

Solid Acids for Green Chemistry

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ABSTRACT

Solid acids and especially those based on micelle-templated silicas and other mesoporous high surface area support materials are beginning to play a significant role in the greening of fine and speciality chemicals manufacturing processes. A wide range of important organic reactions can be efficiently catalyzed by these materials, which can be designed to provide different types of acidity as well as high degrees of reaction selectivity. The solid acids generally have high turnover numbers and can be easily separated from the organic components. The combination of this chemistry with innovative reaction engineering offers exciting opportunities for innovative green chemical manufacturing in the future.

Introduction

Catalytic technologies have played a vital role in the economic development of the chemicals industry in the 20th century, with a total contribution of ~20% of world GNP. In the 21st century, we can expect the drive toward cleaner technologies brought about by public, legislative, and corporate pressure to provide new and exciting opportunities for catalysis and catalytic processes.¹

A rapidly growing area of heterogeneous catalysis is for environmental pollution control. Although heterogeneously catalyzed processes are widely used in large scale petrochemical processes, the majority of fine, speciality, and pharmaceutical chemicals manufacturing processes rely on homogeneous reagents and catalysts, with solid catalysts used in little beyond hydrogenations. Many of these processes were developed about 100 years ago and had been developed simply to maximize product yield, disregarding the environmental impact of inorganic waste and toxic byproducts formed during the reaction. Most of the waste is generated during the separation stage of the process when a typical water quench and neutralization (for acidic or alkaline systems) results in the formation of large volumes of hazardous waste.^{1,2} Increasing waste disposal costs are adding to the environmental costs and the societal costs of an increasingly hostile public toward chemical waste.^{3,4}

The efficient use of solid catalysts and reagents that stay in a phase separate from the organic compounds can go a long way to achieving these goals. Product isolation is simplified and reactions often run under milder conditions and give higher selectivity. The atom efficiency of

the reaction is improved, the process is simplified, precious raw materials used in the manufacture of the catalyst are given increased lifetime (through reuse), and the volume of waste is significantly reduced. Polymer-supported catalysts have been widely used in research and in process chemistry, but their use is restricted due to easy damage to the organic polymer (thermal or chemical).⁵ Zeolites have excellent thermal and chemical stability and have been incredibly successful in vapor phase chemistry, but they are less useful for many organic reactions in which molecular sizes can exceed the small zeolitic pores and where liquid-phase reactions can lead to diffusion control. We have sought to exploit the recent emergence of mesoporous solids in organic synthesis by designing materials that can accommodate most organic molecules and have active surfaces that can catalyze important reactions.⁶ By combining this with innovative engineering appropriate for smaller volume heterogeneous reactions, we hope to develop a range of novel greener processes for the manufacture of higher volume organic chemicals.

Mesoporous Solids

It has been shown that the type of support material used is a critical factor in the performance of the resulting supported catalyst or reagent in an organic reaction system.⁷ The main factors that should be considered when employing a material as a support are

- thermal and chemical stability during the reaction process and for batch reactions during the separation stage and
- accessibility and good dispersion of the active sites.

There are a number of materials that partly or wholly satisfy these requirements, including pillared clays, some carbons, and mesoporous aluminosilicates pioneered by Mobil scientists,⁸ as well as mesoporous silicas. We have studied all of these and have, for example, been involved in the development of commercial clay-based catalysts that are used in some Friedel–Crafts processes.^{1,9} More recently, we have extended our research to mesoporous coals, which we have shown to be amenable to chemical surface modification.¹⁰ Thus, mesoporous activated carbons can be modified either by (a) direct treatment with a silane, such as vinyltriethoxysilane, or (b) initial treatment with the vinylsilane leading on treatment to polymerization of the vinyl groups.¹⁰ It is the micelle-templated silicas (MTS) that have attracted most of our attention in recent years. They offer high surface areas (often to >1000 m² g⁻¹, putting them at the top of the surface area league alongside some carbons) and controllable pore sizes (from ~2–5 nm or larger) that can be important in controlling molecular diffusion and may affect product selectivity. Furthermore, since Pinnavaia's very important work in the 1990s¹¹ we can now add ease of synthesis and "greenness" of the synthesis to the advantages, because the neutral templating method allows simple washing for separation as well as easy recovery and reuse of the template (e.g., a long-chain amine). The silica surface in these materials

