Bases and Basic Materials in Chemical and Environmental Processes. Liquid versus Solid Basicity

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1. Introduction

The development of more efficient, safer, and more environmentally friendly chemical technologies is a major need of humanity. This is in particular true today, when a relevant change in perspective is approaching. A significant decrease in the use of fossil raw materials and a definite increase of the use of renewable raw materials are expected and desired. Acid−base interactions are, together with redox exchanges, the most prevalent phenomenon in all fields of chemistry. Accordingly, bases and acids are among the most important industrial chemical products.[1,2] They find widespread application not only in the chemical industry itself,[3] such as, e.g., hydrocarbon chemistry,[4] all fields of industrial organic chemistry,[5,6] and industrial inorganic chemistry (including metallurgy, semiconductor technology, ceramurgy, fertilizer technology),[7] but also for energy production processes and even for domestic applications. As reviewed recently by ourselves,[8] basic compounds find relevant application in processes aimed at reducing the environmental impact of chemical plants and energy production facilities. On the other hand, both acids and bases may themselves behave as pollutants when dispersed in the environment and/or incorrectly discarded.

Recently, we reviewed the properties and the practical applications of acidic compounds and materials in relation to their use as catalysts in the hydrocarbon industry.[9] In this case. there is an evident trend toward substituting solid acids for liquid acids in order to reduce the environmental impact of industrial processes. The present review will focus on the characteristics of basic compounds and materials largely used in industrial and technological chemistry. We will not discuss the details of reaction mechanisms. Nevertheless, we will summarize the properties of liquid bases, and we will focus on the characterization and use of solid bases. Our contribution is intended to underline the linkage between the chemical knowledge of acid−base interactions and the engineering of chemical processes as well as their environmental impact. Also in this case, we would like to provide evidence of trends aimed at improving process safety and limiting environmental pollution, in particular when they are related to the increased use of solid basic materials.

Guido Busca received his Laurea Degree in Chemistry at the University of Milan in 1977. Next he joined the group of Prof. V. Lorenzelli at the University of Genova (Italy), working in the field of infrared spectroscopy of materials. He was assistant professor of Organic and Industrial Chemistry at the Engineering Faculty of the University of Bologna from 1983 to 1988. In 1988, he became an Associated Professor and, in 2000, he became a Full Professor of Chemistry at the Engineering Faculty of the University of Genova. Since 2004, he has been a Full Professor of Industrial and Technological Chemistry at the University of Genova. He was the Coordinator of the Italian Group of Catalysis from 2000 to 2002. His research interests continue to be in the field of surface chemistry of oxide materials, including heterogeneous catalysis.

2. The Concepts and the Measures of Basicity in the Liquid Phase. A Tutorial

2.1. Basicity in Water Solution

As is well-known, pure water is very weakly dissociated. The water autoprotolysis equilibrium is generally denoted as follows:

$$H_2O \leftrightharpoons H^+ + {}^-OH \qquad (1)$$

and the autoprotolysis constant (or ionic product) of water

$$K_w = [H^+][{}^-OH] = 1.008 \times 10^{-14} \text{ at } 25 \,°C \qquad (2)$$

where the molar concentrations of the species are used as an approximation of their activity.[10] As a result of this, the molar concentrations of both $[H^+]$ and $[{}^-OH]$ are nearly 10^{-7} at 25 °C. When $[{}^-OH] > 10^{-7}$, the water solution is said to be "basic", while when $[H^+] > 10^{-7}$, the water solution is called "acidic".

Actually, the position of equilibria such as eq 1 is strongly affected by the environment of both the reactant and product species. Water (seen as the reactant) is solvated by itself, being involved in a network of hydrogen bondings in which every hydrogen atom bridges two oxygen atoms and each oxygen atom bonds to two protons and H-bonds to two others. Protons and hydroxide anions are also both solvated by water, which also acts as the solvent. As discussed by Kazansky,[11] although the proton is mostly assumed to associate with one water molecule to form the hydronium ion H_3O^+,[10] the actual environment of a solvated proton in water is more like $[H(H_2O)_6]^+$, or even more highly hydrated complexes.

Several theoretical and experimental studies have been reported in very recent years concerning the interaction of the hydroxide anion with water molecules. The very recent experimental and theoretical study of Cwiklik et al.[12] concerning ^-OH impurities in and on ice concluded that the
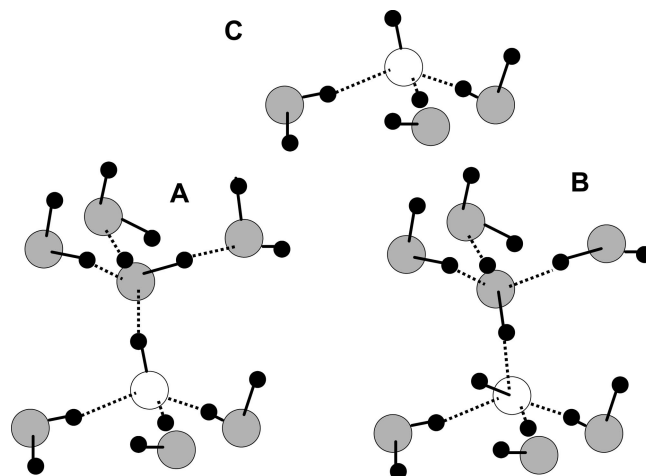

Figure 1. Calculated coordination of the hydroxide ions impurities in and on ice (from ref 12): In-the-lattice (A) and off-the-lattice (B) type of ^-OH structure inside ice. For clarity, hydroxide with only seven nearest neighboring water molecules is presented. (C) ^-OH structure at the surface.

tetrahedral complex A (Figure 1A), in which the ^-OH accepts three H-bonds and donates one, is not stable and leads to ^-OH ejection to the surface via a sequence of (barrierless) proton jumps. Instead, complex B, in which ^-OH accepts four H-bonds and donates none, is stable (Figure 1B). These data could agree with results from IR and Raman spectroscopy, which show a free OH stretching band for hydroxy-groups in water at 3610 cm^{-1}.[13] Studies of the interfacial structures suggest that such ^-OH species, whose proton is not involved in H-bondings, may be located at the water–air surface,[14] like they are at ice crystal surfaces.[12] Neutron diffraction experiments with isotopic H/D substitution suggest that the solvation shell of the ^-OH ions in water has an almost concentration independent structure, although with concentration dependent coordination numbers. The hydrogen site coordinates a water molecule through a weak bond, while the oxygen site forms strong hydrogen bonds with a number of molecules. On the average, this number would be very close to four at the higher water concentrations and would decrease to about three at the lowest one.

The state of the hydroxide ion in basic solutions may be extrapolated from the solid state structures of hydrated metal hydroxides, such as soda hydrates.[15] In the case of NaOH·7H$_2$O, the most hydrated solid soda phase, the hydroxide anions constitute distorted dimeric octahedral complex anions $[(OH)_2(H_2O)_{10}]^{2-}$. The oxygen atoms of the two OH's are H-bonded to five protons of five different water molecules while their own proton interacts with the oxygen of a bridging water molecule (Figure 2). This heptahydrated compound corresponds to 24.1% soda by weight, i.e., a 7.57 M caustic solution, which is to say, a very strongly basic solution. It consequently seems very reasonable to suppose that the hydroxide anion tends to form isolated octahedra $[(H_2O)_6OH]^-$ when in sufficiently diluted water solution and dissociated from the balancing cation. It seems relevant to remark that the oxygen atom of the hydroxyl ion may be involved not only in three but also in five hydrogen bonds.

