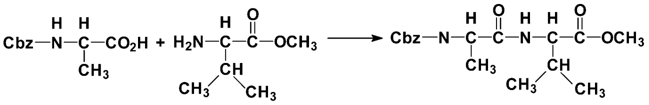
Perfluoro-tagged palladium complexes have been used for the catalytic cyclodimerization of conjugated enynes to give benzene derivatives in fluorous biphasic systems.[292] The catalyst was successfully reused in consecutive runs. The same type of fluorinated palladium complexes have also been used as catalysts for the biphasic fluorous system version of the Suzuki C−C coupling (Scheme 46).[293] Alkylation of allyl substrates by nucleophilic substitution using C-nucleophiles catalyzed by Pd(0) complexes,[294] the Heck reaction,[295] the Stille reaction by coupling aryl halides with tributyltin derivatives,[296] and ring-closing methatesis followed by a consecutive Heck reaction[297] are other C−C bond-forming processes that have been described in fluorous biphasic systems using perfluoro-tagged Pd catalysts.

Scheme 46



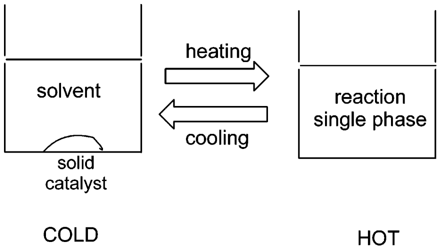
An improvement of the biphasic fluorous strategy consists of adding a commercially available perfluoroalkanoic acid to the fluorinated solvent to form a hydrogen bond with a certain substrate, thus scavenging it from the non-fluorous solvent and solubilizing it into the fluorinated solvent. This concept has been realized to improve the liquid−liquid separation step in *N*,*N*′-di(polyfluoroalkyl)ureas formed as byproducts of the carbodiimide-mediated coupling of carboxylic acids and amines in peptide synthesis.[298] These *N*,*N*′-di(polyfluoroalkyl)ureas experience a dramatic enhancement of the solubility in C_6F_{14} by the presence in this fluorinated solvent of perfluoroheptanoic acid. In this way, Cbz-Ala-OH and H-Val-OMe were condensed with $F_3C(CF_2)_5CH_2CH_2N{=}C{=}NCH_2CH_2(CF_2)_5CF_3$ as coupling reagent in a biphasic CH_2Cl_2/C_6F_{14} solvent system at room temperature for 16 h (Scheme 47). Workup involves washing the reaction mixture twice with a solution of perfluoroheptanoic acid in C_6F_{14} and once again with fresh C_6F_{14}.[298] The obvious drawback of this procedure is the use of extra volumes of C_6F_{14} as well as the need for fluorinated *N*,*N*′-dialkylcarbodiimide. In this regard, recent chromatographic techniques, based on the use of fluorous solid phases, have been developed and used to alleviate the need for using volatile organic solvents to separate fluorous reagents and products.[299−303]

Scheme 47



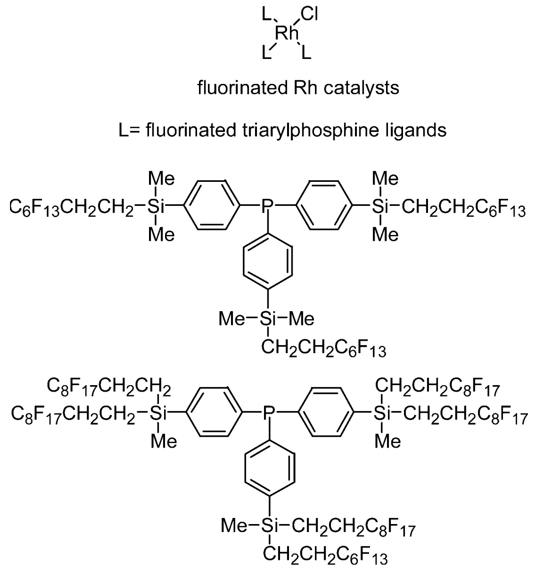
A new variant of the biphasic fluorous methodology based on the low-temperature solid−liquid rather than liquid−liquid separation phase has been recently reported.[304] In this case the catalyst is a fluorinated solid that is insoluble in alkanes at low temperatures, but upon increasing the temperature close to the solid melting point the fluorinated catalyst exhibits a remarkable thermotropic solubility. Thus, the catalytic reaction occurs in a single phase at this temperature. Upon cooling, the fluorinated catalyst precipitates and can be recovered for the next run (Scheme 48).[304] The major advantage of this original approach is that expensive fluorinated solvents are not necessary, but functionalization of the catalyst, normally by attaching a fluorinated tag, is still needed.

Scheme 48

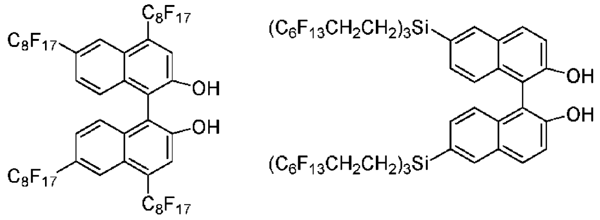


Despite the novelty of biphasic fluorous systems, the list of catalytic reactions for which this methodology has been applied is already quite large, many of them requiring Lewis acid catalysts or being oxidation reactions. Propylene undergoes dimerization in fluorous solvents to 2,3-dimethylbutenes when fluorinated Ni complexes are used as Lewis acids in combination with phosphine ligands and alkylaluminum promoters.[305] Fluorinated phosphine ligands and tris(pentafluorophenyl)borane ($(C_6F_5)_3B$, in place of the organoaluminum co-catalyst) have also been used in this system to improve catalyst solubility in the fluorinated phase.[305] However, although significantly high productivities of 25 000 h^{-1} were achieved, this fluorinated biphasic system suffers from a progressive migration of the catalyst toward the hydrocarbon phase.

Silylation of primary, hydrophobic alcohols with triethylsilane can be effected under biphasic fluorous conditions using dirhodium perfluorocarboxylates having perfluoroalkyl chains from C_7 to C_{13}.[306] Primary alcohols are preferentially silylated in comparison with hydrophilic secondary ones. Hydrosilylation of 1-alkenes using a fluorous rhodium catalyst,[307] and the reverse approach, i.e., hydrosilylation of perfluoro-1-alkenes using a non-fluorinated rhodium Lewis acid, have also been reported.[307]



Several asymmetric Lewis acid-catalyzed C−C bond formations by addition of diethylzinc to aryl aldehydes in fluorous biphasic systems have been reported.[308−311] In some of them, 4,4′,6,6′-tetrakis-(perfluorooctyl)-1,1′-binaphthalene-2,2′-diol was used as a chiral inductor.[311,312] In others, a chiral Ti complex of (*R*)-6,6′-bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl)-1,1′-binaphthalene-2,2′-diol in a toluene/FC-72 biphasic fluorous system was employed for the enantioselective alkylation of aromatic aldehydes using diethylzinc.[309,310] Titanium acts as a Lewis acid site, coordinating with the aromatic aldehyde. Enantiomeric excesses higher than 80% were obtained even in the fifth reuse of the fluorous phase. Hydrolytic kinetic resolution of terminal epoxides can be catalyzed by *light-fluorous* chiral Co(salen) complexes, while heavily fluorinated complexes exhibit low activity.[313] Heterogeneous enantioselective synthesis in the fluorous phase, in which the chiral catalyst is attached to soluble polymeric ligands such as dendritic polymers, allows the use of ultrafiltration in a membrane reactor.[314]



fluorinated 1,1'-binaphthalene-2,2'-diol

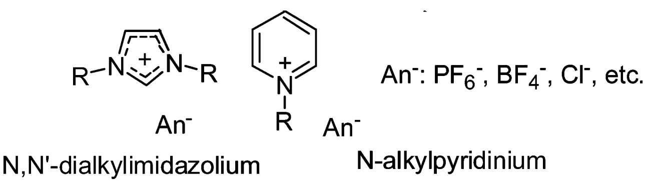
Lanthanide Lewis acids have been converted into recyclable fluorous catalysts by using the tris(perfluorooctanesulfonyl)methide or bis(perfluorooctanesulfonyl)amide ponytails.[315,316] The fluorous ponytails make these catalysts soluble in fluorous solvents, where they remain immobilized or, alternatively, can be used directly as fluorous solids that become soluble upon heating at the reaction temperature and separate upon cooling. These lanthanide complexes are extremely efficient Lewis acids for carbon−carbon bond-forming reactions, including Friedel−Crafts acylation and the Diels−Alder and Mukaiyama aldol reactions, by virtue of the Lewis acidity enhancement originating from the powerful electron-withdrawing effect of the perfluoroalkanesulfonylmethide or amide groups on the lanthanide metal.

L: $^-C(SO_2C_8F_{17})_3$ or $^-N(SO_2C_8F_{17})_2$

4.3. Lewis Acid-Catalyzed Reactions in Ionic Liquids

The use of ionic liquids is now a hot topic in green chemistry, as it is hoped that they constitute an alternative to volatile organic solvents as reaction medium.[285,317−321] From the structural point of view, common ionic liquids are nitrogenated or phosphonated organic cations having inorganic counteranions. Since ionic liquids cannot be distilled and their purification is problematic, they have to be obtained in high purity directly by synthesis.[322] Nucleophilic substitution (formation of the positive organic salt) followed by anion exchange is the most general preparation procedure.[318−321] Enantiomerically pure ionic liquids having substituents from the chiral pool have recently been reported, but are yet to be exploited in asymmetric synthesis.[323−325]

Although ionic liquids, previously known as molten salts, are certainly not a new class of compounds,[326−331] they have recently attracted considerably attention as green reaction media. The most widely used ionic liquids are derivatives of *N*,*N*′-dialkylimidazolium or *N*-alkylpyridinium with inorganic anions such as PF_6^-, BF_4^-, or even Cl^-. They combine a reasonable thermal stability, a sufficient solubility for most organic compounds, a practically zero vapor pressure, and inmiscibility with some organic solvents such as alkanes and ethers. Thus, the catalytic reactions are conducted in a single phase (the ionic liquid) by adding the reagents and catalyst.



After completion of the reaction, the products are recovered by conventional liquid−liquid extraction, while the Lewis acid catalyst is expected to remain immobilized in the ionic liquid. Given the viscosity of the ionic liquid and the limited choice of immiscible organic solvents to recover the reaction products, mass balance indicating the percentage of the initial moles recovered as either unreacted substrate or converted products is an important parameter, particularly for reaction data using fresh ionic liquid as solvent. The need for an organic solvent to extract the reaction products is one of the main drawbacks of the use of ionic liquids as green media. At this point it is worth remembering that, as stated earlier, CO_2, particularly in its supercritical state, is a good solvent to extract products from ionic liquids.

Addition of anhydrous $AlCl_3$ to the Cl^- salt of *N*,*N*′-dialkylimidazoliums gives rise to a distribution of chloroaluminate species $Al_xCl_y^-$ that may exhibit Lewis acidity, depending on the $AlCl_3/Cl^-$ molar ratio.[330] By controlling the proportion of $AlCl_3$ added to the ionic liquid, different species, such as neutral $AlCl_4^-$ or acidic $Al_2Cl_7^-$, can be predominantly present. In the latter case, addition of 2-fold the stoichiometric amount of $AlCl_3$ is required (eq 2). Thus, the catalytic activity of the liquid can, in principle, be tuned. Also the nature of the imidazolium cation plays a role in controlling the melting point, solubility, viscosity, and other parameters influencing the properties of the ionic liquid.

$$Cl^- \xrightarrow{AlCl_3} AlCl_4^- \xrightarrow{AlCl_3} Al_2Cl_7^- \qquad (2)$$

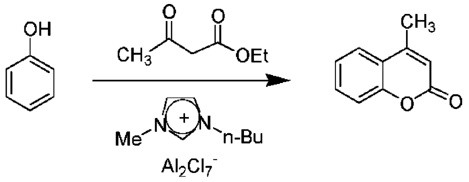
The presence of residual water strongly influences the Lewis acid activity of these ionic liquids, due to the hydrolysis of the $Al_xCl_y^-$ species with formation of HCl and aluminum hydroxides. Moreover, since these melts are highly hygroscopic, the reaction has to be carried out under an inert atmosphere and protected from ambient moisture. The reagents and cosolvents may also need to be dried. Water, hydrochloric acid, and other byproducts likely to be retained on the ionic liquid are also likely to interfere on the reuse of the ionic melt. This is one of the major drawbacks of this catalytic system, the presence of residual water or moisture being a factor responsible for the occasional low reproducibility of the results.

A procedure analogous to that followed to obtain chloroaluminated melts can be used to prepare ionic liquids containing Lewis acids of titanium, niobium, tantalum, tin, or antimony by dissolving halogenated or oxyhalogenated compounds of these metals in the ionic liquid having halide or hexafluoroantimonate as counterion.[332] These Lewis acid ionic melts are particularly active catalysts for the HF hydrofluorination of saturated and unsaturated compounds with C−Cl bonds.[332] In this context, it has been reported that a range of moisture-stable Lewis acidic ionic liquids can be prepared by mixing appropriate ratios of $ZnCl_2$ or $SnCl_2$ and quaternary ammonium salts having hydroxide, chloride, acetate, or benzoate as counteranions.[333]

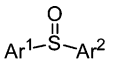
Chloroaluminate salts of imidazolium have shown good activity for a quite large number of acid-catalyzed reactions, including Friedel−Crafts alkylations,[334−336] particularly that of benzene with long-chain α-olefins,[319] a process that is used industrially for the production of linear alkylbenzenes as precursors of alkylbenzenesulfonates which are employed as surfactants.

The acetylation of benzene with stoichiometric amounts of acetyl chloride occurs in complete conversion in 1-ethyl-3-methylimidazolium $Al_2Cl_7^-$ melt.[330] The Friedel−Crafts acylation of toluene, chlorobenzene, and anisole with acetyl chloride has been carried out in 1-ethyl-3-methylimidazolium $Al_2Cl_7^-$, wherein high para selectivity has been observed.[337] The chloroaluminate salt of 1-butyl-3-methylimidazolium, having 2 equiv of $AlCl_3$ per Cl^-, has been found to be an alternative to conventional acid catalysts in the Pechmann condensation of phenols with ethyl acetoacetate, leading to coumarin derivatives (Scheme 49).[338] As an additional advantage of the system, it was found that the reaction time is considerably reduced when this reaction is carried out in molten salts, even at room temperature.[338]

Scheme 49



The previous chloroaluminate melt has been employed as an unconventional medium for the Friedel−Crafts sulfonylation of benzene derivatives with toluenesulfonyl chloride.[339] The substrates exhibit enhanced reactivity at room temperature, yielding diarylsulfones in almost quantitative yields. ^{27}Al NMR has been used to investigate the change in the Al species distribution during the sulfonylation reaction. Before the reaction, $Al_2Cl_7^-$ is the predominant species in the melt, but after the reaction $AlCl_4^-$ predominates.[339] This change was attributed to the trapping by $Al_2Cl_7^-$ of the HCl evolved in the sulfonylation reaction and could eventually modify the catalytic activity of the system, since while $Al_2Cl_7^-$ is acidic, $AlCl_4^-$ is essentially neutral. In fact, acidic chloroaluminate forms of imidazolium molten salts can be buffered to neutrality by addition of an alkali halide[340,341] or $CaCl_2$.[342] $MgCl_2$ only buffers acidic melts partially.[342] It has been proposed that the buffering reaction consists of the formation of tetrachloroaluminate from other acidic polychloride aluminum species, as exemplified by eq 3 for the case of $CaCl_2$.



diarylsulfone

$$CaCl_2 + 2Al_2Cl_7^- \rightarrow Ca^{2+} + 4AlCl_4^- \quad (3)$$

However, $AlCl_4^-$ in ionic melts can behave quite easily as a Lewis acid. Thus, buffered $AlCl_4^-$ melts exhibit what has been termed as “latent acidity”.[340,343,344] The interesting concept of “latent acidity” refers to the fact that weak bases, which normally should not react with $AlCl_4^-$, are able to shift Cl^- from $AlCl_4^-$, forming a Lewis adduct in the buffered melts, as if they were reacting with $AlCl_3$. This effect is due to the driving force introduced in the equilibrium by the precipitation of the halide salts, as exemplified in eq 4.

latent acidity

$$:B + AlCl_4^- + Na^+ \rightarrow +B{:}AlCl_3^- + NaCl_{(s)} \quad (4)$$

In an elegant variant of the use of ionic liquids to conduct Friedel−Crafts aromatic alkylations, immobilization of *N*,*N*′-dialkylimidazolium chloroaluminates on the surface of inorganic porous supports renders a solid catalyst.[345,346] Compared to the use of pure ionic liquid, supporting them on a solid facilitates the separation of the catalyst from products, permits gas-phase reactions to be performed easily, and saves a considerable amount of expensive ionic liquid. Two preparation procedures have been reported to obtain these ionic liquids immobilized in porous supports (Scheme 50). The simplest one (*incipient wetness impregnation*) consists of the impregnation of the required volume of the ionic liquid in its chloroaluminate form to fill the pores of the dehydrated solid. This process needs prolonged stirring to favor uniform deposition and exhaustive solid−liquid extraction with dichloromethane. The fact that HCl is evolved during the impregnation, together with ^{27}Al NMR data, supports that chloroaluminate has reacted with the surface hydroxyl groups. The way in which the chloroaluminate counteranion remains grafted on the silanol groups is analogous to that originally proposed by Getty and Drago for the reaction of $AlCl_3$ and implies a truly covalent bond with the solid walls.[347] Therefore, the amount of ionic liquid retained on the solid after the extraction depends on the density of surface OH groups. Table 3 gives some reported values.[346] An alternative, more elaborate method to anchor the ionic liquid on a solid support consists of the reaction of the chloroaluminate of a 1-triethoxysilyl derivative of 3-methylimidazolium on the walls of silica or MCM-41 (Scheme 50).[345]

Alkylation by 1-dodecene of benzene derivatives and naphthalene has been used as a test reaction.[348] It has been reported that, for the liquid-phase alkylation at 80 °C using immobilized ionic liquids as heterogeneous catalysts, alkylation of benzene results in 98% selectivity toward monoalkylated derivatives

Scheme 50

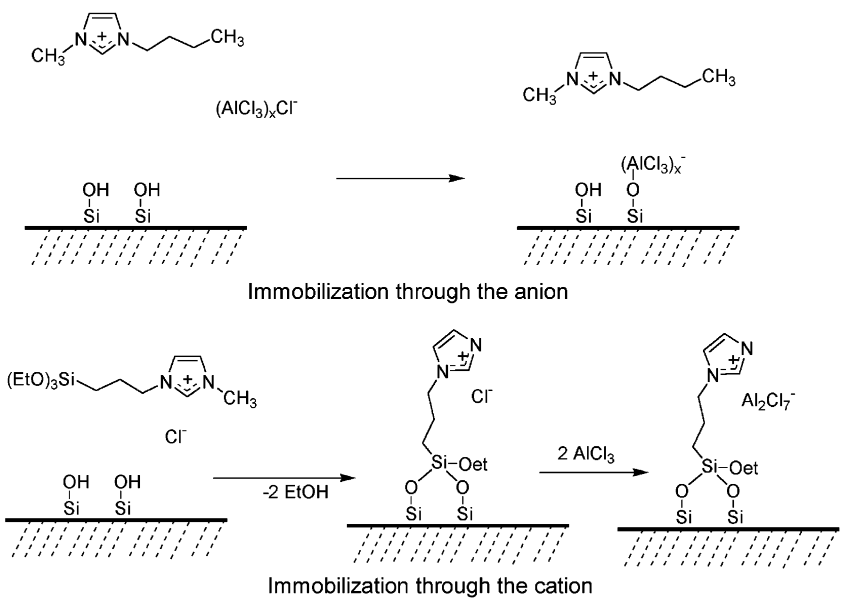


Table 3. Percentage of Ionic Liquid Retained on Various Supports after Impregnation of the 1-Butyl-3-methylimidazolium Chloroaluminate upon Incipient Wetness and Exhaustive Solid−Liquid Extraction with Dichloromethane[a]

solid	percentage of ionic liquid (wt %)
ZrO_2	<5
TiO_2	5
Hβ zeolite	7
Al_2O_3 (Condea Pural SB)	20
SiO_2 (Degussa FK 700)	35

[a] Data taken from ref 346.

at 99% dodecene conversion (Table 4).[348] Catalysts prepared by grafting of the positive imidazolium ring on the silica walls showed activity for dodecene conversion comparable to that of those prepared by the *incipient wetness* technique (anchoring through the chloroaluminate anion), but the solid prepared by grafting had a greater HCl stability.[345]

The same strategy, using Lewis acid ionic liquids supported on inorganic carriers or activated carbon, has been applied to the Friedel−Crafts acylation of aromatics.[349] The ionic liquids consist of 1-methyl-3-butylimidazolium having as counteranions chloroferrate, chloroaluminate, or chlorostannate. The solids were prepared starting from the chloride melt, adding a stoichiometric amount of the metal halide, and stirring the mixture overnight. The supported ionic liquids were tested for the liquid-phase and gas-phase acylation of benzene derivatives. For reactions in the liquid phase, a considerable extent of catalyst leaching was observed.[349] Obviously, leaching does not occur for gas-phase reactions, but deactivation by coking takes place unless the reaction is conducted under optimum reaction conditions.[349]

Lanthanide triflates are widely used as water-tolerant Lewis acids for a variety of transformations (see section 4.4). In this context, it has been recently shown that $Sc(OTf)_3$ catalyzes the Friedel−Crafts alkylation of aromatics with olefins in hydrophobic ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate or hexafluoroantimonate (Scheme 51).[350] In contrast, this reaction is not observed under the same conditions in common organic solvents, water, or hydrophilic ionic liquids such as 1-butyl-3-methylimidazolium triflate or tetrafluoroborate.[350] When lanthanide triflates in ionic liquids are used, the possibility of reuse and the percentage of catalyst remaining in the ionic liquid

Scheme 51

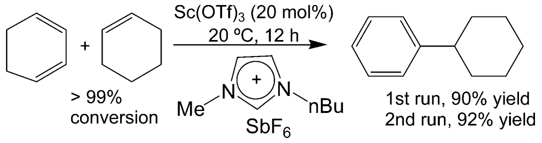


Table 4. Results of Benzene Alkylation by Dodecene at 80 °C after 1 h Reaction Time Catalyzed by Immobilized Acidic $(AlCl_3)_x^-$ Ionic Liquids (6 wt %) Anchored through the Inorganic Chloroaluminate or through the Organic Imidazolium Cation[a]

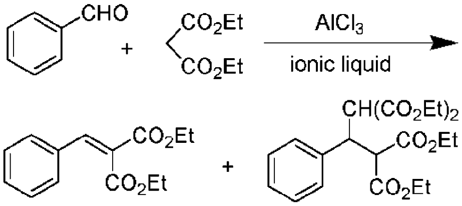
catalyts	dodecene conversion (%)	C_{12} isomerization (%)	selectivity (%) monoalkyl	selectivity (%) heavier products
pure ionic liquid	5	85	14	
pure MCM-41	<5	>95		
SiO_2 anchored through the anion	>95		>95	
SiO_2 anchored through the cation	90	20	75	<5
MCM-41 anchored through the cation	>95	10	85	<5

[a] Data taken from ref 345.

after recovery of reaction products are issues that need to be addressed.