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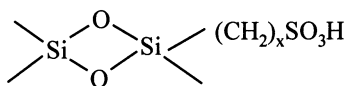


FIGURE 1. MTS-sulfonic acids prepared via in situ sol-gel or post grafting.

consists of two types of functional groups, siloxane (Si–O–Si) and silanol (Si–OH). Chemical surface modification of the preformed silicas can be achieved by reaction of either of these groups via nucleophilic substitution at the silicon or via direct attack on the hydroxyl group. Halogenation, reaction with metal halides, and most commonly, reaction with silanes are all used to modify the silica surface for a particular application. Macquarrie's landmark paper¹² along with others in the same period^{13,14} showed that the simple sol-gel preparation of the materials could be adapted to give inorganic-organic hybrids in situ. This method also gave rise to materials with a much higher degree of functionality (up to ~5 mmol g⁻¹) than was possible through postmodification. Thus, it became apparent that a wide range of organic system compatible mesoporous materials could be prepared in a largely waste-free one-pot process at room temperature in aqueous alcohol – a truly green preparation process for the next generation of green catalysts!

Solid Acids

Solid acids can be described in terms of their Brønsted/Lewis acidity, the strength and number of these sites, and the morphology of the support (typically in terms of surface area and porosity). High product selectivity can depend on the fine-tuning of these properties. Thus, some rearrangement reactions require pure Lewis acidity (e.g., the rearrangement of α -pinene oxide using supported metal halides¹⁵; see later). Friedel-Crafts reactions can require Lewis acidity (e.g., for alkylations using alkyl halides) or Brønsted acidity (e.g., for alkylations using alcohol), or indeed, a combination of both (e.g., for Friedel-Crafts acylations using acid chlorides). Pore constraints may influence product selectivity as a result of the sizes of substrates, intermediates or products (e.g., the improved selectivity to monoalkylaromatics using long chain alkenes using mesoporous silicas compared to larger pore materials¹⁶; see later). At a more fundamental level, the use of mesoporous supports has enabled supported reagents and catalysts to be used in reactions of much bulkier substrates than could be considered for microporous (zeolitic) materials.¹⁷ The synthesis of pure Lewis or Brønsted solid acids is a particularly important challenge where some progress has been made. Chemically modified MTS materials as analogues for sulfonic acids have recently been reported and show great promise as solid Brønsted acids (Figure 1).^{18–20} Pure Lewis acids are more difficult to achieve, because Brønsted acidity often arises from Lewis acid-base complexation (Figure 2).

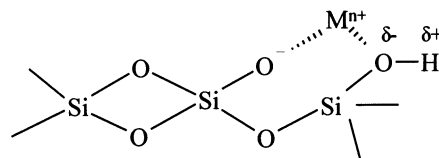


FIGURE 2. Brønsted acidity arising from Lewis complexation on a silica surface.

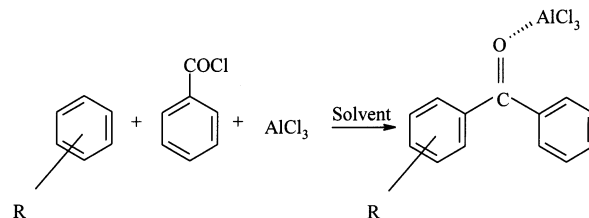


FIGURE 3. Benzoylation of an aromatic substrate using aluminum chloride, leading to a stable Lewis complex.

Silica-Supported Aluminum Chloride

Aluminum chloride is the most widely used of Lewis acids. It is very active, soluble in many organic solvents, and inexpensive. Unfortunately, it is often too powerful an acid, giving unwanted side reactions, and very significantly in the context of green chemistry, it may need to be used in reagent quantities because of its ability to strongly complex Lewis base products, for example, in a benzoylation reaction (Figure 3). When the reaction is complete, the only viable method for separating the aluminum chloride is by a destructive water quench, leading to large volumes of hazardous waste. Thus, the use of aluminum chloride can lead to violations of several of the principles of green chemistry through the release into the environment of hazardous substances, through the use of volatile organic solvents, and through the use of reagent-like quantities that are lost on workup, as well as through unselective reactions that do not lead to the maximum incorporation of starting materials in the product.