In 1884, S. A. Arrhenius[16] defined an acid as any hydrogen-containing species able to release protons, and a base as any species able to release hydroxide ions. This
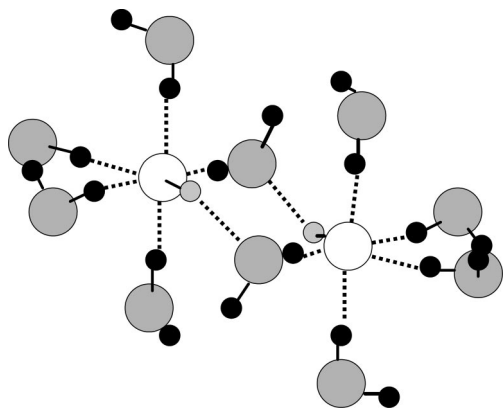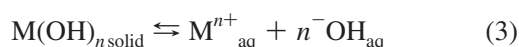
Figure 2. Coordination of the hydroxide ions in solid $NaOH \cdot 7H_2O$ (Redrawn with permission from ref 15. Copyright 2003 Mineralogical Society of America).

approach implies that metal hydroxides are typical basic compounds, as follows:

$$M(OH)_{n\,solid} \leftrightarrows M^{n+}_{aq} + n\,{}^{-}OH_{aq} \qquad (3)$$

where complete dissociation in water solution is supposed. In 1923, J. M. Brønsted[17] and, simultaneously and independently but less precisely, T. M. Lowry[18] modified the definition of a base as follows: a base is any species capable of combining with protons. In this view, acid−base interactions consist in the equilibrium exchange of a proton from an acid HA to a base B, generating the conjugate base of HA, A^-, plus the conjugate acid of B, HB^+:

$$HA + B \leftrightarrows A^- + HB^+ \qquad (4)$$

Thus, basic species in water are either neutral compounds ("molecular bases") that are able to abstract a proton from water:

$$H_2O + B \leftrightarrows {}^{-}OH + HB^+ \qquad (5)$$
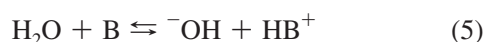
or anionic species (such as anions β^{n-}, arising from the dissociation of salts $M_n\beta_m$) that act in the same way, neutralizing themselves or reducing their charge:

$$H_2O + \beta^{n-} \leftrightarrows {}^{-}OH + H\beta^{(n-1)-} \qquad (6)$$
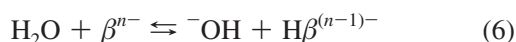
In the Brønsted definition a broader spectrum for the bases is considered than in the Arrhenius definition. The hydroxide anion itself is the basic species, rather than the metal hydroxide.

The strengths of basic compounds in dilute water solution are currently described in terms of Brønsted basicity by the shift of the dissociation equilibrium:[11]
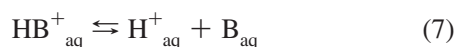
$$HB^+_{aq} \leftrightarrows H^+_{aq} + B_{aq} \qquad (7)$$

$$K_{HB} = [H^+_{aq}][B_{aq}]/[HB^+_{aq}] \qquad (8)$$

$$pK_{HB} = -\log K_{HB} \qquad (9)$$

where B may be neutral or anionic and HB^+ may be positively charged or neutral (or even negatively charged) and the molar concentration of the species is used as an approximation of its activity. K_{HB} is the acidity constant (K_a) of the conjugate acid

HB^+ of the base B. In Table 1 a list of various basic species is reported with their respective pK_{HB} values.

From the value of the autoprotolysis constant (or ionic product) of water (2) and the molar concentration of water, pK_{BH} for the hydroxide anion (i.e., pK_a of water, eq 11) can be calculated to be 15.74. Bases significantly stronger than ${}^{-}OH$ do not exist in water: in fact, they abstract protons from water, thus completely neutralizing themselves and producing hydroxide anions. Those having a basic strength moderately higher than that of the hydroxide anion ($pK_{BH} < 18-20$) may exist with small or very small concentration as such in water solution.

2.2. Lewis Basicity, Hard and Soft Basicity, and Nucleophilicity

In the same year as the Brønsted and Lowry definitions, 1923, G. N. Lewis[19] proposed a different approach. In his view, an acid is any species that, because of the presence of an incomplete electronic grouping, can accept an electron pair and thereby form a dative or coordination bond. Conversely, a base is any species possessing an electron pair which can be donated to form a dative or coordination bond. The Lewis-type acid−base interaction can consequently be described as

$$B: + A_L \leftrightarrows {}^{\delta+}B \rightarrow A_L{}^{\delta-} \qquad (10)$$
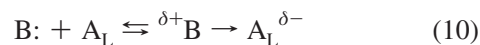
The Lewis classification of acids is broader than that of Brønsted, while Lewis basic species are also Brønsted bases. The Lewis definition is independent of water as the reaction medium. Lewis acid−base interactions are predominant in many practical phenomena, such as in complexation and extraction of metal ions, in adsorption on and dissolution of ionic solids, in solid state and melt reactions, etc.

In 1963, Pearson[20,21] introduced the concept of hard and soft acids and bases (HSAB), which may be taken as an evolution of the Lewis acid and base definition. Hard acids are defined as small-sized, highly positively charged, and not easily polarizable electron acceptors. Hard bases are substances that hold their electrons tightly as a consequence of large electronegativities, low polarizabilities, and difficulty of oxidation of their donor atoms. Hard acids prefer to associate with hard bases, while soft acids prefer to associate with soft bases. These complexes are thermodynamically more stable than mixed complexes and also form faster. According to this theory, protons and hydroxide and oxide ions are all hard, as are most O- and N-terminated anions. C- and S-terminated anions, sulphides, phosphines, and aromatic hydrocarbons are soft bases.

A theoretical assessment of the HSAB theory, which is actually an empirical one, has been given by Klopman.[22] According to this approach (Figure 3), the acid−base interactions depend predominantly on two effects: electrostatic interaction and orbital interaction. Electrostatic interactions predominate for hard−hard or "charge-controlled" acid−base interactions. Orbital interactions occur between the HOMO (highest occupied molecular orbital) of the base and the LUMO (lowest unoccupied molecular orbital) of the acid. The closer in energy these orbitals, the stronger the interaction. This factor is predominant for soft−soft or "frontier-orbital-controlled" acid−base interactions.

Similar interactions occur also with molecules (such as, e.g., CO_2, SO_2, SO_3, carbonyl, and carboxyl organic compounds) that do not actually have nonbonding empty orbitals (as required by the Lewis definition of an acid) but can give rise to empty orbitals during reaction and/or upon rehybrid-

Table 1. List of Basic Compounds with Data on Basicity in the Liquid and Gas Phases