Other reactions reported so far in Lewis acidic ionic liquids include direct carbonylation of olefins[351,352] and alkylaromatics to aromatic aldehydes,[353] cycloaddition of CO_2 to epoxides,[354] Knoevenagel condensation of aromatic aldehydes with ethyl malonate (Scheme 52),[355] Diels−Alder cycloaddition[356] and Claisen rearrangement of allyl aryl ethers[357] using scandium trifluoromethanesulfonate, and acylative cleavage of cyclic and acyclic ethers in the presence of acyl chlorides.[358] Ionic liquids containing HF are particularly active for the liquid-phase substitution of C−Cl by C−F bonds in saturated or unsaturated compounds.[332] Thus, CH_2Cl_2 is converted into a 69:31 mixture of CH_2F_2 and CH_2ClF at 84% conversion.

Scheme 52



As mentioned earlier, the combination of CO_2/ionic liquid permits the design of continuous-flow reactors. A further logical extension of the biphasic supercritical CO_2/ionic liquids is to triphasic systems comprising an ionic liquid, water, and an organic solvent. In these systems the catalyst resides in the ionic liquid, the substrate and products are in the organic phase, and inorganic salts are dissolved in the aqueous phase. Such a system has been developed for the Heck reaction.[359]

Brönsted acidic ionic liquids that are substantially free of Lewis acidity have also been reported.[360] They can be obtained by reacting organonitrogen or organophosphorus compounds with a Brönsted acid in a molar ratio less than or equal to 1. These Brönsted acidic ionic liquids are useful as catalysts for esterification reactions[360] and aromatic hydroxyalkylation with paraformaldehyde.[361] It has been reported that mixtures of Brönsted and Lewis acids can exhibit superacidity in *N*,*N*′-dialkylimidazolium ionic liquids, being stronger acids than sulfuric acid or liquid HF.[362] Thus, it has been reported that benzene can be protonated to cyclohexadienyl cation or that this mixture of acids can catalyze the alkylation of ethylene to isobutane.[318,319,363]

Ionic liquids are suitable conducting media in which to perform electrochemical studies.[336,364−366] It has been reported that the addition of 1 equiv of HCl per available chloride to a mixture 49:51 of $AlCl_3$ in 1-ethyl-3-methylimidazolium results in an expansion of the electrochemical window of the melt relative to that of Lewis neutral melt.[367] This has been interpreted as being due to the formation of $H_2Cl_3^-$ or $HAlCl_5^-$, which maintains low the concentration of free chloride ion. An electrolyte composition consisting of a 58:42 mixture of $AlCl_3$/1-methyl-3-ethylimidazolium chloride or related melts in acetonitrile has been proposed as a component for high-energy density, high-rate batteries.[368] Voltammetric studies indicate that several protic species are present in this melt.[367]

Room-temperature inorganic liquids of high ionic conductivity have been prepared by reacting $AlCl_3$ with sulfonyl chlorides.[369] The liquid has been considered to be in a state between molecular and ionic, and the term "quasi-molten salt" has been coined for them. The interesting opportunities of these "quasi-molten salts" compared to ionic liquids are clear, considering that unlike pyridinium and imidazolium ionic liquids, which are reduced by alkali metals, quasi-molten salts can be used as media for reversible lithium and sodium metal deposition/stripping. Their electrochemical window spans 5 V, and their conductivity is 10^{-4} S cm^{-1}.[369] However, corrosion arising from hydrochloric and sulfuric acid formation in the presence of moisture is a major drawback of this interesting medium.

A final remark concerning the use of biphasic fluorous media and ionic liquids as green media is the paucity of reports addressing their complete life assessment cycle and their toxicity after long-term exposition. Thus, caution should be exercised when considering these two media as "green" until all these data are available. Particularly important are the presumably long-term persistence of perfluorinated compounds in the environment for longer than decades and disposal and regeneration problems for ionic liquids, especially when they contain halogenated or metallic additives. In general, it seems logical that halogenated Lewis acids ($AlCl_3$) should be avoided in ionic liquids, as they are in other media.

4.4. Lewis Acid-Catalyzed Reactions in Water as Solvent

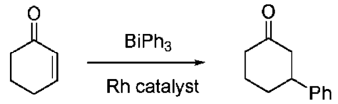
It is a widely accepted belief that Lewis acid-catalyzed reactions must be carried out in the absence of water or even under strict anhydrous conditions. Very frequently, the presence of even trace quantities of water stops completely the Lewis acid-catalyzed reaction because the most common Lewis acid catalysts react immediately with water and instantaneously or progressively decompose to form hydroxides or oxides, losing immediately or gradually their Lewis acid activity. The hydrolysis of anhydrous metal halides such as $AlCl_3$, $TiCl_4$, and BCl_3 are paradigmatic examples of the dramatic negative influence of the presence of water (eq 5). However, it has been reported that $InCl_3$ can catalyze the cross-cyclization of epoxides and homoallyl alcohols to tetrahydropyran derivatives,[370] and therefore, it seems that not all the metal halides should necessarily undergo prompt hydrolysis in water.

$$\mathrm{MeX}_n + n\mathrm{H_2O} \rightarrow \mathrm{Me(OH)}_n + n\mathrm{HX} \qquad (5)$$

From the point of view of green chemistry, water would be the perfect solvent in which to carry out chemical reactions, provided that it dissolves reagents and products and that no polluted wastewaters are disposed.[371−373] A large amount of work has been devoted to performing organic reactions in water, particularly using organometallic chemistry and aimed at C−C bond formation.[372,374−380]

In this regard, a general C−C bond-forming reaction that has been extensively studied in water as solvent is the addition to carbonyl compounds or the conjugate addition to α,β-unsaturated carbonylic compounds under air atmosphere. A considerable number of organometallic compounds, such as aryl- and vinyltin, arylboronic, or triphenylbismuth reagents, can be used and the reaction requires catalysis, Rh(I) complexes being typical catalysts (Scheme 53).[381−387] Formally, this reaction is equivalent to the addition of Grignard and other organometallic reagents, except that those reactions require rigorously anhydrous conditions and cannot be conducted in the open air. Here, in striking contrast, water is the medium. When considering this reaction from the point of view of green chemistry, the convenience of using nontoxic organometallic reagents, for instance those of bismuth, must also be taken into consideration.

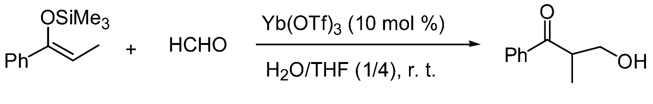
Scheme 53



Another reaction type using organometallic reagents and catalysts to form C−C bonds in water is the Ullmann-type reaction. In these reactions, two aryl halides couple to form a biphenyl, normally in the presence of a copper catalyst in organic solvents. It has been reported that minor amounts of palladium stabilized by complexing 18-crown-6 ether or poly(ethylene glycol)s are able to catalyze the reductive coupling of aryl iodides in the presence of zinc to form Ullmann products in water and under air atmosphere.[388,389]

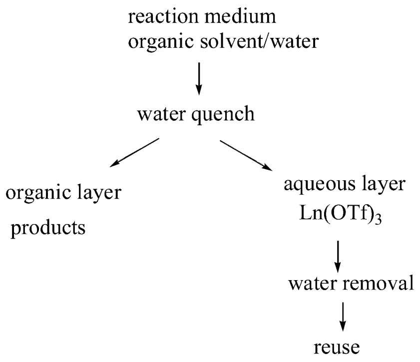
Focusing on Lewis acid catalysts, it has been found that rare earth metal triflates and some other metal salts can be used as water-soluble Lewis acids. Lanthanide [$Ln(OTf)_3$] and other metal triflates undergo slow hydrolysis in water,[390] and they act as strong Lewis acids with hard character and high binding constants with carbonyl oxygens. In fact, while most metal triflates are prepared under strictly anhydrous conditions, $Ln(OTf)_3$ can be prepared in aqueous solution.[391−393] The catalytic activity of $Ln(OTf)_3$ as a Lewis catalyst in mixtures of organic solvent and water as reaction medium was demonstrated in the hydroxymethylation of silyl enol ethers by using commercial formaldehyde aqueous solution (Scheme 54). This reaction is a particular case of the general Mukaiyama aldol reaction of silyl enol ethers with aldehydes that we have commented on earlier, to be generally carried out in organic solvents using $TiCl_4$ as catalyst.[124,394] Among the $Ln(OTf)_3$ tested for aldol reaction, $Yb(OTf)_3$ in 10 mol % was found to be a convenient catalyst, $Sc(OTf)_3$ behaving similarly.[395,396] Besides formaldehyde, $Yb(OTf)_3$ also activates other aldehydes in Mukaiyama aldol reactions with silyl enol ethers in THF/water, particularly those that are water soluble, such as acetaldehyde, acrolein, and chloroacetaldehyde.

Scheme 54



$Ln(OTf)_3$ can be easily separated from the reaction mixture by extracting the products with organic solvents, since $Ln(OTf)_3$ totally remains in the water and can be reused after concentration from the aqueous phase (Scheme 55).

Scheme 55



The percentage of water in the $Ln(OTf)_3$-catalyzed aldol reactions in water/THF mixtures strongly influences the yield of aldol products, there being an optimum concentration for the process. Lower or higher amounts of water in the reaction mixture can remarkably decrease the product yield. For instance, for the reaction of cyclohexanone trimethylsilyl ether with benzaldehyde, 80% aldol yield is obtained when the medium contains 10−20% of water, decreasing to only 10 and 18% for pure THF and pure water, respectively.

Concerning the mechanism of the Lewis catalysis in water, it has been proposed that, upon solubilization of the catalyst in water, hydration occurs immediately, water molecules continuously exchanging in the metal coordination sphere. If an aldehyde exists in the medium, it can coordinate to the metal center, provided that the exchange rate constant for inner-sphere ligand exchange for water is fast. Upon coordination with the metal triflate, the aldehyde becomes activated and the silyl enol ether attacks the Lewis adduct. However, according to this model, it should be possible to predict quantitatively the precise activity of a given metal salt as Lewis acid catalyst in aqueous media from the exchange rate and hydrolysis constants, something that does not agree with the experimental facts.

On the other hand, the possibility that a Brönsted acid generated from the interaction of the metal triflate and water should be the actual catalyst deserves more attention to be completely ruled out. In this way, even if $Ln(OTf)_3$ are Lewis acids in aprotic solvents, in water they could generate an amount of H^+ that is significant from the catalytic point of view.

In a further step toward avoiding totally the use of organic solvents and conducting the Lewis acid-catalyzed reaction in pure water, a variant of the above Lewis acid catalysis has been developed. By

Table 5. Influence of the Nature of the Metal Triflate (20 mol %) and Surfactant (20 mol %) on the Yield of the Aldolic Condensation of Trimethylsilyl with Benzaldehyde in 100% Aqueous Medium[a]

triflate	surfactant	time (h)	yield (%)
$Yb(OTf)_3$		48	17
$Yb(OTf)_3$	SDS	48	50
$Sc(OTf)_3$	SDS	4	88
$Sc(OTf)_3$	TritonX-100	60	89
$Sc(OTf)_3$	CTAB	4	

[a] Data taken from ref 397.

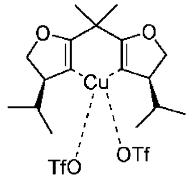
adding a small amount of sodium dodecyl sulfate (SDS) as surfactant, metal triflates can catalyze the aldol condensation in water without any organic cosolvent (Table 5). Cationic surfactants such as cetyltrimethylammonium bromide (CTAB) were found ineffective. On the other hand, the aldol reaction also occurs in neutral surfactants such as TritonX-100/20, although the process requires much longer reaction times.[397]

Further improvement of the use of surfactants to assist the reaction in water is the use of transition metal or rare earth salts of dodecyl sulfate. These salts combine the Lewis acidity of the cation with the surfactant ability of the anion, playing simultaneously the two roles. The structural similarity between the triflate and the alkyl sulfate anions is evident. For this Lewis acid–surfactant combined catalysis of aldol condensation in aqueous media, the nature of the metal cation is of paramount importance. While the Cu salt has the highest relative initial rate, the final yield is lower than that obtained using scandium or ytrium dodecyl sulfate (>90%) due to the concurrent hydrolysis of the trimethylsilyl ether competing with the aldol condensation. Addition of a small amount of Brönsted acid dramatically accelerates the reaction rate of the aldolic reaction.[398,399] No mechanistic insight into the way that Brönsted acids cooperate in the catalysis has yet been gained, but the interconversion Lewis/Brönsted becomes an obvious working hypothesis to be tested.

$$(C_{12}H_{25}SO_3^-)_nM^{n+}$$

metal dodecyl sulfate

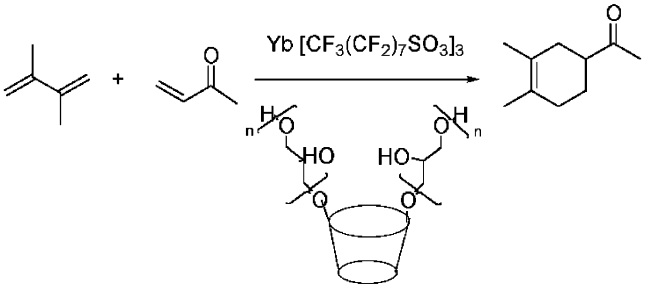
The Lewis acid–surfactant system enhanced by Brönsted acid has been further extended to catalytic asymmetric aldol reaction in water[400] using the copper complex of chiral diisopropyl bisoxazoline. The aldol is formed in low yield (23%) with moderate enantiomeric excess (58%), but addition of a carboxylic acid, particularly lauric acid, as a Brönsted acid improves both the yield (76%) and the enantioselectivity (69% ee). The way in which the carboxylic acid interacts with the copper complex or influences the reaction mechanism has yet to be unveiled.



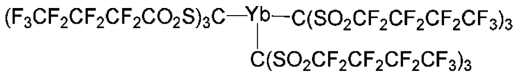
diisopropylbisoxazoline

A move toward heterogenization consists of the inclusion of perfluoroalkyl sulfates of alkali metal, alkaline earth metal, or transition metal ions inside cyclodextrins. The resulting complexes can be easily prepared, separated from the reaction mixtures, and reused as catalysts. Thus, β-cyclodextrin–epichlorhydrin copolymer was treated with ytterbium tris(perfluoroctanesulfonate) in H_2O at room temperature for 20 h to give a complex which is effective as a catalyst for the Diels–Alder reaction of methyl vinyl ketone with 2,3-dimethylbutadiene in H_2O at 30 °C, to give 4-acetyl-1,2-dimethylcyclohexene in 66% yield (Scheme 56).[401,402]

Scheme 56



An analogous type of composite catalyst derived from the same β-cyclodextrin–epichlorhydrin copolymer, but containing this time encapsulated tris(perfluorobutanesulfonyl)methide yterbium salt, was found to act as a Lewis catalyst for the above Diels–Alder reaction in H_2O at 35 °C in 98% yield.[401,402] Complexes of palladium exhibiting Lewis acidity have also been anchored to high-surface-area silicate and used as heterogeneous catalysts for Suzuki cross-coupling.[403]

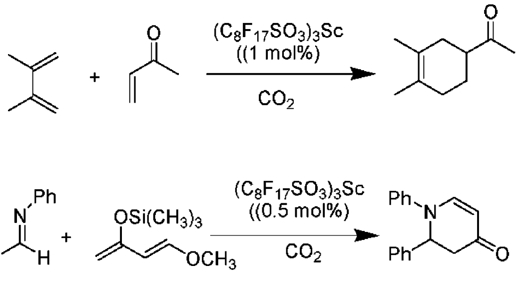


$$(F_3CF_2CF_2CF_2CO_2S)_3C{-}\underset{\displaystyle C(SO_2CF_2CF_2CF_2CF_3)_3}{\underset{|}{Yb}}{-}C(SO_2CF_2CF_2CF_2CF_3)_3$$

tris(perfluorobutanesulfonyl)methide yterbium

As in the case of ionic liquids and fluorous biphasic systems, there are also examples in which Lewis acid surfactants have been used not in aqueous media, but in supercritical CO_2.[404] In particular, scandium tris(heptadecafluorooctanesulfonate) in supercritical CO_2 can catalyze Diels–Alder reactions of carbonyl dienophiles with diene as well as hetero-Diels–Alder reactions of imines and dienes (Scheme 57).

Scheme 57



Although performing organic synthesis in an aqueous medium is a current challenge that will attract considerable attention in the forthcoming years,[405] from the point of view of green chemistry it would be even more convenient to avoid the use of any solvent.[6,406] The current status of solvent-free chemistry has been reviewed recently.[407−409] This approach appears to be particularly appealing when one reagent is a liquid and available in large quantities, such as aromatic hydrocarbons or aliphatic ketones. The latest advances in this area include aldol[410,411] and related reactions,[412] asymmetric-catalyzed addition,[413] and catalyzed cross-coupling reactions.[414−420]

H_2O-stable Lewis acid sites have been obtained by synthesizing metal zeolites in which the metal occupies framework positions. In this way, zeolites such as Ti and Sn zeolites and mesoporous materials are able to catalyze such reactions as epoxidations of olefins, hydroxylation of aromatics, hydroxyalkylation of aromatics, Baeyer−Villiger oxidations, and Meerwein−Pondorf reactions in aqueous media.

5. Characterization of Lewis Acids on Solid Catalysts

There is no doubt that it would be highly desirable to be able to synthesize solid Lewis acid catalysts in which the Lewis acidity could be tuned to cover a large number of reactions with different acid demands.

In the next sections, we will focus in the use of conventional Lewis acids supported on high-surface-area solids (section 6) or truly isotropic solid Lewis acids (section 7) as catalysts. Solid Lewis acids would contribute to overcoming many of the environmental limitations of homogeneous Lewis acids. For this reason, efforts have been made to prepare solid Lewis acids by directly supporting the homogeneous acids or by generating electron-deficient sites on the surface of the solid catalyst. Before commenting in detail on these solid acids, we will describe in this section the series of techniques available to determine and measure acidity in solids. It is worth noting that, while it is relatively easy to distinguish between Brönsted and Lewis acid sites by spectroscopic characterization techniques, a procedure to determine the softness/hardness of the Lewis sites apart from the test reaction commented in section 2 has not yet been developed. Softness/hardness determination in solids would most probably require a comparison of the adsorption of a series of basic probes differing in their softness/hardness character.

5.1. Thermoanalytical Techniques

Among the different thermoanalytical techniques available for characterization of solid catalysts, temperature-programmed desorption (TPD) is a frequent choice to measure acidity because of its simplicity. TPD involves the detection of molecules desorbed from a solid catalyst swept by an inert gas when the temperature of the sample is increased at a constant rate. The molecules desorbed at each temperature can be identified by mass spectroscopy and quantified by using a thermal conductivity detector.

In principle, TPD yields information on the states of binding of chemisorbed molecules as well as on the number of molecules bound in each state.[421,422] It appears then that the TPD of basic amines can give information on acid strength and total number of acid sites on solid catalysts. As basic probe molecules, NH_3 and amines are generally used. However, they adsorb on both Brönsted and Lewis acid sites, and unless this technique is coupled with spectroscopic techniques, it provides limited information of specific Lewis acid sites on solids.