There have been several attempts to immobilize aluminum chloride so as to help overcome these problems. We have found that slow reaction of AlCl₃ with the surface of silica in an aromatic solvent leads to a material with strong Brønsted and Lewis acidity,²¹ presumably arising from the formation of SiOAlCl₂ sites on the surface. The use of controlled-pore MTS materials can give the added benefit of improved reaction selectivity. Thus, in the reaction of aromatic substrates such as benzene with alkenes, 24-Å-pore catalysts leads to an improvement in the yield of the monoalkylate of ~10% for C6–C16.²² This can be further improved through the use of external site poisons. Two methods have been tested. The first involved poisoning the catalyst with a bulky amine, triphenylamine so as to selectively remove the external catalytic sites. The second method, based on essentially the same principle, involved elimination of the external silanol groups of the silica by reacting them with a bulky silane, triphenylchlorosilane, prior to catalyst formation (Figure 4). The effects on the selectivity toward monoalkylation are shown in Figure 5. The catalyst poisoned with triphenylamine shows a gradual loss in activity with increasing chain

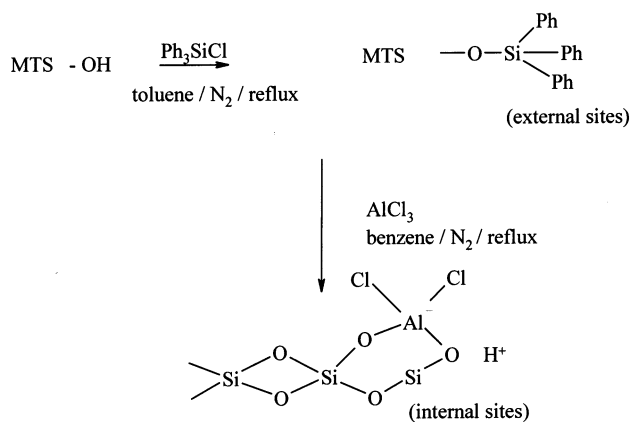


FIGURE 4. Preparation of supported aluminum chloride with blocked external sites to maximize in-pore catalysis.

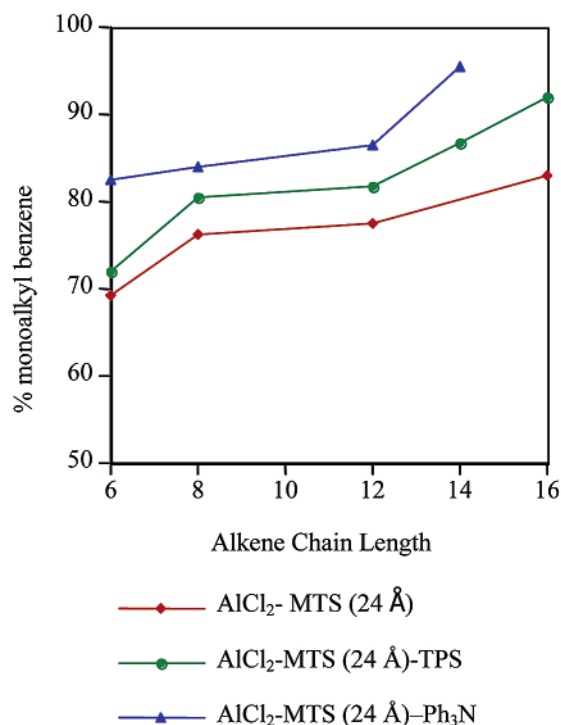


FIGURE 5. Comparison of catalyst selectivities toward monoalkylation in the reaction of benzene with alkenes using modified and unmodified supported aluminum chloride catalysts.

length of the alkene, which is consistent with the pore openings being restricted by the large amine groups, which in turn reduces the alkene diffusion rate through the catalyst. Interestingly, this effect is not observed for the triphenylsilane-blocked catalysts, suggesting that the pore restrictions are not as great. A significant increase in selectivities to the monoalkylated products is observed in all cases, consistent with the catalysis taking place more within the pores. In the case of tetradecene, an increase in the amount of alkene dimerization is observed (this side reaction is not normally significant within these catalytic systems, although it can be in others). This is probably due to the fact that the externally blocked catalyst still possesses Lewis acid sites that are capable of catalyzing alkene oligomerizations. It is also worth noting that these heterogeneous catalytic systems also give useful selectivi-