conjugated acid	base name	formula	pK_a water	pK_a acetonitrile	PA (kJ/mol)
acetonitrilium cation	acetonitrile	H_3CCN	−10.4		783
sulphuric acid	hydrogen sulphate anion	HSO_4^-	−3	7.9	
hydroxonium cation	water	H_2O	−1.74		691
oxalic acid	hydrogenoxalate anion	$HOOCCOO^-$	1.23		
hydrogen oxalate anion	oxalate anion	$(COO)_2^{2-}$	4.19		
anilinium cation	aniline	$C_6H_5NH_2$	4.63	10.6	882.5
acetic acid	acetate anion	H_3CCOO^-	4.8	21.2	
malonic aldehyde MA	MA anion	$^-H_2C(CHO)_2$	5.0		
pyridinium cation	pyridine	H_5C_5N	5.2	12.5	928
carbonic acid	hydrogencarbonate anion	HCO_3^-	6.37		
lutidinium cation	2,6-lutidine	$(H_3C)_2H_3C_5N$	6.75	14.1	963
aziridinium cation	aziridine	C_2H_4NH	8.04		905.5
hydrazinium cation	hydrazine	H_2N-NH_2	8.23		853.2
phthalimide	phatalimide anion	$C_6H_4(CO)_2N^-$	8.3		
trimethylphosphonium cation	trimethylphosphine	$(H_3C)_3P$	8.65	16.6	957
DABCOH$^+$	DABCO^a	$N(C_2H_4)_3N$	8.8	18.3	963.4
acetylacetone	acetylacetonate anion	$(CH_3CO)_2CH^-$	8.9		
ammonium cation	ammonia	NH_3	9.24	16.5	853
hydrogen cyanide	cyanide anion	^-CN	9.31		
phenol	phenate anion	$H_5C_6O^-$	10.00	26.6	
hydrogencarbonate ion	carbonate ion	CO_3^{2-}	10.25		
n-butylammonium cation	n-butylamine	$n\text{-}C_5H_{11}NH_2$	10.64	18.3	920.4
ethylammonium cation	ethylamine	$C_2H_5NH_2$	10.65	18.4	912
methylammonium cation	methylamine	CH_3NH_2	10.66	18.4	899
triethylammonium cation	triethylamine	$(C_2H_5)_3N$	10.75	18.5	981.8
piperidinium cation	piperidine	$(H_2C)_5NH$	11.12		933
ethyl diisopropyl ammonium cation	ethyl diisopropyl amine	$C_2H_5[(CH_3)_2CH]_2N$	11.40		994.3
malononitrile MN	MN anion	$^-[HC(CN)_2]$	11.2	22.2	
DBUH$^+$	DBU^b	$C_9H_{16}N_2$	12	24.3	1048
diethylmalonate DEM	DEM anion	$^-[HC(CO_2C_2H_5)_2]$	13.5	27.8	
guanidinium cation	guanidine	$(H_2N)_2C=NH$	13.6	23	986
tBuP1H$^+$	tBuP1^c	$(tC_4H_9N)_3P=N(tC_4H_9)$	14.9	26.9	997
cyclopentadiene	cyclopentadienyl anion	$(C_5H_5)^-$	15.5		
methanol	methoxide anion	CH_3O^-	15.5		
water	hydroxide anion	HO^-	15.74		
ethanol	ethoxide anion	$CH_3CH_2O^-$	16.0	42	
acetamide	acetamide anion	$(CH_3CONH)^-$	17.0		
isopropanol	isopropoxide anion	$(CH_3)_2CHO^-$	17.1		
terbutanol	terbutoxide anion	$(CH_3)_3CO^-$	19.2		
$N[C_2H_4(CH_3)N]_3PH^+$	proazaphosphatrane^d	$N[C_2H_4(CH_3)N]_3P$		29.6	1025
acetone	acetone anion	$(CH_3COCH_2)^-$	20		
acetonitrile	acetonitrile anion	$(CH_2CN)^-$	25		
acetylene	acetylide anion	$HC\equiv C^-$	25		
tBuP4H$^+$	tBuP4^c	$[(tC_4H_9N)_3P=N]_3P=N(tC_4H_9)$	30.6	42.6	1186
ammonia	amide ion	H_2N^-	33		
ethylene	vinyl anion	$H_2C=CH^-$	44		
benzene	phenyl anion	$C_6H_5^-$	48		
methane	methyl anion	CH_3^-	50		
n-butane	butyl anion	$CH_3CH_2(CH_3)CH^-$	>50		
isobutane	tert-butyl anion	$(CH_3)_3C^-$	>50		

^{a} DABCO = 1,4-diazabicyclo[2.2.2]octane. ^{b} DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. ^{c} Phosphazene bases. ^{d} Verkade base.
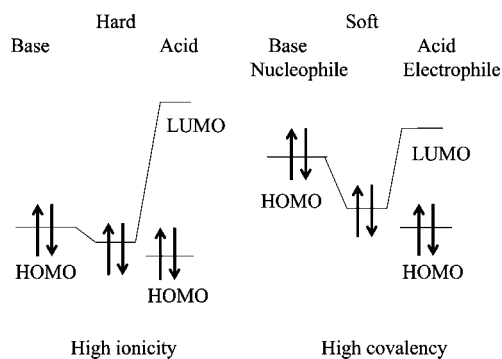
Figure 3. Schematics of the electron energy levels in charge controlled and frontier-orbital controlled effects. Redrawn from ref 22.

ization. The interactions of basic species with electron-poor carbon-containing species belong to this type of interactions but are commonly described by organic chemists in terms of nucleophile−electrophile interactions.[23] Nucleophiles are electron rich chemical species having a full n-type orbital that can react with an electron-poor carbon atom, leading to the formation of a new bond. This occurs in different ways, such as by reacting with (i) an sp^2 hybridized carbenium ion, such as in SN$_1$ nucleophilic substitutions and in electrophilic additions to olefins; (ii) an sp^3 hybridized carbon atom, such as in SN$_2$ nucleophilic substitutions; or (iii) an sp^2 hybridized carbonylic or carboxylic carbon atom, such as in nucleophilic attacks on a carbonyl and in acylic nucleophilic substitution reactions. Actually, the nucleophile−electrophile interactions are mostly evaluated in kinetic more than in thermodynamic terms. A measure of the nucleophilicity of a reactant is in fact usually given as the rate of reaction in a given reaction, such as, e.g., an SN$_2$ nucleophilic substitution. However, the rankings of the nucleophiles in different nucleophile−electro-

phile interactions are generally quite consistent when the attacking atoms are the same, except when very important steric effects are present. This means that the dominant effect in the nucleophilicity scale is the thermodynamic instability of the nucleophile/base, which is also the dominant effect governing basicity.

This is not always true for nucleophiles having different attacking atoms, such as O- and S- compounds. S-compounds are generally less basic but more nucleophilic than the corresponding O-compounds. In fact, since the proton is a hard acid, the Brønsted basicity is stronger for harder oxygenate than for softer sulphide species. In contrast, since any electrophilic carbon is quite a soft acid (and, in any case, a softer acid than the proton), nucleophilicity is stronger for softer bases, such as for sulfur compounds as compared to oxygen compounds.

2.3. Bases Stronger than the Hydroxide Anion and Basicity in Nonprotic Solvents

Bases stronger than the hydroxide anion, including "superbases", can exist as stable species in nonprotic solvents. Based on experiments concerning dissociation or exchange reactions in the presence of strong bases, and correlation between data, the water pK_a scale can be enlarged to values that are not really measurable in water. The pioneering work of Conant and Wheland[24] was the first attempt to assign pK_a values to a number of extremely weak organic acids, including hydrocarbons. The position of equilibria such as

$$HA + KA' \leftrightharpoons KA + HA' \qquad (11)$$
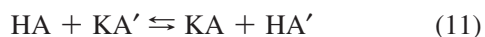
where KA′ is the potassium salt of a very weak acid (e.g., an alkyl-potassium organometallic compound) and HA is another very weak acid (e.g., a hydrocarbon), has been determined in a nonprotic solvent, such as diethyl ether. McEwen[25] extended the study to include a greater number of acids and improved the method quantitatively by using colorimetric, spectroscopic, or polarimetric methods to determine the position of the equilibria, using benzene as the solvent. The equilibrium constant is the ratio between the direct and inverse kinetic constants; thus, kinetic studies of proton or deuterium exchange reactions can also be useful to evaluate the acidity of weak acids. Today many data concerning acidity in nonprotic solvents, mainly from spectrophotometric experiments, are available for comparison with acidities from calculations and acidities measured in water for solvents having different dielectric constants (such as dimethyl sulphoxide ($\varepsilon = 47.2$), acetonitrile ($\varepsilon = 36.6$), tetrahydrofuran ($\varepsilon = 7.58$), dimethoxymethane ($\varepsilon = 7.20$), cyclohexylamine ($\varepsilon = 4.73$), diethyl ether ($\varepsilon = 4.20$), benzene ($\varepsilon = 2.27$), and heptane ($\varepsilon = 1.92$)).[26,27] Leito summarized many recent data in ref 28 and references therein.