5.2. Vibrational Spectroscopy Methods

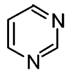
It is possible to identify and quantitatively determine acidic Lewis sites by IR, Raman, ESR, NMR, and XPS spectroscopies, using probe molecules such as NH_3, pyridine, carbon monoxide, NO, H_2, and phosphines.[423]

Pyridine adsorption combined with IR spectroscopy has shown that this probe molecule can serve to determine simultaneously the concentration of Brönsted and Lewis acid sites on solid catalysts.[424−428]

Furthermore, when IR is combined with thermal desorption, it also gives information about acid strength distribution. Pyridine coordinated to Lewis acids gives IR bands at ~1450 and 1620 cm^{-1}. Then, by measuring the intensity of those bands, and from the values of the extinction coefficients,[426,429,430] it is possible to calculate the total number of Lewis acid sites retaining pyridine at different desorption temperatures. Raman spectroscopy[431] can also be used in combination with adsorbed pyridine to specifically identify the pyridine coordinated with Lewis acid sites. In this case, Lewis acid and H-bonding sites can be estimated from the intensity of Raman bands near 1000 cm^{-1}.[432,433] The band position near 1000 cm^{-1}, which arises from the symmetric ring breathing mode of adsorbed pyridine, was found to shift linearly to a higher frequency as a function of the acid strength of the Lewis acids; consequently, pyridine adsorption coupled with Raman spectroscopy can also give information on Lewis acid strength.[434]

Other strong bases, such as quinoline and NH_3, can also be used in combination with IR to determine separately the surface concentration of Lewis acid sites, or at least to establish the relative concentration of those in a series of catalysts.[432,433] Strong basic molecules, however, adsorb strongly and therefore unspecifically even on the weakest acid sites. Consequently, weaker bases have also been used as probe molecules.

In this sense molecules such as 1,3-diazine (pyrimidine), CO, H_2S, H_2, and acetonitrile, among others, have been used to characterize Lewis acid sites on solid catalysts.[435−438]



pyrimidine

The IR spectra of 1,3-diazine and 1,4-diazine are not as informative as the spectrum of pyridine, but the spectrum of 1,3-diazine allows semiquantitative measurement of Lewis and Brönsted acid sites.[435]

Carbon monoxide has been used to investigate the strength and concentration of Lewis acid sites on the surface catalysts.[439−442]

If Lewis acidity is present, interaction between the Lewis site and the CO probe molecule occurs. For instance, in the case of γ-Al_2O_3, which presents a large amount of Lewis acid sites, the carbonyl IR band of CO adsorbed at 77 K and 20 Torr, after evacuation at 77 K, appears as a strong band at 2152 cm^{-1} with shoulders at 2140 and 2188 cm^{-1}.[443] The 2152 and 2140 cm^{-1} bands are associated with H-bonded and CO physically adsorbed,[444,445] and the 2188 cm^{-1} band, which shifts to 2196 cm^{-1} after evacuation, corresponds to a stable surface complex between a Lewis acid site and CO.[446]

The CO adsorption is also used to detect defect sites[447] and to see the effect of introducing anionic promoters on the Lewis acidity of solids. Besides CO, other probe molecules such as N_2[448,449] and deuterated acetonitrile can also be used to monitor Lewis acidity.[450−452] The use of H_2, as simple as it may seem, could also be worth pursuing.

Triphenylphosphine oxide has been proposed as a basic probe to compare the Lewis acid strength of several organotin dichlorides.[453] The parameter to be measured is the shift of the P═O frequency in the IR. Steric factors and the presence of electronegative substituents have been proposed to be largely responsible for the modulation of the acid strength at the Sn atom.[453]

5.3. Probe Molecules Combined with Nuclear Magnetic Resonance and X-ray Photoelectron Spectroscopy

MAS NMR techniques[454,455] have been extremely valuable for determining the Brönsted acidity of solid catalysts. This technique can be used to characterize acid sites directly through the ^1H NMR shift of surface hydroxyls, or indirectly through changes in the chemical shifts of the nuclei in various probe molecules. The acid strength of surface hydroxyl groups in solid acids can be correlated with the ^1H NMR chemical shift.[456] This correlation allows different types of Brönsted acid sites in zeolites to be distinguished.[457,458] However, theoretical calculations indicate that these correlations are applicable only for a series of similar solids.[459] The interaction of acid sites with probe molecules can be studied by measuring changes in the MAS NMR chemical shifts of nuclei such as ^{13}C, ^{14}N, and ^{31}P, and these can be used to characterize both Brönsted and Lewis acid sites.

The NMR technique can also be used to characterize the interaction of amines with Brönsted and Lewis acid sites.[460,461] Unfortunately, the chemical shift measurements are not sufficiently precise to separately quantify each type of acid site. On the other hand, Brönsted and Lewis acid sites can be better discriminated using trialkylphosphines and trialkylphosphine oxides as probe molecules and MAS ^{31}P NMR and CP/MAS NMR.[462−469]

Trimethylphosphine interacts with Brönsted acid sites to form $[(CH_3)_3PH]^+$ adducts that give ^{31}P chemical shifts at ~3 ppm and a J_{P-H} coupling constant of ~500 Hz. On the other hand, the ^{31}P atom of the trimethylphosphine−Lewis acid adduct site appears at considerably higher fields. Direct quantification of Lewis sites can be carried out by monitoring by MAS ^{31}P NMR the adsorption of the more stable trimethylphosphine oxide.[462,463] ^{14}N NMR spectra of adsorbed probe molecules such as N_2O allow the specific determination of Lewis acid sites.[470,471]

Basic probe molecules can also be used in combination with XPS technique to characterize surface acid sites.[472,473] For instance, the N_{1s} lines of ammonia adsorbed on the surface can be decomposed into two component peaks, assigned to Brönsted and Lewis acid sites. The relative area of the two peak components after deconvolution was measured for the quantification of Brönsted and Lewis acid site concentration.[474,475] The XPS technique has been very useful to characterize Lewis acid sites in materials that are difficult to characterize by other techniques, such as sulfated zirconia and tungsten/zirconia acid catalysts.[472,476]

5.4. Radical Cations as Probes of Lewis Acid Sites

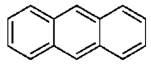
It is a well-documented fact that Lewis acids can abstract a single electron from electron-rich organic molecules having low oxidation potentials.[171] This electron transfer (eq 6) generates an organic radical cation, whose persistence depends on the intrinsic stability of the species (intramolecular reaction pathways) and on the nature of the medium and the presence of nucleophiles or oxidizing species. In some cases, the organic radical cation is persistent enough to be easily detectable by conventional spectroscopic techniques, including optical and ESR spectroscopies.[171]

$$M + LA \rightleftharpoons M^{\bullet +} + \underset{\text{(normally undetectable)}}{LA^{\bullet -}} \tag{6}$$

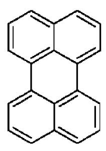
$$(LA = \text{Lewis acid})$$

The way in which Lewis sites act as single-electron acceptors is not yet fully understood. The transfer of a single electron from an organic molecule to conventional Lewis acids or to solids containing Lewis sites can serve to titrate the number and strength of electron acceptor sites associated with Lewis sites.[171] The determination of surface sites that act as acceptors of single electrons is based on the measurement of the spin population after adsorption of an excess of molecules which can easily donate one electron. No signal from the electron accepted by the solid is generally observed, and this has been taken as evidence of a complete delocalization through the solid. Probe molecules suitable for use as electron donors are polycyclic aromatic hydrocarbons such as anthracene,[477] perylene,[477] pyrene,[477] chrysene, phenothiazine, thianthrene,[478] diarylsulfides,[479] and arylamines.[480−486]

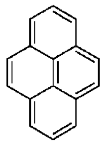
The number of one-electron acceptor sites can be estimated from the intensity of the EPR signals.[487] However, EPR as a quantitative technique requires the persistence of a steady population of the paramagnetic species and is problematic since a standard with a known amount of spin is needed. Unfortu-



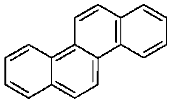
anthracene



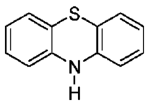
perylene



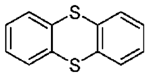
pyrene



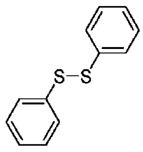
chrysene



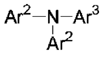
phenothiazine



thianthrene



diphenyldisulfide



$$\begin{array}{c}\mathrm{Ar^2{-}N{-}Ar^3}\\ |\\ \mathrm{Ar^2}\end{array}$$

triarylamine

nately, when a series of polycyclic aromatic compounds were adsorbed on alumina, it was found that a simple correlation between the ionization energies of adsorbed hydrocarbons and the number of the resulting ion radicals does not exist.[488] Today, a wide agreement exists on how to estimate qualitatively the strength of one-electron acceptor sites in solids. It is considered that the one-electron acceptor sites, which can form radical cations from adsorbed perylene in the absence of oxygen, are strong acceptor sites. On the other hand, those sites, which are able to generate perylene radical cation only in the presence of oxygen, are weak one-electron acceptor sites.

The formation of charge-transfer complexes between electron donors and the Lewis acid sites of the solid surface can also be investigated using optical spectroscopy, since formation of these complexes is associated with the appearance of a characteristic absorption band.[489] Given that the electron transfer is normally not complete, the charge-transfer complexes do not exhibit paramagnetic properties in their ground state, and consequently they cannot be observed by EPR spectroscopy. However, the formation of charge-transfer complexes provides useful information about the strength and distribution of the Lewis sites in the solid.

6. Heterogeneous Catalysts Based on Conventional Lewis Acids

6.1. Lewis Acids Supported on Solids

One way to convert corrosive strong Lewis acids into environmentally friendlier catalysts is to heterogenize soluble Lewis acids used in liquid-phase reactions by supporting them on high-surface-area solids such as graphite, Al_2O_3, SiO_2, zeolites, clays, etc. The type of material used as support frequently plays a crucial role in the performance of the resulting supported catalyst. Basically, the support has to be thermally and chemically stable during the reaction process and has to provide accessibility and a good dispersion of the active sites.[490]

Lewis acids such as $FeCl_3$, SbF_5, and aluminum halides can be intercalated between the layers of graphite, increasing the interlaminar spacing and yielding strong acid catalysts. Graphite possesses a highly anisotropic layered structure that is formed by sheets of sp^2 carbon atoms in hexagonal arrays with a C−C distance of 0.142 nm. The distance between the layers is 0.335 nm, and the layers are held together by weak van der Waals forces. The atomic layers are not directly superimposable but alternate in a stack pattern A−B−A−B.[491−493]

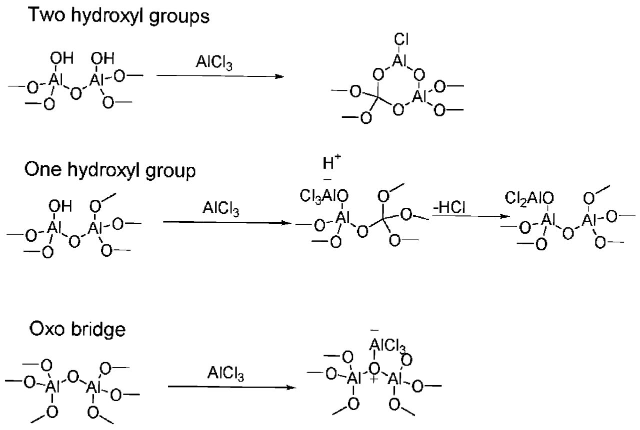
Following Olah et al.,[491] it appears that ions and neutral species enter the interlamellar space of graphite without modifying the layered structure. It has been shown by X-ray diffraction that, when the adsorption has reached equilibrium, a sequence of filled and empty interlamellar voids is favored. During the intercalation, there is a first stage in which all the interlamellar regions start being filled, whereas in subsequent stages, not all but one-half or one-third of the interlamellar regions is filled by the intercalant.[491]

The graphite intercalates can be prepared by heating graphite in the presence of a volatile Lewis acid. In some cases intercalation becomes easier, or at least the material has greater catalytic activity, if the preparation is carried out in the presence of a strong Brönsted acid, fluorine, or a transition metal compound. Highly fluorinated graphite can be prepared by reacting graphite with anhydrous liquid HF containing MoF_6 or SbF_5 as Lewis acid, the former being more effective.[494] The oxidative process takes place at temperatures between 8 and 18 °C. The C/F atomic ratio can be as low as 2.[494] While there is still discussion on the nature of the interactions between the graphite and the Lewis acid intercalated, there is some evidence that a charge-transfer complex is formed upon the intercalation of Lewis acids. Moreover, it appears that the ability of HF and F_2 to facilitate intercalation can be due to the formation of anionic species of the $AlFCl_3^-$ or $SbF_6^-/Sb_2F_{11}^-$ type inside the layers, the proton being the countercation.[495,496] Acetone adsorption monitored by IR spectroscopy has been used as a probe to assess the Lewis acid sites on the surface of carbon-supported catalysts before and after sorption of metal cations such as Ni^{2+}, Cu^{2+}, and Cr^{3+}.[497]

Conventional Lewis acids can be physisorbed, chemisorbed, or anchored on inorganic supports.[498] Strong Lewis acids and different halogenated agents have been supported on Al_2O_3. In the case of the most studied (and probably the most relevant) $AlCl_3$ on alumina, the Lewis acid strongly interacts with hydroxyl or even oxide groups at the surface of the alumina, forming new active sites with the possible alumina local structures (Scheme 58).[499]

Using IR spectroscopy, it has been found[499] that reactions of $AlCl_3$ with one or two hydroxyl groups resulted in complete disappearance of the surface hydroxyls. Further investigations using ESR and IR spectroscopy showed the presence of one-electron acceptor sites, and the absence of IR absorptions due to NH_4^+ after adsorption of NH_3, thus indicating the absence of Brönsted acid sites.

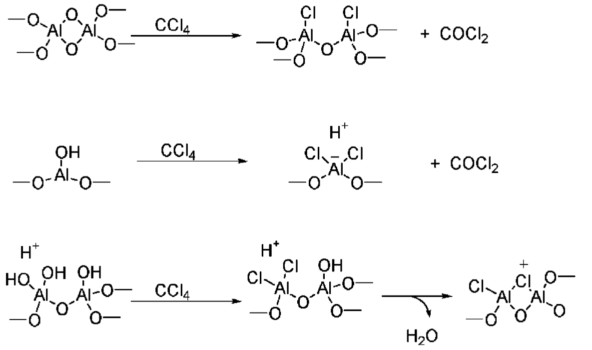
Scheme 58



Molten mixtures of aluminum and manganeous halides have been supported on alumina.[500] The fused salt is thought to be deposited on the carrier as a mixed double salt, perhaps as $Mn(AlCl_4)_2$-type species. The resulting catalyst has longer term stability and higher catalytic activity than supported $AlCl_3$.

The acidity of aluminas can be promoted by fluorination and chlorination. In this way, treatment of alumina with aqueous solutions of ammonium bifluoride leads to incorporation of fluoride into the solid. If the resulting sample is subjected to an adequate calcination temperature (600 °C), strong acid sites develop.[501] Alumina or alumina-supported group VIII metals (Fe, Co, etc.) can incorporate chlorine by treatment with CCl_4, producing strong acid catalysts that are used in the re-forming of *n*-paraffins. The chlorination of Al_2O_3 with CCl_4 has been proposed to occur in two steps, as indicated in Scheme 59.[502]

Scheme 59

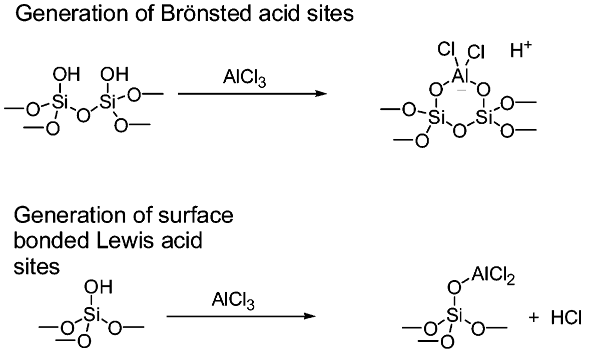


As Scheme 59 indicates, in the first stages the surface Al−O−Al species and isolated hydroxyl groups react with CCl_4, increasing the chlorine content to 7%. In subsequent steps, the number of surface OH groups decreases even further, and the Cl content increases to 14%. It is accepted that the strength of acid sites increases upon chlorination due to the inductive effect of electronegative chlorine atoms on acid sites in the neighborhood.

Fumed aluminas with metal oxides have been chlorinated[503,504] and fluorinated.[505−507] British Petroleum has succeeded in the fluoration of fumed alumina, but the surface areas of the resulting solids are very low. Ayame et al.[508] have prepared a strongly acidic chlorinated alumina by heat treatment of Al_2O_3 with Cl_2 gas at temperatures above 800 °C.

Catalysts based on supporting Lewis acids, particularly $ZnCl_2$, on acid-treated clays are commercially used as replacements for corrosive traditional acids for some Friedel−Crafts reactions.[509−517] Clark and co-workers have used mesoporous silicas to support $AlCl_3$.[518] The reaction of $AlCl_3$ with the silica surface in an aromatic solvent leads to a material with strong Brönsted and Lewis acidity (Scheme 60).[519]

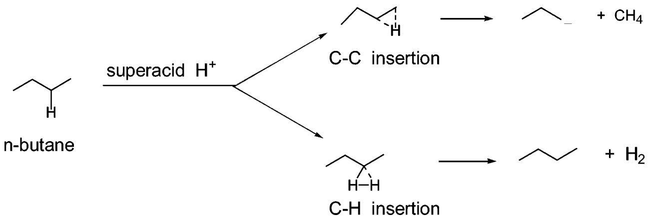
Scheme 60



Direct reaction of BF_3 with the silica surface renders a material that does not exhibit Lewis acidity due to the strength of the B−O bonds.[518] In contrast to the direct adsorption, when BF_3 is physisorbed on mesoporous silica (4 mmol g^{-1}) from its ether or aqueous solution, pyridine characterization of the resulting BF_3/SiO_2 reveals the presence of both Brönsted and Lewis acid sites.[520] The Brönsted/Lewis ratio depends on the solvent used and the adsorption conditions. The use of ethanol to adsorb BF_3 has been studied in detail.[521] Besides protonated ethanol, Brönsted acid sites also come from polarization of the surface hydroxyl groups interacting with BF_3. Ethanol desorption and surface dehydroxylation by heating at 400 °C renders a BF_3/SiO_2 solid with predominant Lewis acid character.

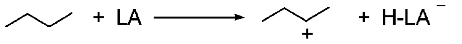
The absence of Brönsted sites on many of the $AlCl_3$/aluminas and halogenated aluminas and the presence of Lewis acid sites suggest that the last type of centers are the actual active sites for some carbocation reactions. For instance, when *n*-butane is reacted with very strong (or even superacid) Brönsted acid catalysts, methane and H_2 are obtained as reaction products (Scheme 61). However, when Hattori[522] reacted *n*-butane at room temperature in the presence of a SbF_5-treated amorphous silica−alumina, no H_2 evolved, and only a small initial amount of methane was detected. Sommer and co-workers have also extensively used H/D exchange of

Scheme 61



alkanes to demonstrate the superacidity of solid acids.[523−525]

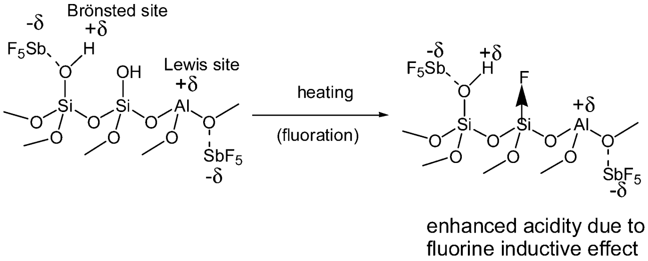
Moreover, the catalyst on which the surface OH groups were isotopically exchanged with deuterium and converted into OD groups forms no CH_3D. These results suggest that Lewis acids, via formation of secondary carbenium ions, could initiate the reaction by hydride abstraction (eq 7). Further evidence in support of a hydride abstraction mechanism for Lewis acids has been obtained from a study with perdeuterated substrates.[526]



(7)

The active sites present on SbF_5-treated amorphous silica alumina have been described as indicated in Scheme 62.

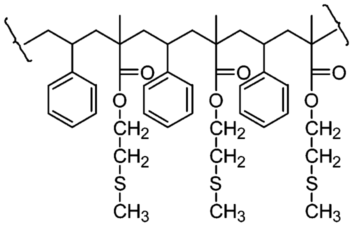
Scheme 62



It has been observed that the gas-phase adsorption of BF_3 on alumina and aluminosilicates is much stronger than that of ammonia as Lewis base.[527] This has been interpreted as indicating the presence of a significant density of basic sites on the surface of alumina.[527] Impregnation of alumina with BF_3 at low temperatures yields a material that has activity toward alkylation of isoparaffins with olefins.[528] Isobutane and *tert*-2-butene react in the presence of BF_3-promoted γ-alumina catalysts to give 95% C_8 products.[528] This type of catalyst can be regenerated by calcination to desorb and decompose the reaction poisons adsorbed on the solid.[529] By studying the cracking of cumene on doped alumina, it was observed that, besides the necessary acid centers for cracking, basic sites on the surface play a positive influence.[527]

A Pt/alumina catalyst without OH groups but with very strong acidities has been prepared by chemical vapor deposition (CVD) techniques.[530] Two catalysts were prepared: one in which $PtCl_2$ was deposited by CVD onto vacuum-dehydrated Al_2O_3 (CVD-$PtCl_2/Al_2O_3$) and a second in which $PtCl_2$ was deposited by impregnation ($PtCl_2$/impregnated Al_2O_3). The two catalysts were activated under the same conditions (500 °C, H_2) before the IR spectra were recorded. The CVD-$PtCl_2/Al_2O_3$ sample does not show IR hydroxyl bands at 3676 cm^{-1}, while the sample prepared by impregnation does show the presence of OH groups. Moreover, the pyridine adsorption titration method for the CVD-$PtCl_2/Al_2O_3$ catalyst gives only the pyridine band at 1450 cm^{-1}, associated with Lewis acids.