Table 1. Comparison of *E* Factors for (Traditional Homogeneous) and Heterogeneous Catalytic Processes for the Alkylation of Benzene

homogeneous; 10:1 ratio of benzene:alkene; 2 wt % catalyst	heterogeneous; 2:1 ratio of benzene:alkene; 2 wt % catalyst
yield 90%	yield 90%
byproducts 10%	byproducts 10%
water quench and wash	filter
90% solvent (benzene) recovery	90% solvent recovery
0% catalyst recovery	100% catalyst recovery
For 1 mole Benzene	
205 g product	205 g product
71 g lost benzene	7.8 g lost benzene
15 g byproducts	2.2 g byproducts
900 mL water	
2.4 g Al(OH) ₃	
30.4 g NaCl	
<i>E</i> = 4.9	<i>E</i> = 0.14 (or 0.16 with no catalyst recovery)

ties to the favored 2-isomer (the isomer with the best biodegradability, which is required in detergent applications). Indeed, by using these supported aluminum chloride systems, we have achieved a selectivity comparable to that when using the large-pore zeolite HZSM-4, even though the latter requires high temperature and pressure for a reaction rate that is achievable at ambient conditions using our catalyst.²³

We can use the alkylation of benzene with a typical alkene as an example to calculate and compare approximate atom efficiencies via the *E* factor²⁴ of the heterogeneous and homogeneous processes (Table 1). For the sake of simplicity, we have made both product yields 90%, although as we have seen, the best solid catalysts are significantly superior to the homogeneous system.

These catalytic systems can be adjusted so as to favor alkene oligomerization. Low-molecular-weight thermoplastic materials with widespread applications, including adhesives and road markings, can be produced by the cationic polymerization of aliphatic refinery feedstreams. The composition of these is variable, but commonly includes monoalkenes and dialkenes as well as non-polymerizable alkanes. The commercial processes normally involve aluminum chloride or other Lewis acids that are destructively separated by a water quench, adding a step to the process and generating large volumes of waste (e.g., aluminous water). Here it is quite possible for the waste disposal costs to exceed the raw material costs. Added drawbacks include the inevitable organic chlorination that occurs and the need to dechlorinate unreacted feed and product, a requirement that is being made more stringent by new legislation. We have found that silica-supported aluminum chloride is an excellent catalyst for these polymerization reactions.²⁵ Reactions proceed under their own exotherms. Instead of the usual water quench, the catalyst is easily removed by filtration or decantation and can then be reused, although it is not as active as a result of relatively large amounts of adsorbed polymer (up to equal amounts by weight). The product yields are lower than those obtained with homogeneous aluminum chloride, although they can be improved by pretreatment of the feed, for example, with alumina and water, to remove catalyst poisons, such as organosulfur species. The mo-