With a slightly different but complementary approach, Hammett[29] first suggested suitable acidity functions applicable to the characterization of superacids and superbases. Strongly basic solutions can be arbitrarily defined as those solutions which ionize acids with an ability equal to or greater than that of aqueous alkali metal hydroxide 0.1 M solutions.[30] To measure their relative ability to ionize weak indicator acids HA, the H_- acidity function was defined as

$$H_- = pK_a - \log([HA]/[A^-]) \qquad (12)$$

where pK_a is the negative logarithm of the thermodynamic ionization constant of the indicator acid in water and $[HA]/[A^-]$ is the measured ionization ratio of the indicator. The acidity function of the solution is thus equivalent to

$$H_- = -\log(a_{H+}f_{A-}/f_{HA}) \qquad (13)$$

where a_{H+} is the hydrogen ion activity in the solution and f denotes the activity coefficients of the indicator. The function H_- becomes identical with pH in dilute aqueous solution, where the activity of hydrogen ion becomes equal to its concentration and the activity coefficients of the indicator approach unity.[31] The function H_- measures the ability of the solution to remove a proton from the acid and makes it possible to measure the strength of weak acids, interpret kinetic mechanistic studies, and investigate the physico-chemical composition of solutions.

Concentrated water solutions of metal hydroxides such as 10 M alkali hydroxides (corresponding to ~30% NaOH or ~40% KOH) have been measured to have H_- values of $16-18$,[30] and similar values for H_- have been found for alcoholic solutions of alkali metal alcoholates. Higher values of H_- should definitely be found for very strong bases measured in less acidic solvents than water.

In Table 1 data about the basicity of several compounds are compared. The effects of destabilization/stabilization of the anionic charge of the base as well as of the cationic charge of the acid on the basicity/acidity are evident. Strong bases have very stable acid forms and unstable basic forms. The reverse is true for acids.

2.4. Superbasicity

Several organic molecules have been synthesized recently and characterized as "superbases". A definition of the term "superbasic" due to Tanabe[32] parallels the definition of the term "superacid" given by Gillespie. Superacids are acids which are stronger than 100% H_2SO_4,[33] i.e. those characterized by $H_0 < -12$, 19 pH units lower than neutrality. Thus, superbases are defined as species whose base strength, expressed by the acidity function H_-, is higher than 26, i.e. 19 pH units higher than neutrality. Very weak acid indicators such as cumene ($pK_a \sim 37$), diphenylmethane ($pK_a \sim 35$), and 4- chloroaniline ($pK_a \sim 26.5$) can be used to determine superbasicity.

Over the past 30 years, research concerning increasing the inherent strength of organic bases has addressed the possibility of including structures allowing extensive delocalization of the cationic charge in the protonated form (Figure 4), thus allowing a very strong stabilization of the HB^+ conjugate acid, which displaces equilibrium 7 to the left. The field was transformed in the early 1990s by Schwesinger and co-workers[34−36] with the synthesis of a series of uncharged strong bases, termed peralkylated polyaminophosphazenes. Compared to traditional organic bases, the peralkylated phosphazene bases demonstrate a dramatic increase in basic strength, up to above 30 pK_{HB} units, giving rise to base strengths comparable to those of organometallic bases. Other extremely strong bases are vinamidine,[37] the so-called Verkade bases, i.e. proazaphosphatranes,[38] as well as the corresponding imides and ylides.[36] It seems that the strongest molecular bases prepared up to now belong to the peralkylated polyaminophosphazene family, with pK_a values a little above 30.
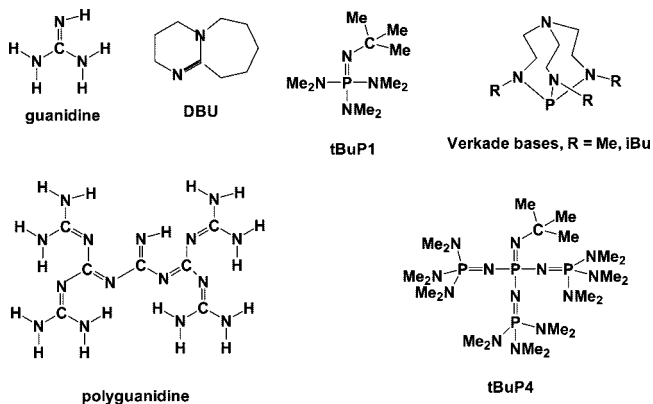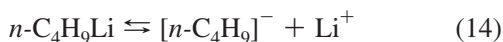
Figure 4. Structures of some strong basic compounds.

The most basic species, with pK_a values up to above 50, arise essentially from organometallic compounds, such as, e.g., the *n*-butyl anion, which is formally the result of dissociation of *n*-butyl lithium,

$$n\text{-}C_4H_9Li \rightleftharpoons [n\text{-}C_4H_9]^- + Li^+ \qquad (14)$$

Similar lithium alkyls, sodium alkyls, and potassium alkyls as well as alkyl-magnesium-halides (i.e., Grignard reagents) are widely used in organic chemistry for nucleophilic alkylations.[39] They may be assumed to be salts of hydrocarbons, which are in fact the weakest protonic acids. Their use as reagents requires using dry solvents and handling in perfectly dry atmospheres to avoid an exchange reaction with water from those sources. The more stable the organometallic compound, the less basic is the derived organic anionic species and the less ionic is its C-metal bond. For this reason, organolithium compounds and organomagnesium halides, both of which have quite covalent C−metal bonds, are those which are produced industrially and are commercially available. They may be converted into even more reactive compounds by transmetalation reactions. Because of the electron donating behavior of methyl groups, the most basic and thus least stable carbanions are those which are branched, such as the *tert*-butyl anion.

A number of solids have also been characterizaed as "superbasic". It is worth knowing, however, that the characterization of superbasicity in solids is mostly done on the basis of titration experiments, whose validity is doubted by some authors (see section 4.2.1.2). A review of the literature[32,41] indicates that metal oxides containing alkali-, alkali-earth, and rare-earth cations may give rise to very strong basicity just at the limit of superbasicity. Alkali metals supported on basic carriers are true superbasic solids. The strongest superbasic solid appears to be Na/NaOH/Al$_2$O$_3$,[40] whose basicity has been evaluated to correspond to $H_- = 37$.

Superbases are often-used reactants in organic chemistry and may be very significant catalysts. In fact, superbases are needed to abstract protons, even those in allylic and benzytlic positions, from most hydrocarbons, which are indeed very weak acids.[41] The most used superbases applied in industrial chemistry are apparently alkali metals, most frequently supported on basic carriers such as for Na/NaOH/Al$_2$O$_3$. This point will be discussed later on, in section 4.3.6.

2.5. Gas Phase vs Liquid Phase Basicity

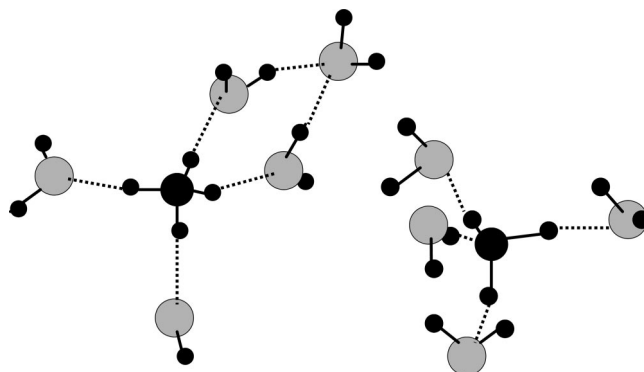As already remarked, liquid-phase basicity is strongly dependent on solvation effects and thus strongly dependent on the solvent, but it may also be affected by steric hindrance. As an example of this, the likely solvation states of ammonia and of ammonium ions, as deduced by calculations,[42,43] are shown in Figure 5. It is evident that the number and strength of the many hydrogen bonds in the first, but also in the second, solvation shell strongly influence the free energy of both the base and the acid in solution, and consequently influence the position of the equilibrium.