Polymer-supported catalysts have been widely used in synthesis.[531] For instance, esterification reactions, such as the reaction of acetic acid with butyl alcohol[532] and the ring aperture of epoxycyclohexane to 1,2-cyclohexanediol,[533] can be catalyzed using strongly acidic cationic exchange resins impregnated with $SnCl_4$. $SnCl_4$ has also been anchored to ion-exchange resins containing tetraalkylammonium chloride side chains and also found to be active for the Prins condensation of isobutene and formaldehyde.[534] Likewise, vinyl ethers can be polymerized in increased yields by using as catalyst BF_3, $SnCl_4$, or $SnCl_2$ bound to a partially cross-linked copolymer of butyl acrylate, acrylonitrile, acrylic acid, and methylol acrylamide.[535] Neodymium chloride has been supported in poly[styrene-*co*-2-(methylsulfenyl)ethyl methacrylate] and used in combination with tris(isobutyl)aluminum in butadiene polymerization.[536]

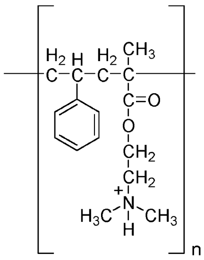


poly[styrene]-co-2-(methylsulfenyl)ethyl methacrylate

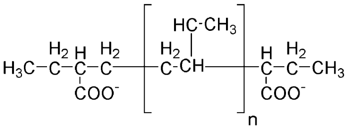
Modification of Amberlyst 15 and Nafion with BF_3 increases their acidity.[537] The result of this acidity increase is an activity increase and a change in their selectivity toward the alkylation of benzene and isoparaffins with light olefins.[537] $AlCl_3$ has also been supported on beds of macroporous, sulfonated polystyrene−divinylbenzene copolymer, generating strong acid sites.[538,539] Sublimed $AlCl_3$ in a stream of N_2 was passed through the macroporous beads of the polymer at 110 °C. HCl was liberated, and the resulting polymer has a S:Al:Cl ratio of 2:1:2, the Al and Cl being uniformly dispersed through each polymer bed. Very strong acid sites were developed, but unfortunately the polymer is degraded.

Polymer chains may define capsules in which mass transfer can occur through the polymer fibers, which may also undergo swelling upon contacting with certain organic solvents. On this basis, a solid catalyst in which $AlCl_3$ has been encapsulated within insoluble polymer walls has been prepared.[540] The polymer walls were formed by the reaction of poly(styrene-*co*-dimethylaminoethyl methacrylate) and hydrogenated telechelic polybutadiene containing COOH groups. The encapsulated $AlCl_3$ is active as a catalyst for the Friedel−Crafts alkylation of benzene with dodecene.[540] The alkylbenzenes were obtained in excellent yields, and the encapsulated $AlCl_3$ catalyst is separated by simple filtration.

These few examples serve to illustrate the vast applicability of polymer-supported Lewis acids. In-depth reviews describing recoverable catalysts based on anchoring the active sites (not only Lewis acids) on a polymer backbone (either insoluble or soluble) have been recently published.[541,542] Nevertheless, catalysts based on high-surface-area inorganic solids may have advantages due to the higher chemical and thermal stability of the inorganic solid and better rates of molecular diffusion through the support.[518,543,544]



poly(styrene-co-dimethylaminoethyl methacrylate)



hydrogenated telechelic polybutadiene

Mixtures of $AlCl_3$ with dehydrated metal salts such as $Ti(SO_4)_3$, $CuSO_4$, $CuCl_2$, and $TiCl_3$ in dry nitrogen atmosphere show very strong acidities.[545–548] The best-studied mixtures were $AlCl_3$–$CuSO_4$ and $AlCl_3$–$CuCl_2$. The catalytic activity of $AlCl_3$–$CuSO_4$ was found to be proportional to the amount and surface area of $CuSO_4$.[548]

In the mixtures of $AlCl_3$–$CuCl_2$, XRD revealed the formation of $Cu(AlCl_4)_2$. This mixture showed high catalytic activity for carbocation reactions. The high catalytic activity of mixtures of aluminum trihalide with metal sulfates and copper dichloride in *n*-pentane isomerization is due to the presence of strong Lewis acid sites.[545,546,548]

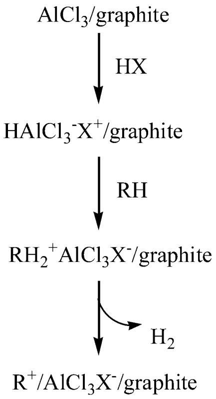
6.2. Catalytic Activity of Supported Lewis Acids

Lalancette et al.[549] have studied graphite–$AlCl_3$ intercalates as catalysts for Friedel–Crafts-type reactions, and more specifically for the alkylation of benzene with ethyl bromide and ethylene. Compared to pure $AlCl_3$, the intercalated solid is less active but more selective, giving fewer polyalkylated products.

An aluminum halide/hydrogen halide/graphite intercalation material is able to isomerize cycloparaffins at low temperatures.[550] There, the $AlCl_3$–graphite intercalate is treated with a liquid mixture of HF and “isomerizable cycloparaffin” in order to give the active form of the catalyst. This treatment may very well form the first intercalated carbonium ion that will intervene in the carbocation chain mechanism as a hydride acceptor (Scheme 63).

Rodewald has shown[551–553] the activity and selectivity of graphite Lewis acid intercalates for the alkylation and isomerization of normal paraffins. Brönsted acids and some transition metals can act as promoters, while addition of Pt metal decreases catalyst decay and improves activity and selectivity. Le Normand et al. have studied the catalytic activity of SbF_5 intercalated in graphite for the cracking and isomerization of methylpentanes.[554,555] A general problem that occurs with acid catalysts intercalated in graphite is that leaching of the acid can occur, and in this case a true heterogeneous catalytic process cannot be claimed. Indeed, Freeman and Goh have shown[556] that a slow release of Lewis acid from the catalyst into the reaction mixture occurs when $AlCl_3$–graphite catalyst is used for the formation of cyclohexylbenzene by the Friedel–Crafts reaction between benzene and cyclohexene. The amount of product formed is due to the amount of $AlCl_3$ extracted from the catalyst. Retention of substantial amounts of Lewis acid in the spent catalyst may reflect blockage of the intermellar regions due to hydrolysis or other forms of $AlCl_3$ decay and poisoning.

Scheme 63



Likewise, leaching of the Lewis acid has been investigated for cracking and isomerization of methylpentanes in the presence of SbF_5–graphite. The behavior of this catalyst was equivalent to that of a low concentration of SbF_5 bled into the liquid phase, suggesting that at least part of the SbF_5 was leached and the activity is not actually due to the graphite intercalated but rather to the fraction of SbF_5 diffused into the solution and that present at the exposed surface area.

$AlCl_3$ immobilized in mesoporous MCM-41 silica shows high catalytic activity for the Friedel–Crafts alkylation of naphthalene with 2-propanol, exhibiting at 85% naphthalene conversion a selectivity toward diisopropylnaphthalenes of 72%, of which 61% is the most important 2,6-isomer.[557] Although it is mentioned that the system can be reused without loss in activity or selectivity, no data about the number of reuses was given.[557] $AlCl_3$ supported on MCM-41 is a suitable solid catalyst for the Friedel–Crafts alkylation of benzene with normal 1-olefins.[519] The activity of the supported $AlCl_3$ is similar to that of unsupported $AlCl_3$, but the selectivity toward monoalkylbenzene using $AlCl_3$ supported on MCM-41 depends significantly on the chain length of the 1-olefin (Table 6).[519] Moreover, each MCM-41 of a series differing in the pore dimension exhibits an optimum selectivity in the linear monoalkylation of benzene for a certain chain length of the 1-olefin that best suits the pore size. MCM-41-immobilized $AlCl_3$ catalyst does not leach out during the alkylation and can be reused as long as it is not exposed to moisture.

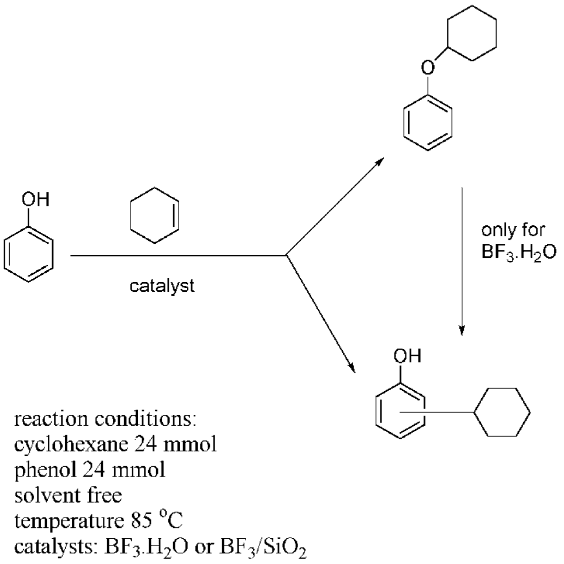
The activity of BF_3/SiO_2 toward the Friedel–Crafts alkylation of phenol with 1-octene[521] or cyclohexene[558] has been studied. A correlation was found between the activity of supported BF_3 and the number and strength of Brönsted acid sites. This work nicely illustrates that, while anhydrous BF_3 in inert solvents is a typical Lewis acid, the assumption that the nature of the acid sites remains the same when

Table 6. Results for the Linear Alkylation of Benzene with 1-Alkenes Using Unsupported (Pure $AlCl_3$) or MCM-41-Supported ($AlCl_3$@MCM-41) $AlCl_3$ as Catalysts under the Same Experimental Conditions

		selectivity (%)	
catalyst	alkene	linear monoalkylated	others
pure $AlCl_3$	1-hexene	58.6	41.4
	1-octene	66.0	34
	1-decene	68.5	31.5
	1-dodecene	72.5	27.5
	1-tetradecene	70.1	29.9
	1-hexadecene	77.5	22.5
$AlCl_3$@MCM-41	1-hexene	79.9	20.1
	1-octene	79.7	20.3
	1-decene	91.1	8.9
	1-dodecene	96.2	3.8
	1-tetradecene	98.5	1.5
	1-hexadecene	>99	<1.0

supported or in the presence of moisture may be misleading. In fact, comparison of the activity and selectivity of $BF_3{\cdot}H_2O$, either unsupported or supported on silica, for phenol alkylation with cyclohexene establishes a remarkably different product distribution.[559] The heterogeneous catalyst forms ether products with a high selectivity that is maintained throughout the reaction, while in the homogeneously catalyzed reaction ethers are primary but unstable products (Scheme 64). When the soluble BF_3 catalyst is used, the yield of O-alkylated compounds reaches a maximum and then decreases as the reaction proceeds, with a concomitant increase in the yield of aromatic C-alkylated products (Figure 1).

Scheme 64



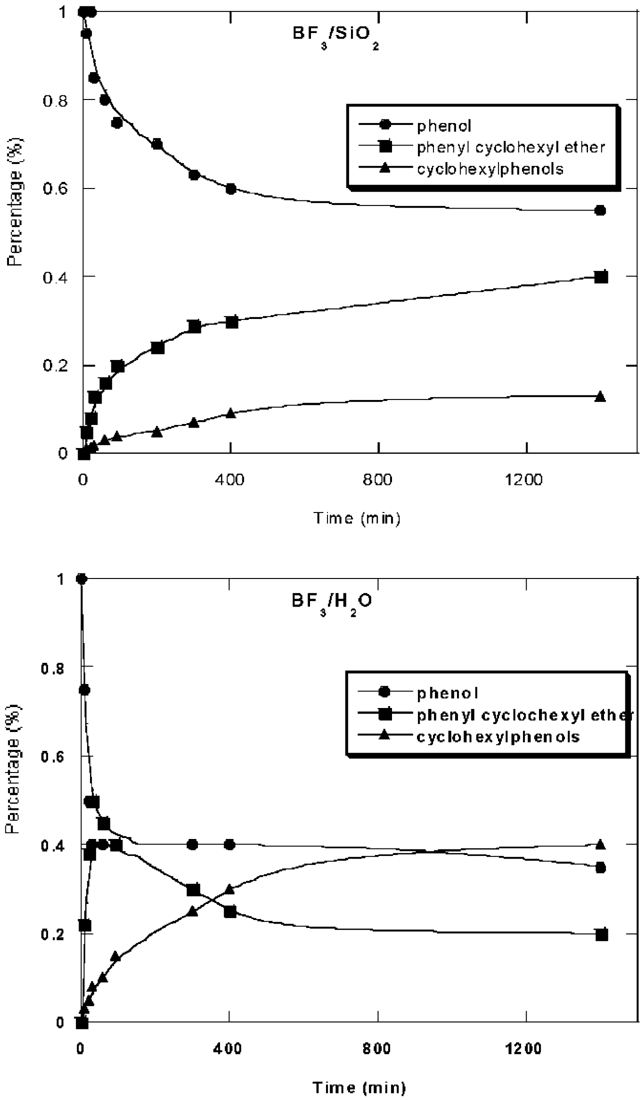


Figure 1. Time–conversion plots for the reaction of cyclohexene and phenol catalyzed by SiO_2-supported BF_3 (upper plot) or by BF_3/H_2O (lower plot). Reaction conditions: cyclohexene and phenol, 24 mmol at 85 °C without solvent. Reprinted with permission from ref 559. Copyright 2000 Elsevier.

Anchoring $SnCl_4$ on silica functionalized with organic quaternary ammonium chloride renders a solid in which the pentacoordinated anionic $SnCl_5^-$ species is formed (Scheme 65). The resulting ionic pair $[NR_4^+][SnCl_5^-]$ resembles an ionic liquid exhibiting "latent acidity" (see eq 4), except that the organic cation is covalently bound to silica. An analogous $AlCl_3$ system in which an imidazolium melt is covalently anchored on the MCM-41 silica walls has been described earlier in the section devoted to ionic liquids.[345,346,348,349] The $SiO_2-NR_4^+[SnCl_5^-]$ catalyst has been found to be active for the Prins reaction of isobutene and paraformaldehyde (Scheme 65).[560] Furthermore, the selectivity toward the desired 3-methyl-3-buten-1-ol, which is a valuable building block for the synthesis of terpenes, largely improves with respect to that of the reaction with unsupported $SnCl_4$. The anchored $SnCl_5^-$ catalyst was reused three times with a very minor decrease in conversion and selectivity (Table 7).[560] No bleeding of tin(IV) from the solid to the solution was observed. Simple adsorption of tetrapropylammonium tin pentachloride exhibits somewhat lower catalytic activity (TON 7.3) than the anchored analogue (8.0).[560]

$InCl_3$ has also been impregnated on mesoporous MCM-41 and the resulting $InCl_3$–MCM-41 solid ($InCl_3$ loading 20 wt %) used as a moisture-insensitive catalyst for the benzylation of benzene[561] and acylation of benzene and other aromatic compounds

Scheme 65

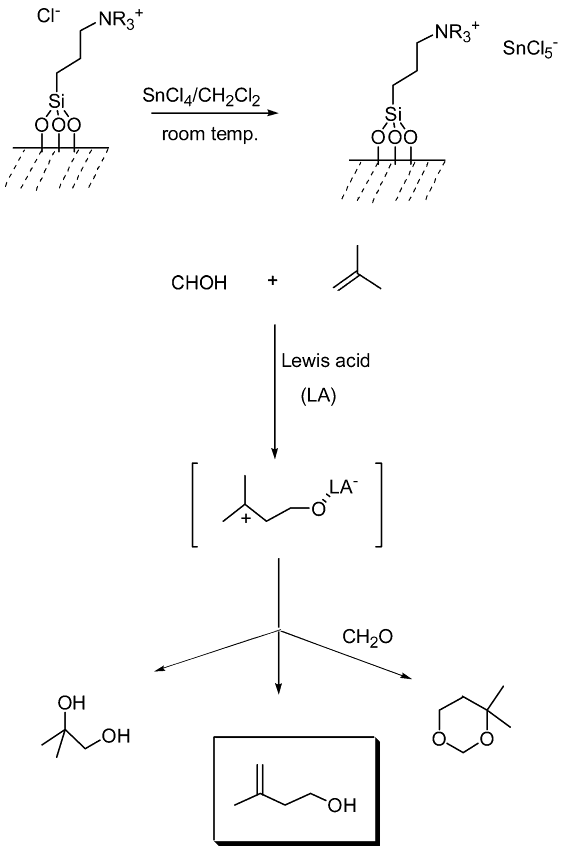


Table 7. Prins Condensation of Isobutene and Paraformaldehyde in Chloroform at 60 °C after 2 h Reaction Time in the Presence of Tin(IV) Chloride Catalysts[a]

catalyst	formaldehyde conversion (%)	3-methyl-3-buten-1-ol yield (%)
none	0	
$SnCl_4$	97.4	54.6
SIL-$NR_4^+SnCl_5^-$ [b]	64.6	92.8
recycle 1	63.3	91.1
recycle 2	61.9	91.0

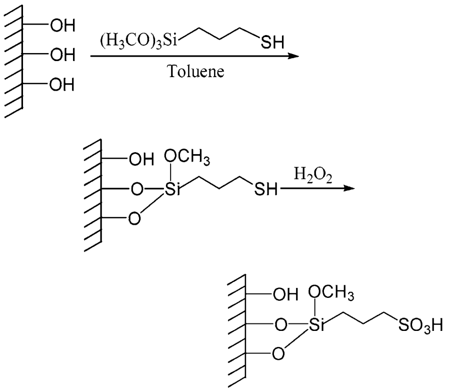
[a] Data taken from ref 560. [b] SIL-$NR_4^+SnCl_5^-$ is tripropylammoniumpropylsilyl anchored on silica, acting as a heterogeneous catalyst.

in dichloroethane.[562] The acylation yields for benzene were much higher than those reported for the same reactions using as catalysts clayzinc,[563] HBeta zeolite,[564] or In_2O_3−MCM-41.[561] It has been proposed, however, that the moisture insensitivity arises from the fact that the acylation is not Lewis acid catalyzed, but it is a redox process. This speculation would need to be supported by a mechanistic study.

As mentioned above for supported Lewis acids, the Brönsted acidity of mesoporous molecular sieves can also be strongly enhanced by grafting sulfonic acid groups to the inorganic surface. A procedure for doing this involves the reaction of silanols with silylating agents having a terminal thiol group. After grafting, this thiol group can be oxidized by H_2O_2 into a sulfonic acid (Scheme 66).[565−567]

Mesoporous sulfonic acids have been successfully applied to D-sorbitol dehydration−esterification, forming isosorbide dilaurate, the liquid biphase preparation of monoesters starting from various polyols and fatty acids,[565] and for the tetrahydropyranylation of ethanol with 2,3-dihydropyran.[568] It has to be noted, however, that the acid strength of these covalently bound sulfonic groups is lower than that of Nafion sulfonic resins, since in the latter the sulfonic group is attached through perfluorinated chains. In this regard, it would be interesting to prepare a hybrid MCM-41/perfluoroalkylsulfonic acid analogous to Nafion.[569]

Scheme 66



$AlCl_3$ supported on alumina or halogenated Al_2O_3 presents strong acid sites and has been used to carry out carbocation reactions from hydrocarbons at low and moderate temperatures. For instance, alkanes and alkenes undergo isomerization at temperatures between 0 and 150 °C in a static reactor in the presence of alumina containing Pt-supported $AlCl_3$. $AlCl_3$ in combination with manganous halides on alumina is active for the skeletal isomerization of alkanes at 82−113 °C in the presence of H_2. AlF_3 supported on Al_2O_3−Cr_2O_3 has been prepared by treatment of the support with CF_3Cl.[570−572] The CF_3Cl-treated Al_2O_3−Cr_2O_3 converts methanol to olefins. In this catalyst the F component was predominantly bound to Al but not to Cr. Al_2O_3 treated with CF_3Cl at 400−420 °C in a recirculation reactor produced a material that was active for the isomerization of butane, pentane, and hexane at temperatures as low as 0 °C. XPS analysis indicates that the active catalyst was AlF_3 formed on the Al_2O_3. This catalyst was active for reactions of benzene with compounds containing the CF_3 group, for instance $CF_3CH{=}CH_2$, CF_3COCF_3, etc.[573] When the same CF_3Cl treatment was carried out with H^+−Mordenite, an enhancement of the activity for isomerization of xylenes, isomerization of *o*-chlorotoluene, and alkylation of chlorobenzene with CH_3OH was observed.

Alumina fluorinated by ammonium bifluoride or ammonium fluoride is active for the isomerization of *o*-xylene at 440 °C, cracking of cumene at 320 °C, dehydration of 1-butanol, and hydroisomerization and hydrocracking of alkanes at 300 °C.[574,575]

Chlorinated alumina is the acid component of *n*-alkane re-forming catalysts. Chlorinated Al_2O_3, prepared by CVD techniques, is also able to alkylate benzene with propylene at room temperature, while benzene alkylation with methanol was, on the other hand, observed at 200 °C.[530] Cl_2 at 800 °C is also able to chlorinate Al_2O_3, giving rise to catalysts that are active for isomerization of short-chain alkanes at low temperatures due to the presence of the very strong Lewis acids formed in the chlorination procedure.[530]

Al_2Cl_6-treated oxides such as SiO_2, Al_2O_3, B_2O_3, TiO_2, and MgO were shown to be active for conversion of *n*-hexadecane to propane, butane, and isobutene at 100 °C.[576]

In summary, it appears that Lewis acids supported on solid carriers are very active catalysts for catalyzing carbocation-type reactions. They show very strong acidities and have the advantage with respect the nonsupported Lewis acids of their easy recovery. Moreover, when bifunctional acid−noble metal catalysts are prepared, long catalyst lifetimes and good selectivities are obtained. Unfortunately, these catalysts are very sensitive to water. Even the presence of a few ppm of H_2O in the reaction medium produces the gradual hydrolysis of the supported Lewis acid, with the corresponding production of HF or HCl and their associated problems of catalyst decomposition, formation of Brönsted acids, and reactor corrosion. As was said above for the case of Lewis acids intercalated in graphite, any catalyst containing supported Lewis acids should be surveyed for leaching when being used in liquid-phase reactions.