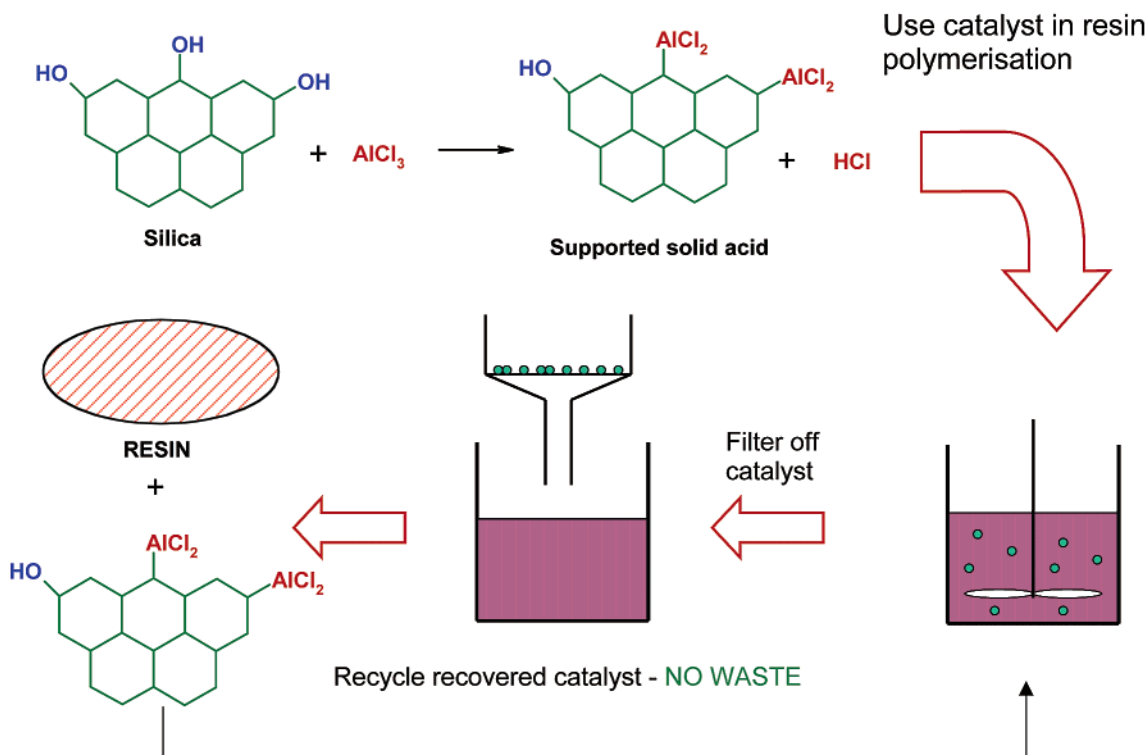


FIGURE 6. Illustration of the use of a solid acid in cationic resin polymerization.

lecular weight data for the products from homogeneous and heterogeneous reactions are broadly similar and, importantly for applications, the heterogeneous system gives a similarly low polydispersity M_w/M_n of <2 . Lower M_z values are obtained with the solid catalyst, probably as a result of the limitations of the pore cavity physically restricting the length of the polymer chain. Low M_z values are important, because they translate to increased compatibility of the resin with other components in an adhesive formulation. Interestingly, at loadings of aluminum chloride above the optimum, the M_z value of the resin obtained rapidly increases, which is consistent with a homogeneous contribution to the reaction.

The homogeneous and heterogeneous reaction systems for producing hydrocarbon resins can be compared in a simple illustrative diagram (Figure 6). It should also be noted that the heterogeneous system offers other important advantages, including very low chloride levels in the organics (as well as very low aluminum consistent with a truly heterogeneous catalyst).

Interesting results are observed as we vary the feed composition. The effect on the standard homogeneous reaction of increasing the ratio of the dialkene to the monoalkene is a steady increase in polymer yield (although at higher ratios, the high M_z values make the product of little practical value). With the heterogeneous system however, there is a maximum in the polymer yield at a ratio of ~ 1 ; at higher or lower ratios, the yields fall.^{24,25} In recent unpublished work on the polymerization of pure alkene monomers with supported aluminum chloride, we again see dramatic differences from the standard homogeneous reactions. Remarkably, we also see nonlinear trends in product yields when studying binary alkene

mixtures, although we have yet to develop a theory to explain such observations. In preliminary investigations on the relative importance of Brønsted vs Lewis acidity, we have found that the Brønsted contribution is very important but can be switched off by selective complexation using the sterically hindered base 2,6-di-*t*-butylpyridine. In this way, we can study the effects of pure Lewis acidity alone, and it is clear that the two types of acidity have very different kinetics and can give different types of products, presumably due in part to the possible cyclization of growing polymers and the effects of this on material properties. Further research is underway in this area.

Other Covalently Bonded Lewis Acids

Direct reaction of BF_3 with the surface of silica to form Si-OBF_2 units is likely to give a rather unreactive material as a result of the strong B-O bond. We decided to tackle this problem by seeking an alternative method of surface attachment via complexation of the intact BF_3 molecule to a surface oxygen with the released proton forming a conjugate cation with a suitable Lewis base. Our preference has been to use alcohols as the base (Figure 7). These solid acids will have limited thermal stability (limited by the volatility of the alcohol) but are useful catalysts for a range of organic reactions, including esterifications, Claisen-Schmidt condensations, and phenol alkylations.²⁶⁻²⁹

Silica-supported BF_3 is a mild solid acid. In the alkylation of phenols, one advantage of this is that ethers can be C-alkylated without the rearrangement of the ether to give poly ring-alkylated products, as occurs with unsupported BF_3 (Figure 8).²⁹ Tanabe and Hattori have made

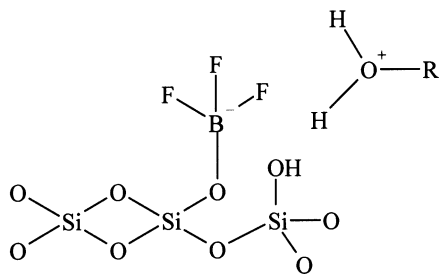


FIGURE 7. Hypothetical structure of the activities in silica-supported boron trifluoride.