Brønsted basicity in the gas phase should, instead, be a "pure" basicity, depending only on the availability of electron pairs on the basic site. The comparison of liquid-phase basicities and gas-phase basicities can consequently give information on just the steric and solvation effects occurring in the liquid phases.[44] Proton affinity (PA) and gas-phase basicities (GB) are experimentally accessible gas phase parameters which allow the determination of basicity in the gas phase. These PA and GB values correspond to the changes in enthalpies (ΔH) and Gibbs free energies (ΔG), respectively, at a specific temperature, usually 298 K, for the reaction in eq 15.

$$BH^+{}_{gas} \rightleftharpoons B_{gas} + H^+{}_{gas} \qquad (15)$$

Most of the available data on gas phase basicities and proton affinities has been obtained from experiments in which the equilibrium constants of proton transfer reactions were determined. Calculations of gas phase basicities allow the ranking of molecular superbases[26,36] and are perhaps easier today than experimental determinations of these rankings. Other parameters concerning gas phase basicity, but more related to Lewis basicity as well as to HSAB behavior, can also be found in the literature. These are cation affinities and cation basicities, such as lithium,[45] sodium,[46] and cesium[47] cation affinities and basicities. However, these data are far less available than those for PA. In Table 1 some data concerning proton affinities are also reported.

3. Liquid Bases and Basic Solutions in Their Practical Applications

There are many industrial as well as household applications of basic solutions. Table 2 summarizes the industrial processes which use bases to abate pollutants. Table 3 lists some applications of liquid bases as catalysts in industrial organic chemistry. Table 4 reports the industrial uses of NaOH as a base. In the following, we review some characteristics of the basic substances frequently used in industrial applications.

Figure 5. Representation of the solvation shells of ammonia (right) and ammonium ion (left) in water, as obtained by calculation. Redrawn from refs 42 and 43.

Table 2. Summary of Environmental Processes for the Abatement of Acidic Pollutants Using Bases (Ref 8 and References Therein)

pollutant	contact	Ad- or absorbent	process	byproduct/waste	application
H_2S	liquid/gas	ethanolamines water solution	regeneration by reboiling	H_2S recovered	natural gas, hydrogen, and refinery gas purification
	solid/gas	caustic	regeneration by sulfur oxidation (chemical or biological)	sulfur recovered	biogas, natural gas purification
		alkali doped active carbons	no regeneration/partial regeneration	AC waste	biogas, natural gas purification
		ZnO	hot process−regeneration by hot hydrolysis	H_2S may be recovered	natural gas purification
		$Fe_2O_3/Fe(OH)_3$	room temp, no regeneration	adsorbent waste	biogas, natural gas purification
CO_2	liquid/gas	HP solution (K_2CO_3−water with activators)	regeneration by reboiling	CO_2 recovered	hydrogen purification, biogas enrichment, CO_2 sequestration from flue gas
		ethanolamines	regeneration by reboiling	CO_2 recovered	
	solid/gas	Na−A (4A) zeolite	regeneration by desorption (PSA)	CO_2 recovered or waste gas	
SO_2	liquid/gas	Na_2SO_3 water solution	regeneration by reboiling	SO_2 recovered	flue gas, tail gas desulphurization
	solid/gas	NH_3 water solution	no regeneration	$(NH_4)_2SO_4$ recovered	
	solid/liquid/gas	$Na_2CO_3/NaHCO_3$	no regeneration	adsorbent waste	
		limestone slurry	no regeneration	gypsum recoverable	
SO_3/H_2SO_4	liquid/gas	caustic	no regeneration	waste water (Na_2SO_4)	abatement from alkylation/sulphonation gases purification alkylated gasoline
	liquid/liquid	caustic	no regeneration	waste water (Na_2SO_4)	purification alkylated gasoline
		NH_3 water solution	no regeneration	$(NH_4)_2SO_4$ recovered	purification liquids in ε-caprolactam/cyclohexanone oxime/nylon 6 syntheses
NO, NO_2	gas/solid	$BaO−Al_2O_3$; $K_2O−Al_2O_3$	reduction by the fuel	N_2 gas went	diesel and lean burn gasoline engine waste gases purification (NSR process)
siloxanes	solid/liquid/gas	wet active carbons	no regeneration/partial regeneration	AC waste	biogas purification
HCl	liquid/gas	caustic	no regeneration	waste water (NaCl)	flue gas, chlorination/oxychlorination gas purification
Cl_2	solid/gas	$Na_2CO_3/NaHCO_3$	no regeneration	adsorbent waste	incinerators flue gas purification
	liquid/gas	caustic	no regeneration	waste water (NaCl, NaClO)	flue gas, chlorination/oxychlorination gas purification
acidic VOCs (phenols)	solid/gas	alkali doped active carbons	no regeneration/partial regeneration	AC waste	industrial gas purification
	solid/liquid	active carbons	no regeneration/partial regeneration	AC waste	industrial wastewater purification
		anionic exchange resins	washing (NaOH, methanol)	waste regeneration solution/ recovery	industrial wastewater purification
heavy metal cations	liquid/liquid	amine, phosphines, phosphine oxides, phosphine sulphides	salt precipitation/extraction	salts/hydroxides recovery	industrial wastewater purification, metallurgy

Table 3. Typical Base-Catalyzed Reactions of Industrial Interest, Usually Performed with Liquid Basic Catalysts (Refs 5, 6, 8, and 23)

reaction name	reactants (example)	products (example)	typical homogeneous catalyst
aldol condensation	heptanal with benzaldehyde	jasminadehyde	NaOH or KOH
Crotonic condensation	*n*-butanal	2-ethylhexenal	30% NaOH
Claisen−Schmidt	2′-hydroxycetophenone and benzaldehyde	2′-hydroxychalcones	NaOH, CH₃CH₂ONa
Henry	nitroalkanes with aldehydes	2-nitroalkanols	amine
Knoevenagel condensation	benzylacetone and ethyl cyanoacetate	2-cyano-3-methyl-5-phenylpent-2-enoate	amine
Wittig	phosphonium ylide and an aldehyde	internal olefin	NaH, t-BuOK, or NaOH
Michael addition	methyl crotonate	3-methyl-2-vinylglutarate	alkoxides
Bailis−Hilman	aldehyde + α,β-unsaturated carbonyl	allyl alcohol	DABCO
Guerbet reaction	*n*-hexanol + H₂	2-butyloctanol	t-BuOK + metal complex
Tishchenko	acetaldehyde	ethylacetate	(CH₃CH₂O)₃Al
Cannizzaro	formaldehyde + trimethylolacetaldehyde	pentaerythrol (+ formic acid)	NaOH, Ca(OH)₂
Meerwein−Ponndorf	aldehyde + alcohol	alcohol + aldehyde	Al isopropylate
Oppenheimer	alcohol + aldehyde	aldehyde + alcohol	Al-alkoxides
cyanoethylation	acetone + acrylonitrile	5-oxohexanenitrile	isopropylamine
addtion of alcohols to α,β-unsaturated carbonyls	methanol + crotonaldehyde	3-methoxybutanal	NaOH
oxyethylation	dodecanol + ethylene oxide	polyethoxylate surfactant	NaOH
transesterification	biodiesel (fatty acid methyl esters)	fats + methanol	NaOH, CH₃ONa

3.1. Metal Hydroxides and Their Water Solutions

Most ionic hydroxides are assumed to be fully ionically dissociated in water solution. Thus, the maximum obtainable concentration of hydroxide anions is determined by their solubilities. As reported in Table 5, the most soluble alkali hydroxides near ambient temperatures are, on a molar basis, Na and Cs hydroxides. At 0 °C, KOH is more soluble than NaOH, but, at 100 °C, NaOH is a little less than 3 times more soluble than KOH. At room or higher temperatures, NaOH is the most soluble hydroxide, and, consequently, concentrated soda water solutions are the most basic and can produce solutions with a pH in the range of 13−15.