7. Solid Catalysts Exhibiting Lewis and Brönsted Acid Sites

7.1. Alumina

Aluminas can show the presence of Lewis acid sites when they are calcined at temperatures above 450 °C. Under these conditions, surface protons and aluminum cations become mobile and start to change their position in the lattice.

Upon calcination, new defects called “surface configurations of low probabilities” are generated.[577] These defects are multiple anionic vacancies, formed by three or more Al^{3+} cations in close proximity, that can act as Lewis acid sites. As mentioned above, those sites are formed at high calcination temperatures, and this has been proved by their ability to generate radical cations upon adsorption of perylene and phenothiazine.[482−484] Indeed, for these two probe molecules, the maximum in the generation of surface radical cations was observed when the alumina was calcined at temperatures above 450 °C.

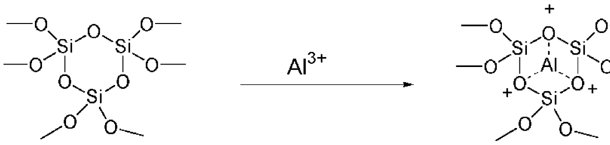
The presence of a large amount of Lewis acid sites in calcined γ-Al_2O_3 has also been deduced from the variations in the wavenumber of carbonyl IR bands of CO adsorbed at 77 K and 20 Torr. A band at 2188 cm^{-1}, which shifts to 2196 cm^{-1} upon evacuation, has been correlated to CO interacting with Lewis acid sites.[443−446,578,579]

7.2. Amorphous Silica–Alumina and Other Mixed Oxides

After the work of Thomas, it was shown that the activity of silica for hydrocarbon cracking was negligible, alumina giving only very low activity.[580] However, the efficiency of hydrocarbon cracking was greatly enhanced when both oxides were combined from hydrogels to form mixed oxides. Thomas explained this activity increase by assuming that alumina in active silica−alumina is in the tetrahedral configuration and a proton is associated with the alumina tetrahedron. In other words, he already claimed that amorphous silica−alumina presented Brönsted acidity and this was responsible for cracking carbon−carbon bonds. The acidity of these materials was more precisely explained by Tanabe through the following two postulates: (a) “the coordination number of a positive element of metal oxide, C1, and that of a second metal oxide, C2, are maintained even when mixed”, and (b) “the coordination number of a negative element (oxygen) of a major component oxide is retained for all the oxygens in the binary oxide”.[581]

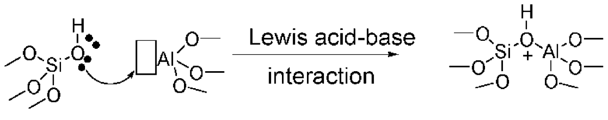
In this way, if a silicon atom is replaced by tetrahedral aluminum, the AlO_4 part is unbalanced electrically, and a negative charge appears that should be compensated by a proton. An alternative interesting model for the acid centers of amorphous silica−alumina catalysts has been proposed by researchers from EXXON,[582] who proposed that a three- or four-member ring structure of SiO_2 reacts with Al ions that become inserted inside the ring of Si atoms (Scheme 67).

Scheme 67



This expanded ring structure is proposed to be the local structure responsible for acidity. When more detailed theoretical work was done on silica−alumina clusters, it was found that the hydrogen atom of the hydroxyl group became protonic by coordination of the oxygen to an Al atom of the silanol (Scheme 68).

Scheme 68



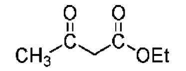
The coordination of the Al to an O atom corresponds to a Lewis acid−base interaction, and the stronger the interaction, the stronger the Brönsted acid strength of the O-associated hydrogen.[583,584]

All the previous proposals could be summarized by saying that Brönsted acid sites of binary silica−alumina oxides are bridged hydroxyl groups and water molecules coordinated on a trigonal aluminum atom.[585]

We note that all the above work has concentrated on the Brönsted acidity of the mixed oxides. However, these materials also present Lewis acidity, and this could be evaluated theoretically through the LUMO energy of the mixed oxide. However, it should be taken into account that the LUMO energy as a measure of Lewis acidity can be used only for comparing Lewis sites of the same central atom in the same valence state and with the same coordination number. Lewis acid sites of silica–alumina are related to coordinatively unsaturated Al species formed upon dehydration at high calcination temperature. The Brönsted and Lewis acidities of silica–aluminas have been extensively investigated by the whole array of the different physicochemical techniques and probe molecules described before.[430,586–592]

For instance, when an anhydrous silica–alumina catalyst was studied with pyridine in different conditions, it was found that the sample contains both Brönsted and Lewis acids. Moreover, the concentration of the Lewis acid sites increases at the expense of the Brönsted sites as the temperature of activation increases.[593] This depletion of Brönsted sites in favor of the Lewis sites is even more pronounced if the samples are steamed.[594]

The most common methods of preparation start from a silica hydrogel with an aluminum sulfate solution in which the aluminum salt is hydrolyzed and precipitated by the addition of aqueous ammonia. In another type of preparation, a co-gel is formed starting from sodium silicate and sodium aluminate. Silica–alumina aerogels and xerogels can be made by a sol–gel process. The drying can be done by supercritical CO_2 or by solvent evaporation. The formation of Si–O–Al bonds, and consequently the formation of Brönsted acid sites, was maximized by chelating the Al precursor with ethyl acetoacetate.[595]



ethyl acetoacetate

Silica–alumina-type clusters can also be formed by grafting silicon alkoxides on δ-alumina.[596,597] It has been shown that the modification of δ-Al_2O_3 with silica leads to creation of both highly acidic Brönsted and Lewis acid sites. The former are generated by isomorphous substitution of Si^{4+} by Al^{3+} in tetrahedral coordination and the latter through formation of tricoordinated Al bound to silicon through oxygen bridges. The relative strength and quantity of these sites reaches a maximum with 40 wt % SiO_2 content, above which the surface of the solid became SiO_2-coated and exhibited acidity approximating that of pure SiO_2.[598]

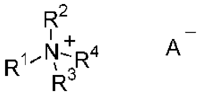
CVD techniques have been employed to coat alumina with $Si(OEt)_4$ in an air and nitrogen atmosphere. By controlling the time and temperature of SiO_2 deposition, a maximum in acid strength at ~14 wt % of SiO_2 has been found to occur. This sample obtained by CVD gave catalytic activity identical to that of commercial silica–aluminas, indicating that in this case availability to reactants of the acid sites located at the outermost layers of the oxide particles can play a major role.[599,600] In principle, one may think that the final properties of the amorphous silica–alumina prepared by CVD of a silicon source on alumina may depend on the surface characteristics of the support. This was studied by Megiris and Glezer, who deposited layers or films in a way that allowed precise control over the growth process during the CVD deposition process on dense α- and δ-alumina.[601] It was demonstrated that the morphology of the support, either α or δ, affects the nanolayer morphology. During CVD, SiO_2 clustering and aggregation occurs even at low Si loading. ^{29}Si MAS NMR showed that, at lower coverages (1.3–4.2 SiO_2/nm^2) bands at −80 to −85 ppm appear which correspond to Si with attached −OAl groups. At the highest level (8.2–17.5 SiO_2/nm^2), the deconvoluted spectrum shows peaks at −108, −100, and −92 ppm. These peaks correspond to $Si(OSi)_4$, $Si(OSi)_3OH$, and mixtures of $Si(OSi)_2(OH)_2$ with OAl^--containing species. Using PMe_3 as probe molecule, a maximum concentration of Brönsted sites was observed at a coverage of 8.2 SiO_2/nm^2 at the same time that the Lewis acid concentration fell to <0.1.[602]

An increase of the SiO_2 coverage leads to a decrease of the amount of Lewis acids, while the area of the Al_2O_3 covered by SiO_2 initially increases linearly with the amount of deposited SiO_2. The acid sites formed initially become eventually covered by SiO_2, leading to a remarkable decline in the amount of Brönsted acidity at higher SiO_2 coverages. In principle, no acidity at all should be expected for a perfect and complete coverage of the Al_2O_3 crystals by a deposition of a multilayer of SiO_2. Despite the sophistication and cost of the CVD preparation methods, the catalytic performance of these materials for acid-catalyzed reactions gives, at the most, the same results that samples commercially prepared by co-gel procedures; therefore, CVD techniques remain limited to structural studies.

Amorphous silica–alumina preparation conditions and the Si/Al ratio have a strong influence on the total acidity as well as on the Brönsted-to-Lewis ratio. Another preparation method involves the modification of surface properties of alumina by silica and silica by alumina layers deposited by the technique of atom layer epitaxy. The resulting material presents both Brönsted and Lewis acid sites.[603]

7.3. Amorphous Silica–Alumina Molecular Sieves

Following the acidity models established for amorphous silica–alumina, it could be expected that a maximum number of acid sites, at least of the Brönsted type, should be obtained when all Al is tetrahedrally coordinated. Moreover, site accessibility and diffusion should also be improved if bottlenecks in the pores are avoided by preparing amorphous silica–alumina with a regular pore size distribution in the range of mesopores. To prepare such type of silica–aluminum, the co-gel synthesis has been carried out in the presence of tetraalkylammonium cations that on one hand should avoid forming Al_2O_3 islands and on the other hand, by changing the size of the tetralkylammonium cation, can change the size of the pores.[604]



tetralkylammonium salt

In this type of synthesis, all NMR-observable Al atoms are initially tetrahedrally coordinated for the as-synthesized materials. However, after calcination, both tetrahedrally and octahedrally coordinated Al exist, giving Brönsted and Lewis acid sites, respectively.[605]

When used as catalysts, amorphous silica–alumina molecular sieves were able to substitute $AlCl_3$ as Friedel–Crafts catalysts for performing cracking or isomerization of paraffins. When tetrapropylammonium hydroxide was used as the tetralkylammonium salt in an alkali-free synthesis mixture, in a Si/Al ratio larger than 60, a precursor of ZSM-5 was obtained that presented a narrow pore size distribution in the range of 3.0 nm.[606] This material, after calcination, was active and selective for reactions such as cracking, hydrocracking, and hydroisomerization of paraffins, as well as for olefin oligomerization.[607] The problem with these porous silica–alumina is structural stability. While silica–aluminas prepared with tetraalkylammonium molecules are stable upon calcination, their pore structure collapses if they are subject to steaming.

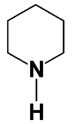
A series of materials, such as MCM-41 and MCM-48, with a regular pore size distribution in the mesoporous range were obtained by Beck, Kresge, et al.[608–611] by carrying out the synthesis in the presence of surfactants. Silica and silica–alumina condense around self-assembled surfactant, and mesoporous structures with different long-range orders (hexagonal, cubic, laminar) are obtained. Today, mesoporous molecular sieves structures have been obtained for a large number of different oxides and surfactants.[612–618] Similar types of materials were also obtained by using surfactants and a solubilized silica source. In this way, the ordered mesoporous FSM-16 has been obtained from kanemite by ion-exchanging interlayer sodium ions of the layered silicate for surfactants. The advantage of kanemite for carrying out this synthesis derives from the fact that this layered material is extremely flexible, owing to the relatively low number of tetrahedra in its structure. Then, upon intercalation with the surfactant, the flexible sheets of kanemite are folded and cross-linked to each other to form a three-dimensional framework.[619–621]

Acidic mesostructured materials MCM-41 and MCM-48 with silica–alumina walls were also synthesized.[622–626] Si/Al ratios as low as 2 have been achieved with the Al in tetrahedral coordination (Al^{IV}). However, after subsequent calcinations at 500 °C, the intensity of the NMR peak corresponding to Al^{IV} decreases while Al in octahedral coordination (Al^{VI}) is formed.[624,627] The presence of Al^{IV} and Al^{VI} leads to anticipate that these materials should present both Brönsted and Lewis acid sites upon calcination. Indeed, Brönsted and Lewis acidity was determined on MCM-41 by pyridine adsorption.[625] The strength of the acid sites of a mesostructured MCM-41 sample is similar to that of a conventional amorphous silica alumina and falls in the range of mild acid sites.

7.4. Activity of Amorphous and Mesostructured Silica–Alumina for Acid-Catalyzed Reactions

It was stated above that δ-Al_2O_3 has only Lewis acid sites, while the incorporation of silica and formation of amorphous silica–alumina introduces Brönsted sites, even though the acid strength of these Brönsted sites corresponds to that of 50% aqueous H_2SO_4 solution.

Thus, silica–alumina containing Brönsted and Lewis acid sites and its catalytic activity may depend on the different population and relative strength of these two types of sites. The presence of Lewis acid sites on silica–alumina is often reflected in its specific catalytic activity. For instance, during the denitrogenation of piperidine on δ-Al_2O_3 and amorphous silica–alumina, the total conversion increases when the total (Brönsted plus Lewis) acidity is increased. However, the formation of hydrocarbons as a result of denitrogenation increases only with increasing the number of Brönsted acid sites, in accordance with a Hoffmann-like deamination mechanism.[628]



piperidine

In another reaction type catalyzed by Lewis acids, such as ethylene polymerization, the larger amount of Lewis acidity on δ-Al_2O_3 gave it an advantage over the silica–alumina catalyst.[629] When the Lewis acid sites of silica–alumina were selectively poisoned by adsoption of pyridine, the catalytic activity of the solid for the polymerization of olefins declined.[630] It is, however, surprising that pyridine can be used as a selective poison for Lewis acid sites. Differences in reactivity between δ-Al_2O_3 and silica–alumina due to their different populations of Brönsted and Lewis acid sites can also be seen during the coking reaction with anthracene.[631] The coking reaction was studied on aluminas and silica–aluminas of varying acidities. Under the same conditions, the amount of coke was larger on silica–alumina than on alumina. The coking reaction appears to be the result of a competition between coke precursors' polymerization and their degradation, which is more favorable at higher temperatures. The different behavior of alumina and silica–alumina is explained by the presence of Brönsted acid sites on silica–alumina, whereas alumina possesses only Lewis acidic sites.[631]

The role of both types of acid sites, Brönsted and Lewis, present on silica–alumina is shown during the isomerization of *cis*-2-butene.[632] This reaction leads to double-bond migration and cis–trans conversion. The deactivation of all the silica–aluminas studied obeys two exponential laws, which allows two initial rates to be calculated. One of them is related to Lewis-oxidizing sites, while the other one is related to the Brönsted acidic sites. It turns out that Lewis acid sites are active but become poisoned faster than Brönsted sites.

From the point of view of their commercial application in catalysis, amorphous silica–aluminas were the first synthetic catalytic cracking (FCC) catalysts, and they are still being used today for catalytic cracking as a part of the matrix surrounding the faujasite zeolite. The presence of a silica−alumina-type component in the FCC catalysts is desired for bottoms upgrading and cracking of reside. In this case, the Brönsted acidity of the matrix after high-temperature steaming correlates well with reside cracking, while Lewis acid sites are postulated to form by interaction between the silica in the binder and active alumina during hydrothermal deactivation in the commercial FCC unit.[633,634] Today, amorphous silica−alumina is used as the acidic component of some hydrocraking catalysts.

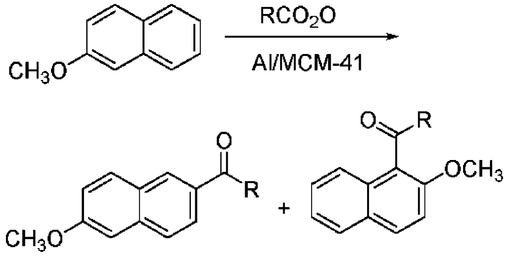
Mesostructured silica−aluminas opened new expectations owing to the regular pore distribution and their potential molecular sieving properties. An obvious reaction that could use these active catalysts was catalytic cracking of heavy oil fractions. It was anticipated that for these heavy feeds, the large reactant molecules would diffuse through the pores of the mesoporous molecular sieves and would reach the internal acid sites. In a systematic work, the gasoil cracking activities of an MCM-41 and an amorphous silica−alumina catalysts were compared, and although similar concentrations of acid sites were present on the two catalysts, as measured by the pyridine adsorption−desorption method, the activity of MCM-41 was higher than that of the amorphous silica−alumina, the selectivity to liquid fuels being also higher for the former.[635] Unfortunately, the stability of the mesoporous molecular sieve is not enough to resist the high-temperature conditions (∼800 °C) in the presence of steam that occurs in the regenerator of the FCC units. Recently, some improvements of the hydrothermal stability of mesoporous molecular sieves have been achieved by changing the thickness of the walls of the channels and/or by "partially" crystallizing the walls.[636,637]

Since the characterization of the acidity of the mesoporous molecular sieves and amorphous silica−alumina indicates that their acidity is mild, one may look for potential applications that do not require the presence of strong acid sites. Thus, hydrocracking of vacuum gasoil, that is already commercially available, using amorphous silica−alumina as the acid component, combining the mild acidity of silica−alumina with the hydrogenating−dehydrogenating activity introduced by Ni, Mo−Ni, or Pt, can be a suitable process for using mesostructured silica−aluminas. Following this, Corma et al. compared the hydrocracking performance of NiMo/MCM-41 with that of NiMo/silica−alumina.[638] The acidity of MCM-41 was similar to that of the amorphous silica−alumina in terms of both the number and acid strength distribution. Furthermore, most of the Brönsted and Lewis acid sites in the two catalysts are of weak to medium strength, as is required for producing diesel in mild hydrocracking operations. When a vacuum gasoil was treated with NiMo/MCM-41, it gave better performance from the points of view of hydrodesulfuration, hydrodenitrogenation, and hydrocracking with higher yield to diesel. This is probably due to the very high surface area and regular pore dimensions of the MCM-41 mesoporous molecular sieves that favor good metal dispersion and site accessibility. This mesoporous material with supported Ni−W has shown good performance for deep hydrocracking of vacuum gasoil to diesel, and for hydrocracking of waxes to produce lube oils.[639,640]

The mild acidity of the mesostructured silica−alumina also makes it possible to perform oligomerization of olefins specially to produce diesel and lube-type molecules. For this process, MCM-41 and silica−alumina obtained with tetraalkylammonium ions, as described before, give excellent results.[606]

Acylation reactions are of general interest and require the use of stoichiometric amounts of $AlCl_3$ to "catalyze" the reaction. Attempts are being made to overcome the waste disposal problems associated with the use of $AlCl_3$ through the use of friendly, easy-recyclable, truly solid catalysts. In this respect, some success has been achieved with zeolite catalyst to acylate activated aromatic rings.[641] Taking this into account, mesostructured silica−aluminas could have utility for carrying out acylation reactions involving bulky reactants and requiring mild acidity. Thus, the production of the anti-inflammatory drug Naproxen involves the regioselective acylation of 2-methoxynaphthalene with acetic anhydride, with the aim of producing the maximum possible acylation at position 6 (Scheme 69).

Scheme 69



MCM-41 was found to be an active catalyst for this reaction, with turnover numbers of 20, 17, and 11 using acetic, benzoic, and isobutyric anhydride as acylating agents, respectively.[642] Interestingly, the catalyst could be easily regenerated and recycled, but unfortunately the selectivity to the product acylated in position 6, which is the desired one, is too low.

These solids could be quite useful for substituting unfriendly mineral acids such as $AlCl_3$, BF_3, HCl, or H_2SO_4 as catalysts for some acid reactions. Moreover, the weak to medium acidities of these structured silica−alumina catalysts may have the advantage over other catalysts with stronger acidities arising from easier product desorption, avoiding undesired consecutive reactions and increasing selectivity and catalyst life. This has been nicely demonstrated for the production of chemicals and fine chemicals formed through acetalyzations, Beckmann rearrangements, glycosidations, hydroxyalkylations, and aldol condensations.[643−650] When stronger acidities are required, mesostructured as well as amorphous silica−alumina can be used to support $AlCl_3$, BF_3, and other Lewis acids such as organic cation−chloroaluminate ionic liquids.[498,518,651] For instance, the catalytic properties of MCM-41 activated with $AlCl_3$, $ZnCl_2$, $FeCl_3$, $NiCl_2$, and $CuCl_2$ were investigated for carrying out the Friedel−Crafts benzylation of PhX (X = H, Me, Br, Cl, F) at room temperature in the liquid phase.[652]

$AlCl_3$/MCM-41 was the most active, followed by $ZnCl_2$/MCM-41, that on the other hand gave better selectivity. The low selectivity exhibited by $AlCl_3$/MCM-41 for the benzylation of substituted aromatics was due to the migration or transfer of the substituent group. The reaction was carried out in a continuous trickle bed reactor with low catalyst deactivation rates. While the results for these catalysts show promise to replace $AlCl_3$ in the industrial manufacture of diphenylmethanes, the potential hydrolysis and deactivation of the catalyst due to moisture has to be taken into consideration.

The chemisorption of trimethylaluminum on mesoporous MCM-41 produces $AlMe_3$-modified MCM-41 materials exhibiting strong Lewis acidic behavior.[653] However, the limited possibilities of catalyst regeneration should also be carefully explored for organometallic Lewis acids supported on silica−aluminas.