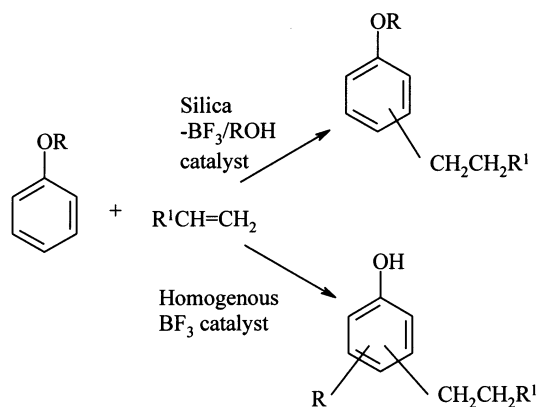


FIGURE 8. Selective C-alkylation of ethers using silica-supported BF_3 .

solid superacids based on silica-supported antimony pentafluoride.³⁰ Antimony trifluoride is a milder Lewis acid that still may be capable of reacting with a hydroxylated surface to form covalent bonds. We have found that by following a similar procedure to that found to be effective for the solid aluminum chloride catalysts, apparently stable forms of supported antimony trifluoride can be made.³¹ Surface areas for these catalysts are generally excellent ($300\text{--}\sim 1000\text{ m}^2\text{ g}^{-1}$ for some of the MTS-based materials). Thermal analysis shows that it is not made up of simple physisorbed SbF_3 . The Lewis acidity of the bound antimony centers is witnessed by the ability to titrate coordinated water molecules. Unsupported SbF_3 in water is very acidic, each mole being titrated by ~ 3 mole of hydroxide. At low loadings on the surface ($<1\text{ mmol g}^{-1}$), each site is also titrated by ~ 3 mole equiv of base, but as the loading increases, the number of equivalents of base goes down (e.g., to 1.5 equiv at 2 mmol g^{-1}). This is consistent with the formation of SiOSbF_2 units on the surface, which at higher loadings interact with each other by SbFSb bridges, effectively blocking Lewis sites (Figure 9).

MTS-supported antimony trifluoride is an active and reasonably selective catalyst for the oxidation of cyclohexanone to caprolactone using hydrogen peroxide (Figure 10). We have been able to obtain 76% of caprolactone (78% peroxide selectivity); this is considerably better than many conventional Lewis acids, including unsupported SbF_3 itself.³²

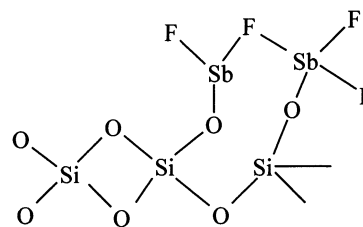


FIGURE 9. Supported antimony trifluoride showing the effect of fluorine bridging between neighboring sites.

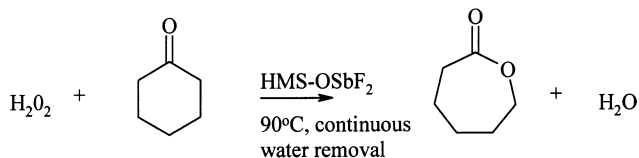


FIGURE 10. The Baeyer–Villiger reaction of cyclohexanone to caprolactone catalyzed by MTS-OSbF_2 .

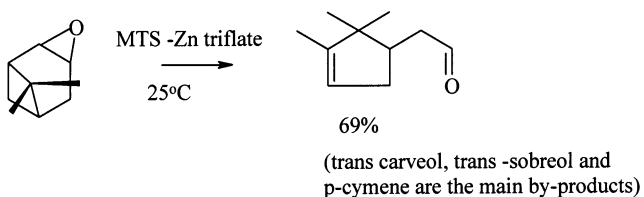


FIGURE 11. Rearrangement of α -pinene oxide catalyzed by MTS-Zn triflate .