The complexation of the cation by water is likely a relevant factor in determining the solubility of metal hydroxides and, consequently, the basic strengths of their saturated solutions. The cations act as Lewis acids with respect to water, forming aquo-ions H-bonded to second sphere water molecules. At least for dilute solutions, these cationic solvation complexes should be quite independent from those of the hydroxide anions. While Li^+ is assumed to coordinate four water molecules in a tetrahedral structure, the coordination sphere of water molecules around Na^+ ions is calculated to be a distorted trigonal bipyramid or a square pyramid.[48] More classical simulations conclude that hexa-aquo complexes $[Na(H_2O)_6]^+$ typically form,[49] as in most hydrated salts. For K^+ the hydration structure is much more sensitive to the environment surrounding the ion.[48] While for Rb^+ the most stable aquo complex species seems to have coordination number 8,[50] and the hydration number of the cesium ion is predicted to be 6.[51] Simulations from first principles of hydrated Mg^{2+} in ambient water showed six water molecules in an octahedral arrangement, in agreement with all known experiments, but for calcium the free-energy curve shows several shallow local minima, suggesting that the hydration structure of Ca^{2+} is highly variable.[52] The coordination of water around Sr^{2+} is even larger, 8 or 9,[53] while, for the aqueous Ba^{2+} ion, the coordination number has been evaluated as 8.3.[54] In the case of poorly soluble amphoteric hydroxides, such as AgOH, Be(OH)₂, Zn(OH)₂, Pb(OH)₂, Al(OH)₃, dissociation of the hydroxide in water solution is incomplete, which means that hydroxide anions participate, even in solution, in the coordination sphere of the cation. It is evident that the metal-to-oxygen bond and the solid state structure stability strongly affect the solubility of metal hydroxides too.

In practice, alkali metal hydroxides (in particular sodium hydroxide, also called "caustic", and potassium hydroxide, or "caustic potash") allow the preparation of quite dense (1−1.5 g/mL) and poorly volatile (1−13 Torr at rt) solutions with pH in the range 7−15.5. Two percent solutions (∼0.5 M) have pH ∼ 13, while the commercial 50% NaOH solution, whose melting point is near 15 °C,[55,56] has pH ∼ 15.28, density 1.540 g/mL at 0 °C and 1.469 g/mL at 100 °C, and a partial pressure of water of 0.9 Torr at 20 °C. The partial deprotonation of very weak acids characterized by $pK_a \sim 20-25$, such as most carbonyl compounds, can be obtained with these solutions. In some cases, such as "caustic fusion" processes, melts of dry solid NaOH (melting point 318 °C[57]) may also be used as extremely basic media. Since it is also a quite cheap material, sodium hydroxide is by far the most widely used base today. In Table 4 some common examples of industrial applications of caustic are summarized. Most of these have been discussed in ref 8.

Almost all processes performed with NaOH, as described above, can also performed with KOH with similar results, and they are in fact applied with KOH in several cases. Rarely, however, evident advantages (or differences) come from the use of KOH instead of NaOH. One case where KOH gives different results is the production process for soaps. In fact, K^+ salts of fatty acids are essentially liquid soaps at room temperature while the corresponding Na^+ salts are solid. However, the very high conductivity of concentrated KOH solutions,[58] which is higher than that for NaOH solutions, is a very significant property justifying the use of 30−35% KOH solutions as typical electrolytes for alkaline water electrolysis cells (AWE), for alkaline fuel cells (AFC),[59,60] and for manganese dioxide−zinc alkaline batteries as well as for rechargeable Ni−Cd and Ni−metal hydride alkaline batteries. KOH is also used as a component of melts for the production of industrial glasses and in the production of fertilizers such as potassium chloride, sulfate, and nitrate.

Ca(OH)₂, also called hydrated or slaked lime, is slightly soluble in water (0.05 mol ⁻OH/L) to give weakly basic solutions (a saturated solution at 25 °C, containing 1.8 g/L, gives a pH of 12.45). This justifies its use to neutralize acid solutions as well as to act as a basic reactant and a basic catalyst, e.g. for industrial aldol condensation reactions.[61]

Table 4. Industrial Application of Sodium Hydroxide (Ref 8 and References Therein)

	final product (example)		starting material			intermediate product or byproduct
caustic fusion	zirconium metallurgy	metallurgy	zircon minerals, ZrSiO$_4$	650 °C	dry solid/melt	Na$_2$ZrO$_3$ + Na$_2$SiO$_2$
	recovery of diamonds	diamond mining	rocks (silicates)		dry solid/melt	sodium silicates
caustic leaching of metal ions	Al hydroxides/alumina	wet metallurgy	Bauxite	110–250 °C	10–25%	Bayer process, sodium aluminate solution
production of sodium salts from acids	soaps (Na salts of fatty acids)	chemical industry	free fatty acids		5–15%	
	detergents (sodium alkylbenzene-sulphonates)		alkylbenzenesulphonic acids			
extraction of acidic components from/purification of organic solutions	paper/cellulose	paper making	wood chips	150–180 °C	5–10%	lignin
	alkylated gasoline (sulphuric acid process)	refinery	product of alkylation (sulphuric acid process)		12%	
	desulphurized gasoline or diesel fuel	refinery	S-containing gasoline or diesel fuel		5–25%	production of Na-mercaptures/disulfides
	sodium phenate/phenol	chemical industry	phenol-containing organic solutions			
abatement of acid compounds from industrial and waste gases	edible vegetable oils	food engineering	vegetable oils	40–90 °C	3–25%	soaps
	ethylene/propylene	petrochemistry	steam cracking gas		8–12%	"red oil" formation
	purified waste gases	refinery	H$_2$SO$_4$ contaminated gases from alkylation processes		12%	
	purified waste gases	chemical industry	HCl contaminated gases from chlorination/oxychlorination processes			
	purified waste gases	energy production	H$_2$S from natural gas—biogases			
basic reactivity in organic chemistry	vinylidene chloride	chemical industry	1,1,2-trichloroethane	60–110 °C	10–15%	
	epoxy resins	polymer industry	bisphenol A (BPA) and epichlorohydrin (ECH)	100 °C, two steps	48% caustic	
basic catalysis	2-ethyl-2-hexenal	chemical industry	butanal	80 °C	30%	Mitsubishi
	biodiesel (methyl esters of fatty acids)	chemical industry/fuel production	oils + methanol	60–80 °C	concentrated	Lurgi
nucleophilic reactivity	phenols	chemical industry	arylsulphonic acids	320–340 °C	dry melt or 50%	
	benzyl alcohol		benzyl chloride	90 °C	10%	
	soaps (Na salts of fatty acids)		fats	100 °C	6–10%	
neutralization of waste acid solutions	neutral solutions to be discarded	chemical industry, metallurgy	spent acid solutions			
cleaning of apparata	clean apparata/spent soda solutions	chemical/food industry	dirty apparata	rt to 100 °C	2–20%	

Table 5. Solubilities of Metal Hydroxides in Water

compound	mol wt (g/mol)	solubility (g/L_{H_2O})		
		0 °C	20 °C	100 °C
LiOH	23.95	127		175
NaOH	40.00	420	1090	3470
KOH	56.11	970	1120	1780
RbOH	102.48		(15 °C) 1800	
CsOH	149.90		(15 °C) 3955	
Mg(OH)$_2$	58.32		(18 °C) 0.009	0.04
Ca(OH)$_2$	74.09	1.85	1.65	0.77
Sr(OH)$_2$	121.63	4.10		218.3
Ba(OH)$_2$	154.00	16.7	38.9	(80 °C) 1014
Al(OH)$_3$	78.00		(18 °C) 0.00104	

However, its use instead of caustic soda is relatively rare, mainly occurring only when the use of sodium hydroxide causes some safety problem. Common applications of slaked lime are[62] in the recovery of ammonia in the Solvay process for the production of soda ash (Na$_2$CO$_3$), in the "causticization" process to produce NaOH from soda ash, in the regeneration of soda solutions in the Bayer alumina synthesis process, in the production of magnesia, and in various water treatment processes.