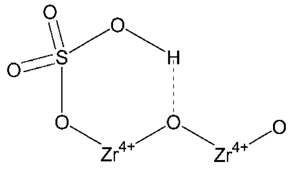
7.5. Mixed Oxides Other than SiO_2–Al_2O_3

Besides silica−alumina, other mixed oxides such as silica−magnesia, silica−zirconia, alumina−boria, titania−boria, tungstate−alumina, and tungstate−zirconia, can also be prepared, and they present Brönsted and Lewis acidities. As mentioned earlier when discussing the acidity models for silica−alumina, the current model structure of mixed oxides is based on the two postulates stated by Tanabe. Tanabe et al. reported[581] that the increased acidity of binary oxides is caused by an excess of positive charge in the crystalline structure. With respect to the acid strength of mixed oxides, Shibata et al.[654] found a correlation between the acid strength of the binary system and the averaged elecronegativity values of the cations. Apparently, the acid strength of the binary mixtures correlates well with the average Sanderson’s electronegativity. The concept of mean Sanderson electronegativity of the framework is quite useful to predict acidity in zeolites, that at the end can be considered as a “binary mixture” of silica and alumina. The acid strengths of Lewis acid sites in more than 30 binary and primary mixed oxides have been measured and interpreted on the basis of the different polarizing powers of the cation involved.[655]

Alumina-supported tungsten or niobium oxides function as effective acidic catalysts for hydrocarbons cracking, with high resistance to hydrothermal treatments.[656,657] HRTEM could not detect WO_3 clusters, even at 25 wt % loading of WO_3. A sample of WO_3 (10 wt %)/Al_2O_3, after steaming at 900 °C, gave similar results. EXAFS studies failed to show the presence of W−O−W bridge bonds in a sample with less than 10 wt % loading, indicating highly dispersed WO_3 on Al_2O_3, in agreement with thermal analysis and controlled-atmosphere electron microscopy. It is not obvious why WO_3 forms an X-ray and microscopically amorphous, highly dispersed phase on the Al_2O_3, or how these two oxides interact to form strongly acidic sites. Nevertheless, the results indicate a strong and specific interaction between the two oxides that occurs even in the presence of a large amount of a potentially competitive binder such as SiO_2. The acid strength and water stability of this system make it interesting for studying Friedel−Crafts reactions, and it is surprising that researchers have paid such little attention to these materials as acid catalysts.

More attention, however, has been paid to the system tungsten−ZrO_2. This type of catalyst is prepared by impregnating $Zr(OH)_4$ with aqueous ammonium tungstate, followed by evaporating the water, drying, and calcining in air at 600−1000 °C.[658,659] XPS showed this catalyst to be WO_3 supported on ZrO_2.[660] The acid strength of this catalyst was estimated to be ($H_o \leq -14.52$), and even if this type of acidity measurement is inappropriate, these binary oxides show activity for isomerization of butane at temperatures as low as 50 °C. It is believed that, in these solids, strong acid sites (or at least sites that are highly active for carbocation reactions) are formed not by impregnation of the crystallized oxide, but on the amorphous form whose calcination then converts to the crystalline form; i.e., tungsten oxide combines with zirconium oxide at the time when a tetragonal system is formed.[661−664] Similar preparation methods using MoO_3 on ZrO_2 also produce acid catalysts with acidities of $H_o \approx -13$.[658]

A considerable number of reports dealing with sulfated zirconia have appeared since the original report by Hino et al. showing that the acid strength increases upon sulfation of zirconia.[665,666] Reviews on the catalytic activity of these materials have been regularly published.[25,423,507,661,667] Sulfated zirconia can be prepared by calcining ammonium sulfate-impregnated zirconia. Sulfuric acid or ammonium sulfate can be used as the sulfate source. It has been demonstrated that the sulfate precursor, the zirconia preparation procedure, the calcination temperature, and the sulfur content play an important role in governing the acid strength distribution of the solid.[666,668−672] Sulfated zirconia and related transition metal-promoted or -supported materials have been often considered superacidic due to their catalytic activity toward isomerization of small alkanes, particularly *n*-butane, at low temperature.[25,491,673] The Lewis or Brönsted nature of acid sites on sulfated zirconia is controversial, and, most probably, both types of sites are concurrently present in the solid.[674−678] A proposed structure of the acid sites in sulfated zirconia involves the coordination of hydrogenosulfate groups on zirconia atoms.[678]



Structure of sulfated zirconia acid sites

More recently, it has also been reported that the addition of Al to sulfated zirconia or supporting sulfated zirconia over γ-Al_2O_3 enhances significantly the activity and stability of sulfated zirconia toward the *n*-butane isomerization at 250 °C in the presence of H_2.[678,679]

Pyridine is the most widely used base probe to determine the nature (Brönsted and Lewis), population, and strength of acid sites present in solid acids. FT-IR spectroscopy is the technique to monitor the nature and quantify the amount of the chemisorbed pyridine. However, despite the advantage of using pyridine as a basic probe and IR monitoring of its aromatic region, this standard technique has been reported to have limitations and may lead to erroneous overestimation of the concentration of acid sites in certain solids. This is the case of sulfated zirconia, in which it has been reported that pyridine can compete as a ligand with sulfate anions, replacing them in the coordination sphere of metallic cation. This leads to an artifact overestimated evaluation of surface Lewis acidity of sulfated zirconia that does not take place when weaker CO is used as a base.[680]

In this context, Sommer and co-workers have proposed that the rate of H/D exchange for methane offers a simple way to assess the relative acidity and reactivity of sulfated zirconia.[523,681] In fact, H/D exchange has been used to develop quantitative methods for Brönsted acid sites titration.[525,682] A study on the H/D exchange between methane and deuterated sulfated zirconia, deuterated sulfated zirconia supported on δ-alumina, and deuterated Al-promoted sulfated zirconia has shown that the apparent activation energy is the same for all the sulfated zirconia solids and smaller than that of HZSM-5.[523] Therefore, the acid strengths of all the sulfated zirconia solids are identical and stronger than the acid strength of ZSM-5.

Temperature-programmed desorption and frequency response methods have been used to study the dynamics of ammonia sorption over sulfated zirconia, and the results have been compared with those from samples of zirconia, sulfated zirconia/titania, and zeolite HZSM-5. Strong Brönsted and Lewis acid sites were detected for all the solids. The Lewis acid sites were fully covered by ammonia at all the temperatures studied, showing that they are very strong acid sites.[683] A ^{31}P solid-state NMR study using trimethylphosphane as a basic probe has revealed that Brönsted acid sites, which do not exist on zirconia, appear in sulfated zirconia.[684]

Normal sulfated zirconia is microporous, making it more suitable for vapor-phase applications than for liquid-phase reactions. Mesoporous sulfated zirconia has been found to exhibit good activity for the liquid-phase alkylation of long-chain alkenes, the preparation of linear alkylbenzenes,[685] and the Friedel−Crafts benzoylation of benzene.[518] Although totally dehydrated sulfated zirconia is a Lewis acid, the easy adsorption of water from the ambient, solvents, or substrates converts Lewis sites into Brönsted sites.

In conclusion, it has been shown that, by proper preparation of mixed oxides, it is possible to obtain solid catalysts that are able to promote acid-catalyzed reactions under experimental conditions in which only superacids in homogeneous systems work. These materials exhibit promising catalytic activity for substituting unfriendly superacid catalysts, as we will show in the next section when discussing substitution of environmentally unfriendly acids by friendly solid catalysts in industrial processes.

8. Replacing Lewis Acids in Industrial Catalytic Processes

8.1. Oil Refining

The oil refining industry and the automotive fuel industry are the industrial chemical processes consuming the largest amounts of catalysts. The largest catalytic process is the catalytic cracking of hydrocarbons to produce liquid fuel. The process is carried out today in riser-type reactors and is named fluid catalytic cracking (FCC).

One of the first industrial examples in which a friendly solid acid (amorphous silica−alumina) was able to substitute an unfriendly Lewis acid ($AlCl_3$) was the catalytic cracking of oil to produce gasoline. Indeed, the first commercial trial of catalytic cracking was carried out in 1915. A. M. McAfee of the Gulf refining company discovered that aluminum chloride, a Friedel−Crafts catalyst known since 1877, could effect the cracking of heavy oils. The catalytic process increased the gasoline yield by 20−30% with respect to the thermal cracking process. However, the high cost of catalyst recovery and the tarry residues produced, together with plant corrosion problems, prevented the implementation of the cracking process using $AlCl_3$ catalysts. The discovery that acid-treated clays and, especially, also amorphous silica−alumina have acidity opened the possibility of using friendly solid acids as catalysts on a commercial scale. The first trial was made by Eugene Houdry, who produced gasoline by cracking gasoil and showed the suitability of the gasoline obtained by running it in his Bugatti racing car. In 1936, the first 2000 billion pound per day (BPD) commercial cracking unit was started, and in 1940 the worldwide installed capacity was already 140 000 BPD.

Zeolites are used today for catalytic cracking. For these crystalline, microporous solids, the total number as well as the nature and the strength of the acid sites depend on the framework (Si/Al ratio) and extraframework (Al and other cations) composition. However, zeolite acidity, while being an important catalyst factor, is not the only parameter in the case of FCC, since other factors such as site accessibility (formation of mesopores in the zeolite crystals during catalyst activation−regeneration) and zeolite stability play a major role.

The number of Brönsted acid sites and the hydrothermal stability of a zeolite are determined by its framework Si/Al ratio, which on the other hand is related to the unit cell size of the zeolite. For instance, in the case of Y zeolite that is the one used in larger amounts in catalysis, the higher the framework Si/Al ratio, the lower will be the total number of Brönsted acid sites and the higher will be the zeolite stability.[686] Thus, zeolite Y, which is initially synthesized with a Si/Al ratio of ~2.7, becomes dealuminated during its activation process, during its use as catalyst, and also during the high-temperature thermal treatment that occurs in the regeneration of the FCC unit.[687] Dealumination and consequently the final framework Si/Al ratio are controlled by introduction of different levels of rare earths by ion exchange. The larger the amount of exchanged rare earth, the lower the Si/Al ratio in the final stabilized material. This parameter also controls the final selectivity of the catalyst, since the higher the framework Si/Al ratio, the lower the selectivity toward liquid fuels and coke, and the larger the amount of gases and olefins.[688]

With respect to the Lewis acidity, this property is associated with the presence of extraframework Al species produced during the zeolite activation–dealumination process and any other cation exchange.[689]

The extraframework Al species behaving as Lewis acids play an important role in cracking bottoms, but also tend to produce more gases and coke.[690,691] It is remarkable that, while the effect of Lewis acidity (extraframework Al) is clear when cracking vacuum gasoil, there is a controversy about the role played by this type of acid sites when cracking pure hydrocarbons.[692−695]

Besides Brönsted and Lewis acidity, the third important variable in FCC is site accessibility. It should be taken into account that vacuum gasoil and oil resides, which are the most common FCC feeds, have average size molecules of 2.0 and 4.0 nm, well above the pore size of Y zeolite (0.74 nm). Therefore, primary feed cracking occurs on the matrix and on the external surface of the Y zeolite crystallites. To increase the accessibility of the feed to the zeolite active sites, one can generate mesopores in the crystal or reduce the crystallite size, increasing therefore the ratio of external to internal surface. This increases the access of large gasoil molecules to the acid sites, which results in higher activity and reduced secondary reactions.[696,697] Secondary reactions are responsible for coking formation and saturation of olefins. Unfortunately, zeolites with smaller crystallites have lower hydrothermal stability, and they have to be synthesized with higher Si/Al ratios in order to retain higher crystallinities after the treatments.[696]

Today, besides Y zeolite, FCC catalysts also introduce other zeolites, such as ZSM-5[698] or even Beta zeolite,[699] to produce more liquefied petroleum gas olefins and gasoline with higher octane numbers. For the latter purpose, it is necessary to control the reaction conditions, ZSM-5 composition, crystallite size, and postsynthesis treatments.[700−704]

8.2. Olefin Oligomerization

Short-chain olefin oligomerization can give gasoline, middle distillates, and lubricant oils. The first studies and demo plants used $AlCl_3$ as catalyst. However, catalyst deactivation by impurities and corrosion problems, together with difficulties in catalyst recovery, led to the development of a new generation of environmentally more acceptable catalysts, based on silica-supported phosphoric acid. Nevertheless, this type of catalyst is still not completely environmentally friendly due to the gradual loss of phosphoric acid during operation. Recently a series of real solid catalysts based on zeolitic molecular sieves has been developed. Commercial processes such as the Mobil olefins-to-gasoline (MOG) and distillate (MOGD) processes and the Shell polygasoline and kerosene (SPGK) process are based on zeolites as solid acid catalysts.

Zeolite ZSM-5, with a pore diameter of ~0.55 nm, is able to convert light alkenes into gasoline products through a complex network of reactions that include oligomerization and hydrogen transfer.[705] Oligomerization is favored by a high acid density, while moderate acid strength minimizes cracking and coking. An optimum acid distribution can be achieved in the case of ZSM-5 zeolite by the proper steam-calcination treatment.[706] Another way of controlling acidity, and therefore selectivity, is by using medium-pore silicoaluminophosphates (SAPOs: SAPO-11, SAPO-31) instead of ZSM-5. It appears that the milder acidity of SAPOs limits cracking, aromatization, and coking reactions, improving the selectivity to gasoline, which is mainly formed by alkanes.[707,708] Incorporation of Mn or Fe into the SAPO framework increases skeletal isomerization, with a corresponding increase in gasoline octane number.[708]

The MOGD process is also carried out using ZSM-5 zeolite as catalyst, working at high pressure and low temperature.[709,710] The product is formed by monobranched alkenes, which give after hydrotreating an excellent distillate with low aromatics, cetane number of ~52, and a pour point of −70 °C.

The SPGK process converts C_2-C_5 olefins to gasoline, kerosene, and distillate at temperatures of 200−300 °C and pressures in the range of 10−50 bar. The catalyst is Ni/mordenite, which produces mainly isoalkenes. The gasoline has research octane numbers above 90, and motor octane numbers close to 80. The distillate product, after hydrotreating, is of very good quality.[711]

Oligomerizing C_3-C_6 alkenes using medium-pore unidirectional zeolites such as ZSM-22, ZSM-23, and ZSM-35, whose pore dimension inhibits by shape selectivity the formation of branched products, can produce synthetic lubricants with good pour points and viscosity indexes. The selectivity can be further improved by deactivating the sites at the external surface.[712,713] Longer chain *n*-olefins with 10 or more carbons can be converted at low temperatures and pressures into dimers and trimers, which are useful lubricant base stocks with a very high viscosity index and low pour point. In this case, large-pore zeolites such as Y faujasite or even mesoporous molecular sieves are good catalysts for the process.[714,715]

8.3. Isomerization of Short-Chain Paraffins

Light straight-run gasoline is formed mainly by *n*-pentane and *n*-hexane, which have octane numbers of 62 and 25, respectively, too low for them to be introduced into reformulated gasolines. It is possible, however, to increase the octane number of this fraction up to close to 80 by *n*-alkane isomerization. The reaction temperature has to be as low as possible in order to shift the thermodynamic equilibrium toward branched products. We have seen earlier that low-temperature *n*-alkane isomerization requires as catalyst strong Brönsted or Lewis sites, such as $AlCl_3$

and SbF_5. During World War II, butene was isomerized on $AlCl_3$ to produce alkylate for aviation fuel. The use of $AlCl_3$, however, introduced practical and environmental problems, and it is not employed in current commercial units. Instead of $AlCl_3$, bifunctional, amorphous catalysts of platinum on chlorinated alumina, such as those whose preparation has been described earlier in this review (Section 6.2), are used commercially to isomerize C_4-C_6 *n*-alkanes at temperatures ~150 °C. These catalysts, which work well, are very sensitive to small amounts of water and sulfur compounds and require a severe pretreatment of the feed. Furthermore, it is still necessary to supply continuously chlorine in the feed to replace the fraction of chlorine depleted from the catalyst during the process, which causes corrosion and contamination problems. These problems are avoided by using an environmentally friendlier Pt/modernite zeolite catalyst that can perform the isomerization of C_5 and C_6 *n*-alkanes. However, this less acidic catalyst produces a gasoline with an octane number approximately 2 octane units lower than that obtained when working with the chlorinated alumina catalyst. On the positive side is the fact that, when working at temperatures ~240 °C, the zeolite catalyst is less sensitive to H_2O and sulfur. When the zeolite is submitted to the appropriate dealumination procedure, it is possible to produce very active and selective Pt/modernite catalysts, with sulfur resistance of up to ~100 ppm sulfur in the feed.[716]

A compromise between performance and the advantages of Pt/modernite catalyst over chorinated alumina is achieved by using Pt/sulfated zirconia and even Pt/tungstene–zirconia as isomerization catalyst. It has been demonstrated that these catalysts work well at temperatures of about 180 °C.[717–719] However, these zirconia-containing Pt catalysts are quite sensitive to H_2O and sulfur. Recently, Corma et al. have developed by high-throughput combinatorial catalysis an isomerization catalyst for light straight-run naphtha that can still work at a temperature of 180 °C but presents a higher resistance to sulfur and H_2O than Pt/sulfated zirconia.[720,721]

8.4. Catalytic Dewaxing and Isodewaxing

Catalytic dewaxing improves the cold-flow properties of lube oils and middle distillates by selectively cracking *n*-alkanes. This can be done by using medium-pore-size zeolites such as ZSM-5, ZSM-23, and ferrierite as catalysts, ZSM-5 being the preferred one for the Mobil distillate dewaxing (MDDW) and Mobil lube dewaxing (MLDW) processes.[722] Modernite-based dewaxing catalysts have also been developed by BP, UNOCAL, and AKZO. However, the lube oil yield can be increased if *n*-alkanes are isomerized instead of cracked. This process is named isodewaxing and requires shape-selective catalysts that inhibit the formation of multibranched paraffins. This is done by using unidirectional medium-pore zeolites (ZSM-22, ZSM-23, Theta-1) and SAPO structures such as SAPO-11, SAPO-31, and SAPO-41.[723]

Monodirectional medium-pore zeolites and SAPOs present good selectivities for producing monobranched alkanes owing to their pore diameter of 0.42–0.47 nm and the unidirectionality of the channels.[724–726] Recently, SAPO molecular sieves have been synthesized that present very high activity and selectivity for isodewaxing.[727–729]

8.5. Isobutane/Butane Olefin Alkylation

Gasoline is produced by reacting isobutane with C_3-C_5 olefins. The resultant mixture contains highly branched alkanes with very high research and motor octane numbers. This is a commercial process that, since its introduction during World War II, still uses unfriendly acid catalysts such as HF and H_2SO_4. HF is especially dangerous owing to its high volatility, toxicity, and corrosiveness, increasing the environmental risk in the case of eventual HF leaks to several miles around the plant.[730] Even if the risk associated with HF has been mitigated by the use of additives that decrease the HF volatility, it would be highly desirable to develop an alternative nontoxic and noncorrosive solid acid catalyst that can be active and selective for alkylation of isobutene.[690,731] The easiest solution would be to support or immobilize the liquid acids such as H_2SO_4 and/or trifluoromethanesulfonic acid (triflic acid) on SiO_2.[732] Lewis acids such as BF_3, $AlCl_3$, SbF_5 supported on SiO_2, Al_2O_3, cation-exchange resins, and even pillared layered compounds have also been claimed as alkylation catalysts.[528,733] Of special relevance is the catalyst developed by Catalytica-Conoco-Neste, which consists of BF_3 supported on γ- or δ-alumina.[528] As we described before when discussing supported Lewis acids as catalysts, small amounts of water and an additional amount of free Lewis acid have to be introduced during the operation. It appears then logical that the behavior of this catalyst approaches that of HF. Fluorinated silica and alumina have also been used as alkylation catalysts, but the selectivity to the desired high-octane trimethylpentanes is too low.[734] Ionic liquids formed by $AlCl_3$ with quaternary ammonium halides are also active for isobutane/butene alkylation[317,735,736] and would be worth supporting it on an inorganic carrier.

True solid acid catalysts such as large-pore zeolites,[635,737,738] sulfated metal oxides,[669,739–743] heteropolyacids and their salts,[744–746] Nafion, and Nafion–silica composites[747,748] have also been used for isobutane/butene alkylation and related reactions. Unfortunately, all these catalysts decay very fast,[749] and they need continuous regeneration. This is done in two steps. In the first step, the catalyst is washed out with liquid isobutane to remove weakly adsorbed hydrocarbons. The strongly retained hydrocarbons are removed by hydrocracking at moderate temperature, forming lighter hydrocarbons that are then desorbed. As far as we know, the only plants using these processes are demonstration plants based on SiO_2-supported triflic acid[750] and a demonstration plant with UOP's technology based on an undisclosed solid catalyst, working in a riser unit. To increase the life of the catalyst, a process is also claimed that uses zeolite catalyst in the supercritical phase of isobutene or isopentane.[199]

8.6. Alkylation Process for Gasoline Desulfuration

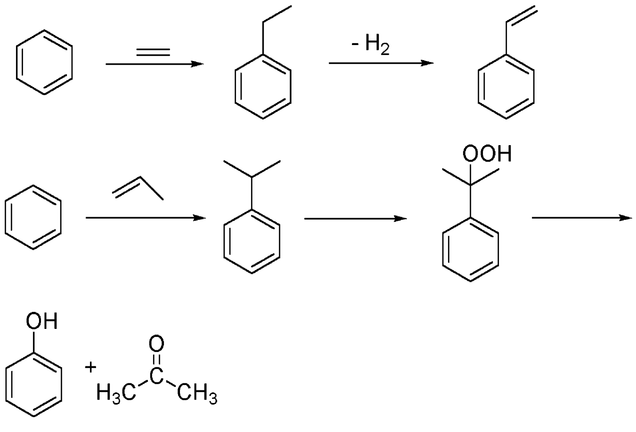
Environmental legislation requires the the sulfur content of gasoline to be reduced to 10 ppm by the year 2005. Several alternatives are being considered to deal with the gasoline stream of the highest sulfur content, even 1000 ppm, i.e., FCC gasoline. Potential solutions for decreasing the sulfur content of this fraction involve FCC feed hydrotreating or FCC gasoline postreating. Postreating the gasoline for sulfur removal can be done by hydrotreating, selective adsorption, selective oxidation, or selective alkylation of sulfur compounds. Among the different possibilities, selective alkylation of sulfur compounds makes use of acid catalysis. This process has been announced to become commercial by BP, and it consists of the removal of sulfur species in cracked naphthas by passing the naphtha over an acid catalyst to alkylate the thiophenic compounds, using as alkylating agents monoolefins and diolefins already present in the naphtha. By doing this, alkylated thiophenes are concentrated in the heavy portion of the naphtha or even in diesel, and they can be distilled out. For this process, which is in its infancy, the development has been claimed of a true solid catalyst that avoids olefin oligomerization and aromatics alkylation in order to decrease catalyst deactivation and the loss of gasoline and octane.[751−754] However, the use of PO_4H_3/SiO_2 solid catalyst is far from ideal, and efforts are being made to replace it by a truly solid acid catalyst.