Supported Zinc Salts

The original solid Lewis acid developed in our laboratory was supported zinc chloride.^{33,34} This is an acid-treated clay-based material that was the basis of a commercial catalyst for Friedel–Crafts reactions still on the market today.³⁵ Analogues based on mesoporous silicas were subsequently discovered and shown to be more active if also more expensive. We have since extended the materials chemistry to clay- and silica-supported zinc bromide as catalysts for the bromination of activated and moderately deactivated aromatic substrates (PhEt , PhMe , PhBr , PhCl , Ph^tBu) under mild conditions.³⁶ Paraselectivities of up to 11:1 (p/o ratio) can be obtained (typically 3 with the unsupported salt).

We have also found that zinc triflate is amenable to supporting on a mesoporous silica. We have developed a 2.4-nm pore MTS-based material for the selective rearrangement of α -pinene oxide to campholenic aldehyde (Figure 11).¹⁵

Interestingly, the best results in terms of selectivity to the aldehyde (the favored product in the fragrance industry, where it is used in the synthesis of sanatol) are achieved using a very low-loaded catalyst ($0.01\text{ mmol g}^{-1}\text{ Zn}(\text{OTf})_2\text{-MTS}_{24}$) – up to 69% selectivity of 100% substrate conversion in 60 min at ambient temperature. These materials are reusable giving the same selectivities, although activities may be reduced somewhat because of further reactions of the aldehyde. The currently favored commercial procedure uses homogeneous zinc salts, but they have poor turnover numbers (<10) compared to the supported catalysts ($\text{TON} > 3000!$). Thus, the solid catalysts process significantly reduces the volume of hazardous

metal waste, which is consistent with the principles of green chemistry.

The nature of the zinc triflate-support interaction is unknown. We have proven that under the conditions of our experiment, hydrolysis to triflic acid does not occur. Loss of zinc in reaction is $<0.5\%$ for the most useful 0.01 mmol g^{-1} catalyst. To further confirm catalyst stability under reaction conditions, filtration completely stopped the reaction ("hot filtration test").

Collaboration between chemists and chemical engineers will be essential if new green chemical technology is to be exploited commercially. The fine, speciality and pharmaceutical chemicals industries are not particularly accustomed to using solid catalysts, although there have been some successful applications.³⁵ Formed catalysts can be made, enabling their use in plugged flow or other (semi)continuous reactors. One innovative method we are exploring is to bind solid catalysts on a plate suitable for use in a high-throughput reactor. In this way, we have been able to develop the first examples of catalytic spinning disk technology with the combined advantages of good heat and mass transfer characteristics, high throughput, and selective catalysis. They are safer to use than conventional reactors, which is consistent with this aspect of green chemistry. These reactors are suited for fast reactions, since they involve short residence times on the catalytic disk. This is ideal for reactions such as the α -pinene oxide rearrangement in which short reaction times favor higher selectivity.³⁷

Mesoporous Zirconia-Based Solid Acids

Although silicas and aluminosilicates have attracted the greatest attention as oxide supports, there are others that offer the necessary properties of high surface area, chemical and thermal stability, and an active surface. Zirconia is one such material. When its surface is derivatized with sulfated functions, "sulfated zirconia" (SZ) is an interesting and useful solid acid.³⁸ SZ has attracted a lot of attention because of its high catalytic activity for the conversion of small hydrocarbons, especially *n*-butane isomerization. We have, however, been interested in the much less exploited potential of SZ for liquid-phase organic reactions.^{39–41} Normal SZ is microporous in nature, making it suitable for traditional vapor-phase applications but less amenable to liquid phase reactions. However, mesoporous versions can be made. Both the surface area and the sulfate loading of SZ materials decrease on increasing the calcination temperatures, especially at $>550 \text{ }^\circ\text{C}$.³⁹

We use FTIR spectroscopic titration with pyridine to study the nature of the surface acidity of these materials.⁴⁰ Catalysts calcined between 500 and $600 \text{ }^\circ\text{C}$ and subsequently cooled in a desiccator exhibited only Brønsted acid sites. This is in contrast to previous reports in which sulfated zirconia was reported to exhibit significant amounts of Lewis acidity. We believe that this is due to the rapid adsorption of water from the atmosphere or from organic solvents or substrates on cooling, which converts Lewis into Brønsted acid sites. Practically, it