The use of cesium hydroxide, in spite of its very high solubility, is very limited, probably because of its cost.

The use and manipulation of concentrated hydroxide solutions (pH > 11.5) is associated with safety and corrosion problems.[41] In fact, accidental contact of the human body with such solutions may cause injury to tissues with severe burns and deep ulceration.[63] In addition, the susceptibility of currently used materials (e.g., mild steel) to caustic cracking requires the use of more resistant and expensive materials. In concentrated caustic soda at operating temperatures above 50−80 °C, the use of Ni-alloys is advisible.[56]

3.2. Salts with Basic Hydrolysis: Solutions and Slurries

Inorganic salts characterized by basic hydrolysis, i.e. the salts of weak acids, produce basic anions by dissociation and, thus, may also be used to increase pH in water solution (eq 6). Among the salts most typically used in this way are carbonates, bicarbonates, acetates, and phenates. The pK_{HB} values for these anions are in the range 4.8−10.25. Most of these salts have quite high solubilities (see Table 6). Consequently, these salts allow the formation of moderately basic solutions with pH ∼ 7−13.

Sodium and potassium carbonates and bicarbonates are soluble salts characterized by basic hydrolysis. Potassium carbonate and bicarbonate are the most soluble (more so than their sodium analogues) and, thus, are more widely used. These salts allow the neutralization of acids, such as, e.g., the production of soaps from fatty acids. Among the largest applications of potassium carbonate is the so-called Hot-Potassium Carbonate (HP) process[64] used to recover carbon

Table 6. Solubilities of Metal Salts in Water

compd	mol wt (g/mol)	solubility (g/L_{H_2O})		
		0 °C	20 °C	100 °C
NH$_4$HCO$_3$	79.06	119	210	
NaHCO$_3$	84.01	69		(60 °C) 164
KHCO$_3$	100.11	224		(60 °C) 600
Na$_2$CO$_3$	106.00		(30 °C) 505	455
K$_2$CO$_3$	138.20	1055	1105	1557
Na(CH$_3$COO)	82.04	1190		1701.5
K(CH$_3$COO)	98.14		2530	

dioxide from hydrogen and from waste gases (Table 2). Corrosion problems have been reported for these processes.[65] Solid sodium carbonates, which are cheaper, are used as adsorbants for purification/dechlorination of incinerator waste gases.[66]

Limestone, one of the most common constituents of the earth's crust, is a readily available and cheap mineral based on calcium carbonate, CaCO$_3$, and is very poorly soluble in water. Limestone, mostly in the form of slurries but also as a dry powder, is widely applied in the field of Flue Gas Desulphurization (FGD) technologies,[67,68] i.e., for the abatement of SO$_2$ from coal-fired power plant combustion waste gas and other gases. This process may produce "FGD-gypsum", which is a useful byproduct. Limestone is widely used to produce lime in the cement industry and is used to regenerate caustic in the kraft process for papermaking.[69]

3.3. Molecular Bases

Ammonia and N-containing organic compounds such as amines are typical molecular bases. Ammonia is a gaseous molecule (boiling point −33.43 °C at 101.3 kPa) with very high solubility in water and weak basicity. A 1 N solution of ammonium hydroxide has a pH of 11.77 at 18 °C. The toxicity and odor of ammonia vapors is a drawback to the use of such volatile ammonia solutions.[70] The use of pure ammonia is additionally hampered by the flammability and explosivity of air/ammonia mixtures. However, ammonia is used in a great number of industrial applications, several of which are related to its basicity. In organic chemistry, it is widely used as a nucleophilic reactant to produce, e.g., amines from alcohols. It is also applied as a base to neutralize acid solutions such as sulphuric acid effluents from aromatic amine extraction processes from coal tar distillation fractions.[71] Similarly, ammonia is used to neutralize sulphuric acid in the BASF process for the production of ε-caprolactam, the monomer for nylon-6.[72] Finally, it can also be used to abate SO$_2$ in FGD processes.[67,68] It is also widely used in the production of ammonium salt fertilizers.

Aliphatic amines are typically characterized by pK_{BH} roughly ranging from 8.04 for aziridine (CH$_2$)$_2$NH to 11.40 for the "Hunig base", i.e., ethyl diisopropyl amine. Thus, amines allow the production of water solutions with pH in the range 7−13. The various effects playing a role in determining the basic strength of different amines are evident from the data summarized in Table 1. The possibility of delocalizing the cation charge by the presence of electron donating alkyl groups is partially opposed by increased steric hindrance, as is found for primary, secondary, and tertiary amines. Strain tends to decrease the basicity of amines.[73] Extensive charge delocalization through delocalized π-orbitals, such as occurs, for example, in the case of protonated guanidine (Figure 4), makes this imine−diamine molecule, with a pK_{BH} of 13.6, more basic than akylamines.

A large number of amines have useful basic properties and may be occasionally used as basic compounds. Several amines are used as organocatalysts,[74−76] and in particular, aymmetric amines are useful as catalysts for asymmetric synthesis. Superbasic compounds, such as those belonging to the phosphazene family, are becoming interesting for industrial syntheses. Very recently, Cerro-Alarcón et al. proposed the use of these bases as catalysts for a water-free transesterification process for the synthesis of biodiesel with water-free glycerin as a coproduct.[77]

One of the most useful applications of amines as bases in industrial and environmental chemistry is their use in washing hydrogen, natural gas, refinery gases, or even waste gases to abate hydrogen suphide, mercaptans, carbonyl sulphide, and/or carbon dioxide. To this end, the so-called "ethanolamines" (i.e., monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA), dimethylethanolamine (DMEA), and methyldiethanolamine (MDEA) are the most often applied.[78,79] These compounds do not form azeotropes with water and do boil above 170 °C, but they do begin to decompose above 200 °C. They are used as 10−40% (1.5 M) aqueous solutions, giving pH values in the range 8.5−12.

Other basic compounds, such as phosphines, phosphine oxides, phosphine sulphides, and also phosphate esters, are used as extractants to separate organics from water and to extract and separate heavy metal ions. In particular, some of them are used in the separation of the uranyl ion from leaching solutions in the preparation of nuclear fuels.[80]

Obviously, drawbacks on the use of such molecular bases are their often high toxicity, sometimes aggravated by high volatility, and their corrosive effects on production apparatus.

3.4. Basic Ionic Liquids

Ionic liquids are organic salts characterized by a low melting point. A "low" melting point, in the most usual definition, is one below 100 °C or even one less than room temperature.[81] Although the first of these compounds, ethylammonium nitrate, had apparently been synthesized as early as 1914,[82] deep investigation into the potential of these compounds is a very recent matter. Because of their very low vapor pressure, their apparent nonflammability, and their low toxicity, ionic liquids are considered to be green chemistry products[83] useful as solvents for organic reactions and for the preparation of inorganic materials[84] as well as excellent liquid catalysts.[85] Ionic liquids frequently have a predominantly acidic character, but several of them have been classified as "basic". As reviewed by Conrad Zhang,[85] salts formed by the combination of bisalkylimidazolium or alkylpyridinium chlorides with $AlCl_3$ are characterized by Lewis basicity and are active as catalysts for typically base-catalyzed reactions (such as, e.g., Knoevenagel condensation), if the molar ratio between the organic salt and $AlCl_3$ is less than 1.

The combination of a "neutral" anionic liquid, such as butylmethylimidazolium fluorophosphate $[BMIM]^+ [PF_6]^-$, with a hydroxide produces a basic catalyst, probably due to the formation of the corresponding hydroxide salt $[BMIM]^+[HO]^-$.[86] The use of hydroxide ionic liquids such as choline hydroxide[87] and butylmethylimidazolium hydroxide $[BMIM]^+[HO]^-$ (refs 88 and 89) as catalysts is the object of increasing attention and may have industrial interest.[86] This is an interesting field of new research.