8.7. Petrochemicals

8.7.1. Aromatics Alkylation

Important applications of the Friedel−Crafts alkylation of aromatics include the production of ethylbenzene and cumene via alkylation of benzene with ethylene and propylene, respectively. Styrene and phenol are the final products in these processes (Scheme 70).

Scheme 70



Valuable products and versatile intermediates are also produced from dialkylates of benzene and polynuclear aromatics. In this way, diethylbenzenes are used for the production of divinylbenzenes. Para and meta isomers of diisopropylbenzene are used for the manufacture of hydroquinone and resorcinol, respectively, after forming the corresponding hydroperoxides and decomposing them in a subsequent step.

In the production of ethylbenzene, $AlCl_3$ is still used commercially, reminiscent of old times. As was explained before, the primary function of the metal halide is to generate a carbocation. Since this is easily achieved by abstracting a halogen atom from an alkyl halide, alkyl halides are added as co-catalysts during the alkylation reaction. Environmental problems and the corrosive nature of the system have provided an incentive to develop solid acid catalysts for this reaction.

Today there are successful commercial processes that use solid acids as catalysts. As solid acids zeolite ZSM-5 (Mobil-Badger process),[755,756] Y (UNOCAL-ABB Lummus Crest Liquid-Phase Ethylbenzene Process and CDTech Catalytic Distillation Technology),[757] and MCM-22 are being used.[758,759] The process involves two reactors. In the first one, ethylbenzene and diethylbenzenes are formed. Ethylbenzene is separated out and the diethylbenzenes are sent to a transalkylation reactor.

Ethylbenzene can also be obtained by alkylating benzene with ethanol using Fe−ZSM-5 zeolite. This process can be of interest for countries with a high production of ethanol derived from biomass.

Cumene has been historically produced—and in some places it is still this way—by alkylation of benzene with propylene over supported phosphoric acid Friedel−Crafts catalyst. Since, as mentioned before, this catalyst also has problems of corrosion and waste disposal, new solid catalysts have been developed and new commercial processes implemented. Catalysts and processes do not differ much from these devoted to alkylation of benzene with ethylene. MCM-22 zeolite is an active and selective catalyst for cumene production.[758] Thus, the Mobil−Badger cumene process uses MCM-22 zeolite instead of ZSM-5. The pore topology of this zeolite is formed by a system of a circular 10-member-ring (MR) pore channel system and a 12-MR system of large cavities connected to each other by 10-MR windows. It has been presented that, while benzene and propylene can diffuse through the 10-MR pores and windows, cumene diffusion is hindered; consequently, the reaction occurs mainly at the external part of the crystals, i.e., at the external “cups” open to the exterior.[760] To increase the external surface, the laminar precursor of MCM-22 has been delaminated, and in this way the external surface of the resulting material (ITQ-2) is in the range of 600−800 $m^2\ g^{-1}$, with a corresponding increase in the rate of cumene formation.[761] Beta zeolite is also used for the manufacture of cumene by Chevron, UOP, and ENICHEM.[762] The catalytic behavior of MCM-22 and Beta zeolite for alkylation of benzene with propylene has been compared recently,[758] and similar results were found.

There is a commercial CD Tech cumene process, which is essentially the same as the CD Tech ethylbenzene process described before. The alkylation step is again followed by distillation, and the diisopropylbenzene formed in the alkylation reactor is converted to cumene in a separate transalkylation reactor. The solid catalysts used are most likely modified Y zeolites.

The Dow 3-DDM process is suited to produce cumene by alkylation of benzene with propylene over dealuminated mordenite catalysts.[763,764] Concerning the isomer distribution of the diisopropylbenzenes, the mordenite pore size is not large enough (0.67 nm × 0.70 nm) to allow rapid diffusion of the wider ortho and meta isomers; therefore, formation of the para isomer is increased by diffusion shape selectivity. The key point in mordenite preparation is the formation during dealumination of a system of mesopores that communicate the 12-MR zeolite pores between them, conforming a pseudo-three-dimensional system instead of the unidimensional pore system in the original zeolite.

It can be said that actual solid acid molecular sieve catalysts are able to carry out very efficiently the Friedel–Crafts alkylation of benzene with ethylene, propylene, or 2-propanol.[765] The challenges remain to further decrease the yield of *n*-propylbenzene, which is highly unwanted and difficult to separate, to decrease or even avoid the formation of polyalkylated products, and to increase the life of the catalyst, even though they last today about two years, before replacing them with fresh catalyst.[766] A new zeolite named ITQ-21 has been synthesized recently[761] with a very open structure that appears specially suited for maximizing the ratio of cumene to *n*-propylbenzene during the alkylation of benzene with propylene. Other large-pore tridirectional zeolites of interest for cumene production are ITQ-16[767] and ITQ-17.[768]

Alkylation of polynuclear aromatics such as biphenyl or naphthalene produces valuable intermediates. In particular, 4,4′-dialkylbiphenyl can be converted into the corresponding dicarboxilic acid, which is a monomer for a variety of high-performance polymers and liquid crystal applications. Similarly, 2,6-dialkylnaphthalene is the raw material for the manufacture of high-quality polyester fibers and plastics. The use of conventional Lewis Friedel–Crafts catalysts has been avoided by using the dealuminated mordenite described by Dow, which is prepared to present mesopores that convert this zeolite in a pseudo-tridimensional system of pores.[769,770] It appears then that properly tailored zeolites can offer still new advantages for Friedel–Crafts-type alkylations.

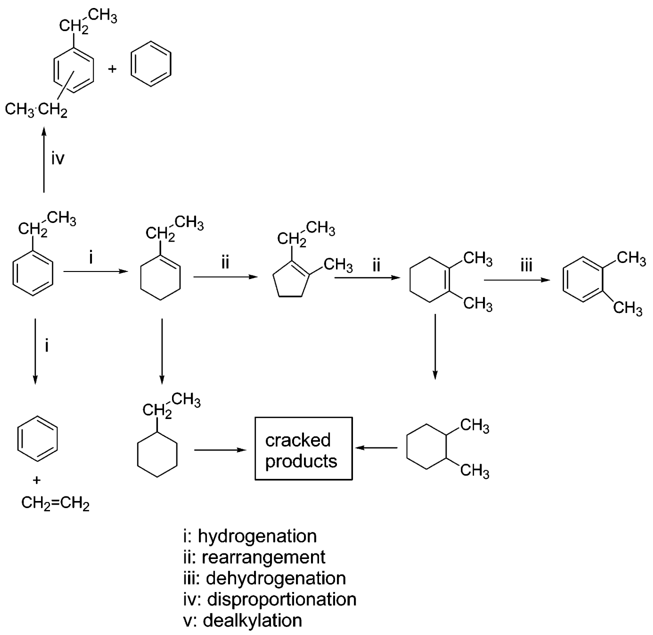
8.7.2. Isomerization of C_8 Alkylaromatics

The C_8 alkylaromatic fraction produced in the reformate contains a mixture of *m*-, *p*-, and *o*-xylenes and ethylbenzene. The product in highest demand is *p*-xylene, which is used to make terephthalic acid for the production of polyester fibers and other plastics. It would be then highly desirable to isomerize the C_8 alkylaromatics to produce the maximum amount of *p*-xylene while removing the ethylbenzene that becomes accumulated during recycling of the unconverted feed. Classical Lewis acids ($AlCl_3$) are active for carrying out the isomerization of alkylaromatics but present no activity to convert ethylbenzene, and the product distribution in the xylene fraction corresponds to the thermodynamic equilibrium. Over amorphous catalysts, transalkylation reactions to produce toluene and unwanted trimethylbenzenes compete with the desired xylene isomerization.[771,772] An important step forward in the isomerization of C_8 alkylaromatics was the discovery of the medium-pore ZSM-5 zeolite. With this zeolite, the xylene transalkylation is strongly diminished because there is not enough room in the ZSM-5 pores to accommodate the bulky bimolecular transalkylation transition state involving to two xylene molecules.[773] The steric constraints are much smaller for ethylbenzene disproportionation to benzene and diethylbenzene, which are separated from xylenes by distillation. There are two commercial processes based on ZSM-5 as catalyst. The Mobil high-temperature isomerization process (MHTI) operates at temperatures above 400 °C to favor dealkylation of ethylbenzene[774] and uses a bifunctional Pt/ZSM-5 catalyst. The process produces a product enriched in *p*-xylene and converts 40–50 wt % of the ethylbenzene. In the Mobil high-activity isomerization process (MHAI), the reactor contains two beds of ZSM-5 catalysts. The one at the top has highly dealkylation activity and the one at the bottom has high isomerization activity. The advantage of this MHAI process with respect to MHTI is the lower operation temperature, with the corresponding longer catalyst lifetime, higher conversion of ethylbenzene, and lower losses of xylenes.

In any case, the two processes described above rely on ethylbenzene dealkylation–disproportionation to decrease the concentration of this product. These processes are acceptable if the prize of benzene is sufficiently higher than that of xylenes. However, if this is not the case, it would be more attractive to be able to isomerize ethylbenzene into xylenes. There are processes based on bifunctional Pt/mordenite catalysts that combine ethylbenzene isomerization with xylene isomerization. The isomerization of ethylbenzene into xylenes requires a partial hydrogenation of the aromatic ring, followed by ring contraction and expansion with formation of an isomerized six-member ring. The reaction mechanism ends with the dehydrogenation of the cycle to form the xylenes. A mechanism of this type requires the presence of two catalytic functions, i.e., hydrogenation–dehydrogenation and acid function (Scheme 71).[774–777] It has been presented that, during the isomerization of ethylbenzene to xylenes on Pt/mordenite, other unwanted metal- and acid-catalyzed reactions occur, such as dealkylation and transalkylation of ethylbenzene, total hydrogenation of ethylbenzene, and cracking of intermediate products (Scheme 71).[778]

In a complex reaction network like this, the final product distribution will be dependent on process conditions as well as on the fine-tuning of the metal and acid properties of the catalyst. For instance, the formation of naphthenes is thermodynamically favored at low temperatures; consequently, losses due to naphthene formation can be decreased by operating at higher temperatures. However, higher temperatures favor dealkylation, transalkylation, and cracking reactions rather than isomerization of ethylbenzene and also decrease the xylenes yield owing to their transalkylation to give toluene and tri-

Scheme 71



methylbenzenes.

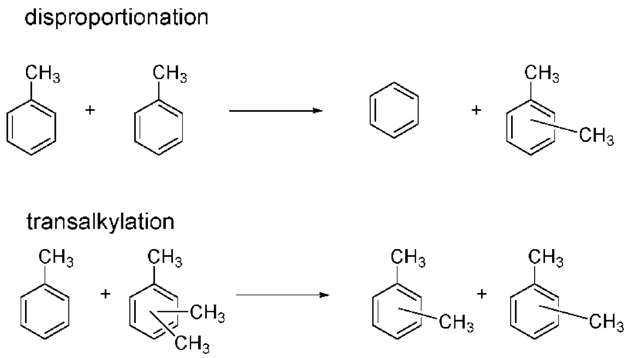
With respect to the catalyst, active-site accessibility and acid strength are important variables. The generation of mesopores on the zeolite crystals favors diffusion of products, increasing selectivity to xylenes.[778] On the other hand, decreasing the acid strength of the zeolite by calcium exchange decreases cracking reactions as well as dealkylation and transalkylation of ethylbenzene and increases selectivity to xylenes, close to 50% at 60% ethylbenzene conversion when the process is carried out at ~400 °C and 15 bar pressure. Taking into account the above results, it would appear that a large-pore SAPO molecular sieve with somewhat lower acid strength than zeolites could be an appropriate solid catalyst for the combined isomerization of xylenes and ethylbenzene. Rabo et al. have reported[779] that the large-pore SAPO-5 catalyst gives a high ethylbenzene conversion, but xylene losses due to transalkylation and cracking are large. On the other hand, the medium-pore SAPO-11 gives ethylbenzene conversion similar to that achieved with mordenite, but selectivity to xylenes is higher.

In summary, it is possible to say that, besides the MHTI and MHAI processes that use ZSM-5 catalyst to dealkylate ethylbenzene in technologies developed by Engelhard (octafining process), UOP (isomer process), and Shell, mordenite is used for a process that involves the isomerization of ethylbenzene into xylenes.

8.7.3. Toluene Disproportionation and Transalkylation

Toluene disproportionation was also performed using $AlCl_3$ and HCl as co-catalysts. But obviously, the commercial processes use solid acid catalysts to convert toluene to a mixture of benzene and xylenes, and transalkylation of toluene with trimethylbenzenes to produce xylenes (Scheme 72).

Scheme 72



Toluene disproportionation with a ZSM-5 zeolite catalyst produces initially a mixture of *p*- and *o*-xylene that rapidly isomerizes to yield, inside the pores, the thermodynamic equilibrium composition. However, in ZSM-5 a diffusion shape selectivity occurs, by which the smaller *p*-xylene diffuses more rapidly out of the pores than the other two isomers. Any *o*- and *m*-xylene remaining in the pores is converted to *p*-xylene in order to maintain the thermodynamic equilibrium. When conversion increases, *p*-xylene can react on the nonselective external surface of the zeolite, with the corresponding decrease in *p*-xylene selectivity.[780-782]

Deposition of MgO, phosphorous boron, or even the coke deposited during the process not only passivates the nonselective sites located close to the external surface but also blocks some pores, resulting in an increase of the average length of the diffusion path. The molecules should travel longer distances to find an open pore, and this results in a higher selectivity to *p*-xylene operating at toluene conversions of ~30% (Mobil selective disproportionation process).[783]

A process combining the disproportionation of toluene and transalkylation of toluene with C_9 aromatics to produce xylenes in a single step has been developed by Toray and UOP (Tatoray process) using Ni/mordenite as catalyst, although no selectivity toward *p*-xylene occurs. On the other hand, transalkylation and disproportionation have been carried out in two separate steps using a surface-modified ZSM-5.[784]

8.7.4. Linear Alkylbenzenes

Linear alkylbenzenes (LABs) are used in the detergent industry since they undergo biodegradation better than branched alkylbenzenes. The process is carried out commercially by alkylating benzene with linear α-olefins using HF and $AlCl_3$ as catalysts. It is interesting that, until the past decade, no alternative solid catalyst was used commercially, even if monodirectional zeolites such as ZSM-12 appeared as interesting catalysts. UOP and CEPSA subsidiary Petresa have developed a new process for production of linear alkylbenzenes that work in the liquid phase in a fixed-bed reactor. This process has replaced HF and $AlCl_3$ by an environmentally friendlier nonzeolitic solid catalyst. The catalyst is probably based in amorphous silica–alumina, whose acidity was perhaps enhanced by fluoride treatment. The selectivity of the solid catalyst is as good as that of HF, and the solid catalyst lasts for two years or more. The suitability of HF as catalyst for the preparation of LABs can be deduced from the results obtained with the older isobutane/butene alkylation process for producing gasoline using HF. Indeed, it was observed there that HF was not able to isomerize the double bond of the olefin, and this is also desirable for producing LABs by alkylation of benzene with linear α-olefins. Thus, the solid catalyst to be used should minimize the isomerization of the double bond by having acidity behavior like that of HF, or should avoid alkylation of the olefins with internal double bonds by shape-selective alkylation.

8.8. Chemicals and Fine Chemicals

In the previous section, we have shown that petrochemistry and the industry of bulk chemicals has moved over the years to the replacement of conventional Lewis acid with reasonable solid acids. The number of commercial processes that use environmentally friendly solid Lewis acids in petrochemistry is considerable by now. This situation contrasts with the case of fine chemicals. Fine chemicals are characterized by lower production volumes, higher added value, and more complex and diverse chemical structures. In this section we will present some representative examples to illustrate the tendency to move toward new environmentally friendly catalysts and processes. Some reviews have specifically focused on this aspect.[785,786]

8.8.1. Hydration of Olefins

Ordinary protonic acids such as sulfuric and *p*-toluensulfonic acids can be used to carry out the hydration of olefins to the corresponding alcohols. These unfriendly acids have been substituted successfully by heteropolyacids (HPA) for the industrial hydration of C_3-C_4 olefins,[787] with the advantage in the corresponding waste stream disposal. Table 8 summarizes the industrial hydration processes developed using HPA as catalysts.

Table 8. Industrial Processes for Hydration of Olefins Using Heteropolyacids (HPA) as Catalysts

reactant	phase	capacity (10^3 t/year)	start	remarks
propene	liquid (aq)	50	1972	first process (diluted HPA)
n-butene	liquid (aq)	40	1985	to MEK
isobutene	liquid (aq-C_4)	56	1984	C_4 separation (concd HPA)

By using relatively low concentrations of HPA, Tokuyama Soda was able to produce isopropyl alcohol from propylene and H_2O with 70% conversion and 99% selectivity.[788]

Isobutene is hydrated selectively in the mixture of butenes present in the C_4 streams from steam or catalytic cracking. For the selective hydration, an aqueous solution of highly concentrated (up to 0.8 M) HPA at 60−80 °C is used. When the process is carried out in a multistage reactor, isobutene is 100% converted, while the *n*-butenes hydrated are lower than 1%.[789] HPA has tendency to decompose during the process. However, the rate of decomposition can be very strongly reduced by partial reduction of Mo or W and by the coexistence of an organic base with phosphoric acid.

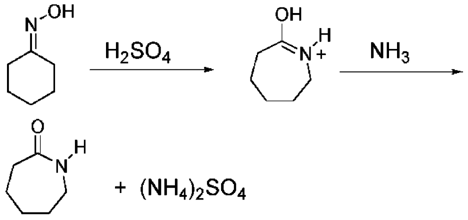
It would be interesting to immobilize the very active HPA into an insoluble, readily recoverable solid acid. This has been tried by supporting HPA on active carbon or silica or by forming insoluble salts and using them to catalyze liquid-phase reactions in polar media. This system, while active, suffers from a reduction of the HPA acid strength and leaching of the active phase. Recently, it has been shown that HPA could be effectively immobilized in a silica matrix by means of the sol−gel technique to form silica-occluded HPA.[790,791]

It is clear that, for commercial hydration processes, friendlier acids should replace H_2SO_4, supported HPA being a candidate.

8.8.2. Production of ϵ-Caprolactam

ϵ-Caprolactam is the monomer used in the production of Nylon 6 and is commercially produced by the liquid-phase Beckmann rearrangement of cyclohexanone oxime in pure anhydrous sulfuric acid (oleum). The product is obtained as a sulfate salt, and ammonia is used to liberate ϵ-caprolactam while forming ammonium sulfate as byproduct (Scheme 73).

Scheme 73

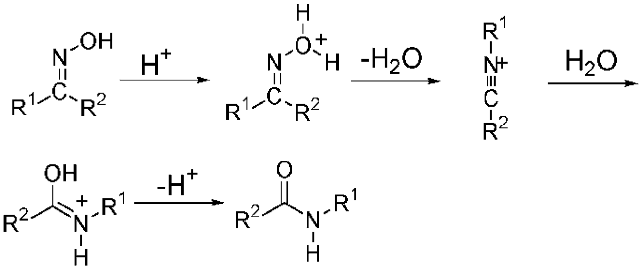


Since cyclohexanone oxime is itself produced from cyclohexanone and hydroxylamine sulfate in the presence of ammonia, the global process from cyclohexanone to ϵ-caprolactam produces between 1.6 and 4.4 tons of ammonium sulfate byproduct per ton of ϵ-caprolactam.[792] It becomes clear that the use of a solid catalyst that could substitute oleum for the Beckmann rearrangement will be highly desirable from the environmental point of view.[793,794] Already, 25 years ago, aluminas modified by the addition of B_2O_3 were used for the rearrangement of cyclohexanone oxime to caprolactam with good selectivities.[795] Other alumina modifiers, such as Cl^-, PO_4^{3-}, and SO_4^{2-}, gave worse results.[796] Other amorphous acid catalysts used for the reaction are boron and aluminum phosphates and Pt/sulfated zirconia, as well as amorphous and mesostructured (MCM-41 and FSM-16) silica−alumina.[797−800]

The most widely accepted reaction mechanism for the Beckmann rearrangement involves a protonation of the oxime oxygen atom to give the corresponding oxonium cation, which undergoes the migration of an alkyl group concurrently with the release of H_2O, giving a nitrilium cation. The nitrilium cation reacts with a water molecule to form the amide tautomer and, finally, the amide (Scheme 74).[801]

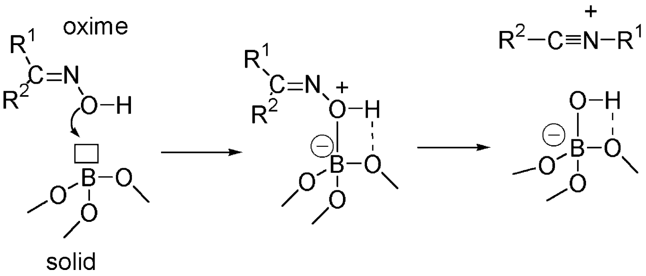
A mechanism of this type involves Brönsted acid sites as catalytic sites,[802,803] the role of the acid site being to convert the poor leaving group OH of the

Scheme 74



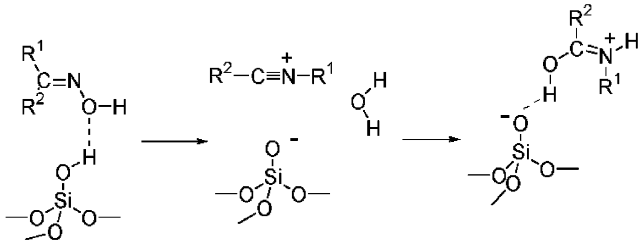
oxime into a better leaving group by protonation. However, Lewis acid sites have also been claimed as the active sites when boron phosphate catalysts were used.[797] It was postulated that the oxime is adsorbed on the trigonal boron (Lewis acid) site to form an intermediate complex and that simultaneous H-bonding of the oxime OH group to the oxygen connected to the boron resulted in alkyl migration to give the nitrilium cation intermediate (Scheme 75). Lewis acid sites have also been postulated to intervene in the reaction when fluorinated Al_2O_3[804] are CeY zeolite[805] are used as catalysts.