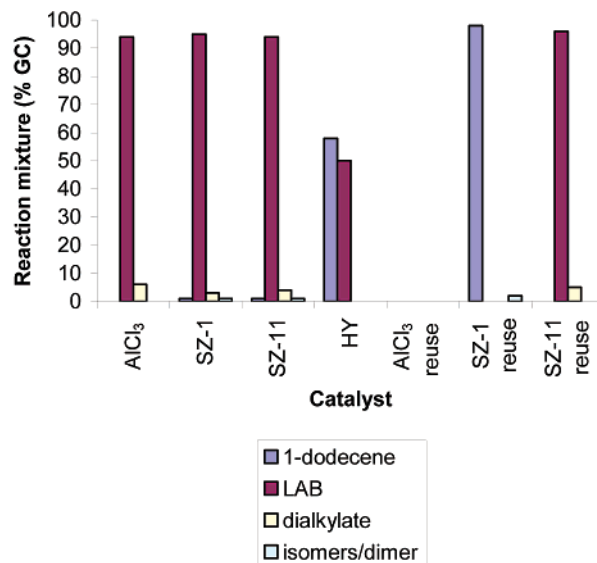


FIGURE 12. Comparison of the activity (first and second uses) of mesoporous SZ with AlCl_3 and HY in the alkylation of benzene with 1-dodecene.

means that for liquid-phase organic reactions in conventional batch-type reactions carried out in normal laboratories or manufacturing plants, SZ can be expected to behave as a solid Brønsted acid.

The Brønsted acidity of SZ combined with its mesoporosity and its excellent thermal stability makes it a very good candidate for aromatic alkylation reactions using long chain alkenes, which are prone to competitive polymerization easily, causing pore blockage (such heavy organics can be more easily removed from a more thermally stable material). This, indeed, proves to be the case.⁴⁰ We used the commercially important reaction of benzene with 1-dodecene as a test reaction for the preparation of linear alkylbenzenes (LABs). LABs are the most important commercial class of alkylated aromatics as a result of their better biodegradability, among other useful properties, and dodecylbenzene, in particular, is manufactured on a very large scale for detergency uses. By comparing mesoporous, optimally activated SZ with AlCl_3 (the traditional catalyst for such reactions) and HY zeolite (one of the modern catalysts for the reaction), we were able to show that the SZ has activity comparable to AlCl_3 and is more active than HY (Figure 12). Furthermore, the mesoporous SZ shows excellent activity on reuse.

The reaction seems to be general for several alkanes. C6–C16 alkanes give almost identical rates of conversion (complete conversion of the alkane in $<1 \text{ h}$ at $35 \text{ }^\circ\text{C}$ using excess PhH) and selectivity to the corresponding mono-alkylbenzenes (90%).

Friedel–Crafts acylations represent one of the greatest challenges in organic chemistry to the green chemist. They consume reagent-like quantities of "catalyst" and produce greater quantities of waste than product. Friedel–Crafts acylations are normally run with AlCl_3 , except for activated substrates in which milder Lewis acids, such as FeCl_3 , may be sufficient. Solid acids are generally more weakly acidic than AlCl_3 , and at least at a simplistic level, this may help

explain why they have yet to make major inroads into commercial Friedel–Crafts processes. A zeolitic-based process has been developed for the acylation of anisole⁴² and a clay-based catalyst has been proven for some benzylation and sulfonylation reactions.³⁵ But these few success stories rely on highly activated substrates or forcing conditions that can destroy less robust catalysts, such as clays. We have found that mesoporous SZ will catalyze the benzylation of benzene under moderate conditions (85 °C). Reactions are run in excess benzene, thus avoiding another organic component (a solvent) and are quite slow (reactions can take 20+ h for complete conversion of the substrate), but the SZ is *genuinely catalytic*. The catalyst is easy to separate at the end of the reaction and can be reused (turnover number >20) with unreacted benzene being recycled. Although the reaction benefits could certainly be improved, the process has many green credentials.

I would like to thank the past and present members of the York Green Chemistry Group who have contributed to the work described here. I am also grateful to our many sponsors, notably the U.K. research council EPSRC, the Royal Academy of Engineering, and a number of chemical and materials companies.

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