Scheme 75



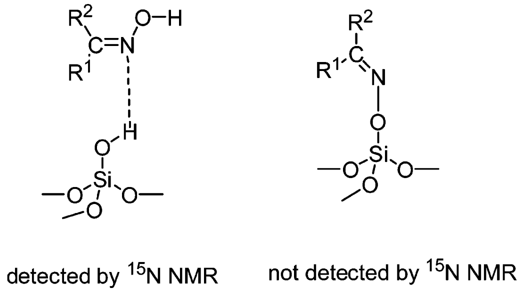
While most Beckman rearrangements are carried out in the presence of Brönsted acid sites, Sato proposed an alternative mechanism via oxime–silyl ether to explain the rearrangement of cyclohexanone oxime on “neutral” silanol groups (Scheme 76).[793]

Scheme 76



By means of ^{14}N NMR spectroscopy, the chemical species formed upon adsorption and heat treatment of 2-butanone [^{14}N]oxime on silicalite was found to be a H-bonded oxime form, whereas no other species were detected upon heating (Scheme 77).[806]

Scheme 77



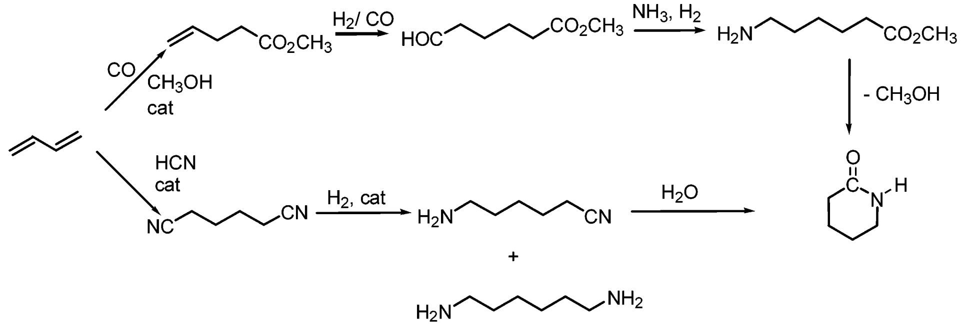
Since Brönsted acid sites were generally thought to be necessary to carry out the Beckmann rearrangement, a large amount of research work has been done using the H^+ form of zeolites as catalysts. Large-pore zeolites such as Y, mordenite, L, and OFT have been used for the gas-phase reaction of cyclohexanone oxime diluted in benzene or alcohols.[643,802,807–813] In general, it can be said that the catalysts deactivated fast and selectivity was not always good. To improve selectivity and perhaps catalyst life, the reaction has also been conducted in the liquid phase using Y and Beta zeolite. These studies have shown that the selection of an appropriate solvent can strongly increase catalyst life.[814,815] Indeed, low temperatures should favor lactam selectivity, while the product occluded in the zeolite could be desorbed more easily in the liquid phase by the solvent, increasing in this way the catalyst life. This concept has been followed by Mitsubishi, which has developed a process for production of ϵ-caprolactam in the liquid phase using zeolites and claiming alcohols as solvents.[816–819] With respect to the catalyst, Corma et al., working in the liquid phase, showed that Beta zeolite could be an adequate catalyst, provided that internal silanol groups are generated.[815] These authors have found that samples of Beta zeolite containing only external silanol groups and neither internal ones nor bridging OH groups were almost inactive for the Beckmann rearrangement.

In the case of medium-pore zeolites and, more generally speaking, molecular sieves, it has been found that highly siliceous ZSM-5, SAPO-11, TS-1, TS-2, and ZSM-5 borosilicates give good performance.[820–824]

The most successful zeolite catalyst has been highly siliceous ZSM-5 zeolite, on which the external silanol groups are claimed to be responsible for the Beckmann rearrangement of cyclohexanone oxime in the vapor phase.[825] The ZSM-5 catalyst still deactivates relatively fast, while the selectivity to lactam decreases over time. However, the deactivation rate can be slowed by the addition to the cyclohexanone oxime feed of methanol and a small amount of H_2O.[826] In addition to diluent gases, the deactivation was also diminished when, besides methanol, the catalysts were modified with noble metals.[827] Since it appears that catalyst deactivation is due to the strong adsorption of the product on the catalyst surface, better desorption of the lactam must be accomplished in order to increase catalyst life. To achieve this one should use polar solvents, lower acidities, and higher reaction temperatures. However, one should be careful with the last parameter since a penalty on selectivities may occur when working at high temperatures.

In the year 2000, Sumitomo announced the construction of a commercial plant for production of ϵ-caprolactam which avoids the formation of am-

Scheme 78



monium sulfate by using a high silica ZSM-5 zeolite.[828] This process requires continuous regeneration of the catalyst and is combined with ENI's process for "in situ" production of hydroxylamine with NH_4OH and H_2O_2 using TS-1 catalyst.[167]

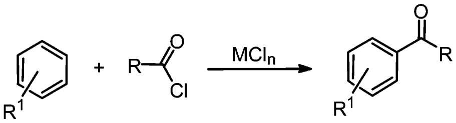
A new route to produce ϵ-caprolactam has been presented by DuPont.[828] This process starts from butadiene via adipic dinitrile, partial hydrogenation, and gas-phase rearrangement to ϵ-caprolactam (Scheme 78). This route also enables the production of hexamethylenediamine for Nylon 6,6 through a complete hydrogenation of adipic dinitrile. Alternatively, butadiene can be selectively carbonylated and hydroformylated in two catalytic steps.[828]

It is worth mentioning that a noncatalytic approach for Beckmann rearrangement has been presented to occur near the critical temperature (374 °C) in subcritical or supercritical water.[829] The development by the Japanese company ASAHI of a new environmentally friendly solid acid-catalyzed process for the production of cyclohexanol from cyclohexene has opened new possibilities for production of adipic acid and ϵ-caprolactam.[787,830] The ASAHI process involves the highly selective partial hydrogenation of benzene and the highly selective hydration of cyclohexene in the presence of a hydrophobic ZSM-5 zeolite, characterized by small crystallite sizes ($<0.1\ \mu$m), which determines that the ratio of external to total acid sites is higher than 0.07. Using this catalyst and working between 100 and 120 °C, a conversion of cyclohexene of ~15%, with selectivity to cyclohexanol higher than 98%, has been achieved. While the traditional system for production of ϵ-caprolactam involves the hydrogenation of benzene, the oxidation of cyclohexane to cyclohexanone, the oximation of cyclohexanone, and the final Beckmann rearrangement, the alternative route based on the ASAHI process involves the production of cyclohexanol and its oxidation to cyclohexanone oxime by hydrogen peroxide through ammoxidation on TS-1.

8.8.3. Friedel–Crafts Acylations

The Friedel–Crafts acylation and the related Fries rearrangement of aromatic compounds are very convenient methods for preparing aromatic ketones, which are important intermediates for the production of fine chemicals.[787,830,831] The acylations of aromatics are usually carried out with organic acid chloride using Lewis acids such as $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, and $TiCl_4$, or with acid anhydrides and Brönsted acid sites such as polyphosphoric acid or HF (Scheme 79).

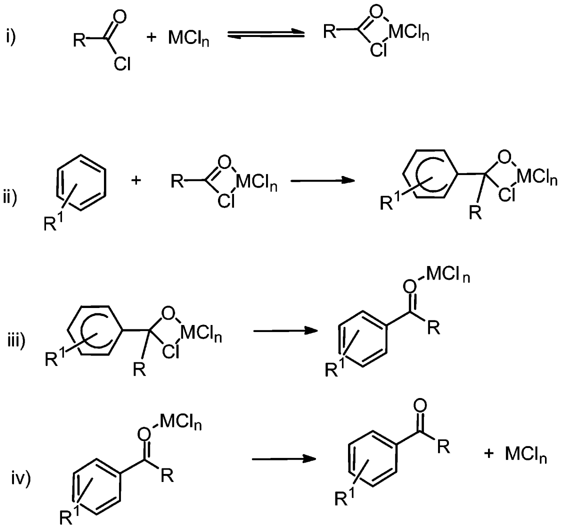
Scheme 79



Unfortunately, the Friedel–Crafts reaction using conventional Lewis acids as catalysts requires stoichiometric quantities of catalyst relative to the acetone formed. This introduces an effluent problem during industrial operation.

A four-stage reaction mechanism has been postulated for acylation: (i) activation of acid chloride by the Lewis acid; (ii) reaction of the activated acid chloride with the aromatic compound to give a complex; (iii) aromatization of the complex; and (iv) decomplexation between the Lewis acid and the aryl ketone formed (Scheme 80).

Scheme 80



Taking into account the above reaction mechanism, the necessity of using stoichiometric amounts of the Lewis acid catalyst (MCl_n) can be understood, considering that the complex formed between the catalyst and the aryl ketone is much more stable than the one formed by the acid chloride and Lewis acid. If this is so, then the acid site would not be regenerated, and the catalyst turnover number would be 1. This assumption has been proven to be true by carrying out the competitive adsorption of acetyl chloride and 4-methylacetophenone on metal ha-

Table 9. Competitive Complexation in Solution of 4-Methylacetophenone and Acetyl Chloride on Different Metal Halides Lewis Acids[a]

Lewis acid	% complexed 4-MeC_6H_4COMe	% complexed CH_3COCl
$AlCl_3$	92	4
$AlBr_3$	92	0
AlI_3	100	0
$SnCl_4$	96	13
$SnCl_2$	0	0
$TiCl_4$	100	14
$FeCl_3$	62	30
$GaCl_3$	100	16
$SbCl_5$	100	29
$SbCl_3$	42	12
$NbCl_5$	100	8

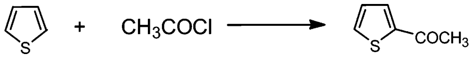
[a] Data taken from ref 832.

lides.[832] The results shown in Table 9 indicate a considerable preference of 4-methylacetophenone over acetyl chloride.

From the above discussion, it is understandable why there is a strong incentive to develop solid acylation catalysts with high turnover numbers. To do this, several directions have been undertaken. One involves finding weaker metal halides, such as $BiCl_3$, for which the complexation with aryl acetones is not so strong, favoring comparatively the complexation with the chlorine in the acid chloride.[833] Another potential solution would involve using less complex forming salts than metal halides with aryl ketones in the same way as rare earth triflates are used.[834,835] Finally, a better solution can be the use of a solid catalyst in order to hinder aryl ketone complexation.

Acid solid catalysts such as montmorillonite and Nafion were used already in 1947 and 1982 for the acylation of the very reactive thiophene with acetyl chloride (Scheme 81).[836,837]

Scheme 81

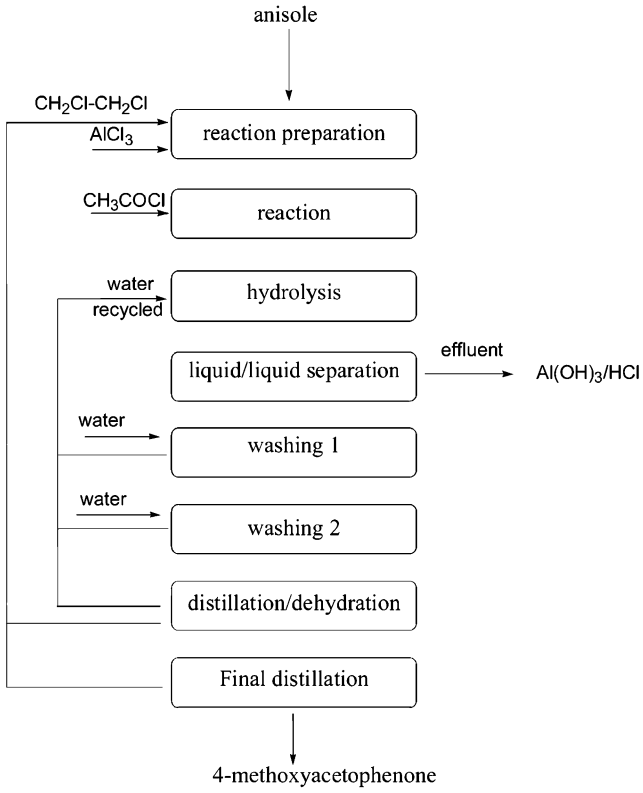


Other activated aromatics, such as anisole, veratrole, and 2-methoxynaphthalene, were acylated with acid anhydrides using zeolites exchanged with iron, copper, aluminum, zinc, and cobalt.[838,839] While these catalysts are active and selective for carrying out acylations, leaching of the exchanged metal can be an important drawback. MCM-41 mesoporous molecular sieves have been used as catalysts for the acylation of 2-methoxynaphthalene.[642] Since no geometrical restrictions exists with the mesoporous material, the acylation occurs primarily to position 1. However, when MCM-41 was impregnated with Zn and nitrobenzene was used as a solvent, a high selectivity to 6-acetyl-2-methoxynaphthalene occurred. Again, care should be taken when addressing the possibility that metal leaching could occur from this catalyst. Unexpectedly, graphite has been reported to be an active acylation catalyst, while carbon black is inactive.[840] In the case of graphite, the catalytic active sites can be associated with the precence of metal impurities. Other catalysts, such as hydrated zirconia, sulfated zirconia, heteropolyacids, Nafion, and (even better) Nafion/silica composite materials, have been reported as catalysts for the acylation of aromatic compounds.[841−846] The problem associated with these catalysts is their regeneration that cannot be done by calcination in air.

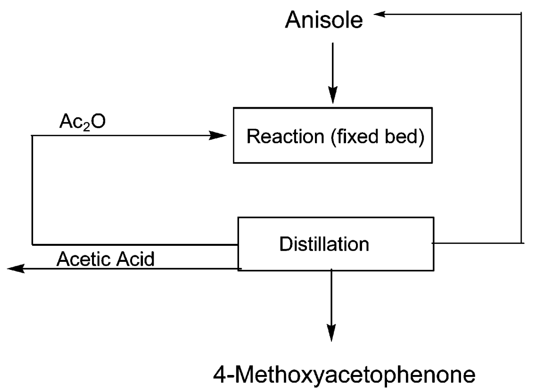
An important step toward the use of solid catalysts for acylation of aromatics was the use of microporous molecular sieves, more specifically zeolites. These can present Brönsted (bridged hydroxyl groups) and Lewis acids (exchange ions and extraframework aluminum). Ce^{3+}-exchanged Y zeolite showed good activity and very high para selectivity for the acylation of toluene with organic acids with 8−12 carbon atoms.[847] Anisole has been acylated successfully with different acylating agents using Y and Beta zeolites.[848−850] Isobutylbenzene is acylated with acetic anhydride to give *p*-isobutylacetophenone, which is an intermediate in the synthesis of the anti-inflammatory ibuprofen. With H Beta zeolite as catalyst, the reaction at 140 °C gives in 1 h a yield of 86%, with 96% para selectivity, although the acylating reagent/catalyst ratio is high. Other less activated aromatics such as toluene and xylenes have also been acylated using zeolites.[851−854] Beta zeolite was particulary active for acylation of toluene with acetic anhydride, with arene-to-anhydride molar ratios of ≥ 10. Better results were obtained when nanocrystalline Beta zeolite was used with a low framework Si/Al ratio.[851] The catalyst is poisoned by adsorption of the acetophenone formed, and the production of organic deposits limits the extent of the reaction. Deactivation was minimized by using the nanocrystalline zeolite as catalyst, in which the role of the external surface is preferential.

Acetylation of 2-methoxynaphthalene to give 2-acetyl-6-methoxynaphthalene, which is a precursor of the anti-inflammatory (*S*)-Naproxen, is carried out commercially using $AlCl_3$ as catalyst. Environmentally friendly zeolite catalysts such as HY, ZSM-12, ZSM-5, modernite, Beta, and and ITQ-7 have been used to carry out this reaction.[855−860] Two major products, 1-acetyl-2-methoxynaphthalene and 2-acetyl-6-methoxynaphthalene, together with small amounts of 1-acetyl-7-methoxynaphthalene, are obtained. The acylation generally occurs at the kinetically favored 1-position, giving the 1-acetyl-2-methoxynaphthalene product, which is the undesired one. Beta zeolite should increase the selectivity to the 2,6-isomer by shape selectivity, since it has been shown that the energy barrier for diffusion of the 2,6-isomer is smaller than that of the other isomers in the case of Beta zeolite.[861] However, the active sites at the external surface decrease the selectivity to the 2,6-isomer. Elimination of the external acid sites of Beta zeolite by coating of the crystals with a layer of amorphous silica or using large zeolite crystals with a low ratio of external to internal acid sites increases the zeolite selectivity.[855] A tridirectional zeolite (ITQ-7) with pores slightly smaller than the larger pores of Beta zeolite gives a higher selectivity to 2-acetyl-6-methoxynaphthalene than Beta.[860] It has been shown by molecular dynamics calculations that this is due to the much lower diffusion coefficient of 1-acetyl-2-methoxynaphthalene in Al−ITQ-7 than in

Scheme 82



Scheme 83



Beta. Polymorph C of Beta (ITQ-17) has also been used as a selective catalyst for acylation of 2-methoxynaphthalene.[860]

The accumulated knowledge and the systematic studies carried out at Rhodia have led to the first industrial application of solid catalysts (zeolites) to the acylation of anisole and veratrole using a fixed-bed reaction process.[862,863] This considerably simplifies the process and leads to an increase in para selectivity, a reduction of operating cost, and a dramatic reduction of effluent volume (as can be seen by comparing the block diagrams in Schemes 82 and 83 for the processes catalyzed by $AlCl_3$ and zeolites, respectively).[864]

Even though commercial applications of solid catalysts as a substitute for $AlCl_3$ have started with the case of anisole and veratrole, the application of solid catalysts to other processes, such as the acylation of 2-naphthol or 2-methoxynaphthalene, is still limited due to catalyst poisoning and the low selectivity to the desired isomer. These are two points on which further research needs to be done.

9. Prospects and Concluding Remarks

The possibilities of implementing new processes in the oil refining industry and in the preparation of bulk chemicals are becoming relatively small, given the large effort in research and development that has been already done, the huge capital investment needed, and the anticipated oil shortage in forthcoming years. The consequent obvious move toward renewable and sustainable feedstocks has already started with the compromise of the European chemical industry to reach 20% of sustainable feedstocks in the next five years.

In contrast to the situation in refining and petrochemistry, it can be easily foreseen that there will be a revolutionary change in the base, intermediate, and fine chemical sector, in which the requirement to comply with green chemistry principles will be enforced in the near future. Friedel−Crafts acylations and the Beckmann rearrangement are perhaps the most important challenges, together with the development of new catalytic C−C bond-forming reactions under mild conditions and the introduction of enantioselectivity. The fixation of CO_2 will appear as an attractive industrial process. Given that the processes for the production of fine chemicals are in the liquid phase, the nature of the medium has to play a central role. Here, the first obvious option is to develop solventless processes when one of the reagents is a liquid, but there is no doubt that other green solvents discussed earlier (water, supercritical fluids, ionic liquids, fluorous phases) will become of paramount importance.

Concerning the catalysts, the tendency toward reusable solids will accelerate in the near future. Supporting Lewis acids in solids is a viable alternative, provided that the ubiquous leaching of the active sites is adequately solved. But in order to avoid leaching and increase the durability and stability of the catalyst, isotropic solid acids, either amorphous or crystalline, are in principle the best options. For these solid acids, the problem is poisoning and deactivation of the active sites, which makes reactivation a key issue of the process. Also of prime consideration is the acid demand of the reaction. The acid strengths of the solid acid sites are typically lower than those of conventional metal halides, and methodologies to enhance them may be needed. Also, studies addressing in-depth the influence of the nature of the support or the solid considered as a macromolecular ligand are necessary. Through fine-tuning of the surroundings of the sites, modulation of the soft/hard nature of the Lewis acidity and, therefore, a selectivity increase could be achieved.

10. Acknowledgments

We are grateful to all the colleagues and co-workers who have been collaborating with us over the years in the field of solid Lewis acids. Continued financial support by the Spanish Ministry of Education is gratefully acknowledged.

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CR030680Z