3.5. Alkali and Alkali Earth Metals and Organometallics

Strictly speaking, organometallics are compounds with a carbon−metal bond. However, commonly used basic species such as alkali alkoxides, alkali amides, and alkali hydrides are sometimes included together with alkali or alkali earth alkyls and aryls in the term "organometallics". Alkali alkoxides may be produced even in water solution by reacting alcohols with concentrated soda caustic solutions. This is

because of the acidity of alcohols, which is comparable to or only slightly lower than that of water. Dry alkoxides are produced by the reaction of alcohols with alkali metals. Alkoxides are slightly more basic than caustic soda, which allows the formation of enolate anions from carbonyl and carboxyl compounds. Thus, they are typical homogeneous "catalysts" for industrial biodiesel production by transesterification of vegetal oils with methanol[90,91]

$$(RCOO)_3C_3H_5 + 3CH_3ONa + 3H_2O \rightarrow C_3H_5(OH)_3 + 3RCOOCH_3 + 3NaOH \quad (16)$$
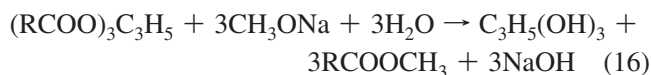
and also for aldol-like condensations,[92] which have industrial applications, mostly in the fine chemistry field (see Table 3).

True organometallic compounds are produced either by reaction of the metals with alkyl chlorides in nonprotic solvents such as tetrahydrofuran (THF), diethyl ether, dioxolane, dimethoxyethane, or n-pentane, as in eq 17,[93]

$$n\text{-}C_4H_9Cl + 2Li \rightarrow n\text{-}C_4H_9Li + LiCl \quad (17)$$

or by direct deprotonation by the metal of a hydrocarbon with "activated" CH bonds, as in eq 18.

$$C_6H_5CH_3 + Li \rightarrow C_6H_5CH_2Li + {}^1/_2H_2 \quad (18)$$

Organosodium and organopotassium compounds that contain carbanions with localized charge are extremely reactive and exhibit saltlike properties such as high melting point, low vapor pressure, and very low solubility in nonpolar solvents such as pentane or hexane. They are generally produced and used in diethyl ether or tetrahydrofuran. Similarly, alkali amides are produced by the reaction of ammonia or amines with metals. The reaction of these compounds with water or moisture is dangerous because of the formation of hydrocarbons along with considerable heat, which together in air easily produce explosions or flames.

Metal alkyls, aryls, and amines are more basic and more nucleophilic than metal-alkoxides and are used mostly as alkylating nucleophiles in aliphatic or acylic nucleophilic substitutions as well as in attacks on carbonyl compounds, with wide application in the fine organic chemistry field.

4. Solid Basic Materials

The concepts of Brønsted and Lewis basicity, as well as of nucleophilicity and the HSAB theories, are obviously also applicable at the surface of a solid in contact with an aqueous or nonaqueous liquid environment, or at a gas−solid interface.[32] In fact, the concepts of the thermodynamic stability/ instability and reactivity (both on kinetic and on thermodynamic bases) of electron rich centers are also applicable at solid surfaces. As we shall see later on, basicity is a typical characteristic of many solids and is relevant to both their practical and industrial applications. According to the above definitions, basicity is related to the presence of electron rich centers. This is consequently typical of ionic solid structures. In this sense, metal hydroxide and oxide structures constitute typical solid bases, although other solids also have some surface basicity. Many metal hydroxides, however, are unstable toward decomposition into oxides under mild conditions and thus are barely usable as bases in the solid state.

4.1. Application of Solid Bases in Industrial and Environmental Chemistry

Basic solids find a number of useful applications in industrial and environmental chemistry.[3,8] Several basic solids are used as heterogeneous catalysts in the chemical industry, as reviewed some years ago by Tanabe and Hölderich,[94] and discussed in several other recent reviews[95−98] and comprehensive papers.[99−104] A short summary of the actual industrial application of solids as base catalysts is reported in Table 7. Basic solids are also used as adsorbents in waste purification or in separation technologies.[8,96] Some of them behave as basic refractories to protect the walls of furnaces from basic vapors.[7] Others are used as precursors in the preparation of glasses.[7]

4.2. Basicity on Metal Oxides

Metal oxides are certainly the most investigated solids with respect to their surface acidobasic properties[105,106] and also in relation to their interaction with aqueous solutions and microbial organisms.[107] Much work has been reported in the field of solid basic materials, covering the topics of both the techniques for surface characterization of basic solids in particular and the relation of their surface characteristics to their catalytic activity.[32,95−97,99,102,108] Although actual current applications of basic solids as catalysts are relatively limited (some examples are reported in Table 7), it seems likely that they will increase in the near future as a result of extensive research. Here we will briefly summarize, from our point of view, some data concerning the studies of the surface basicity of solid oxides.

4.2.1. Techniques for Characterization of the Surface Basicity of Solids

4.2.1.1. Direct Evidence of Basic Surface Sites: UV and XPS Spectroscopy and the Concept of Optical Basicity. Techniques which detect surface anionic centers can give "directly" information about basic surface sites of solids. Among these techniques, UV absorption spectroscopy and luminescence spectroscopy have been most commonly utilized.[109] After the original first paper of Nelson and Hale,[110] fundamental work on this subject was done in the 1970s by Zecchina and Stone,[111,112] who provided evidence of typical surface $O^{2−} \rightarrow M^{2+}$ (M = Mg, Ca, Sr, Ba) charge transfer (CT) transitions on alkaline earth oxides under vacuum. As rationalized and discussed by Garrone et al.,[113] such surface CT transitions occur in the near UV range, i.e., at much lower energy than the corresponding bulk CT transitions, which correspond to valence band $\rightarrow$ conduction band transitions. They are due to low coordination oxide and M^{2+} ions differently exposed at the surface and located at energies definitely lower than those for bulk CT transitions. Coordinatively unsaturated (cus) atoms, denoted as O_{5C} (coordination five, on faces), O_{4C} (on edges), and O_{3C} (on corners), were found to exist at the surface of cubic alkaline earth oxides for which the full coordination of bulk oxide ions is six. For MgO, surface CT transitions were found at 6.6, 5.75, and 4.6 eV, for O_{5C}, O_{4C}, and O_{3C}, respectively, in contrast to the bulk absorption found near 7.8 eV. However, their position is also somehow dependent on particle size.[114] Photoluminescence spectra of vacuum treated MgO show an intense peak, due to emission from surface sites, at 3.18 eV, i.e. at definitely lower energy than the bulk gap. The
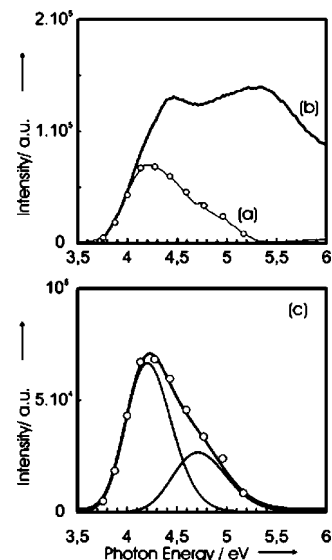
Figure 6. Optical surface properties of CaO particles: the excitation spectrum (a) is obtained in two different ways: by directly measuring the emission intensity at 3.0 eV on tuning the excitation monochromator (solid line) and by plotting the integral emission intensities as a function of the excitation energy (open circles). For comparison, an optical absorption spectrum (Kubelka−Munk function) of the same material is plotted (b). The intensity ratio between its plotted absorbance and the excitation spectrum is arbitrary. Spectrum c demonstrates the decomposition of the photoluminescence excitation spectrum (a) into two components at 4.2 and 4.7 eV. (Reprinted with permission from ref 114. Copyright 2006 American Chemical Society).
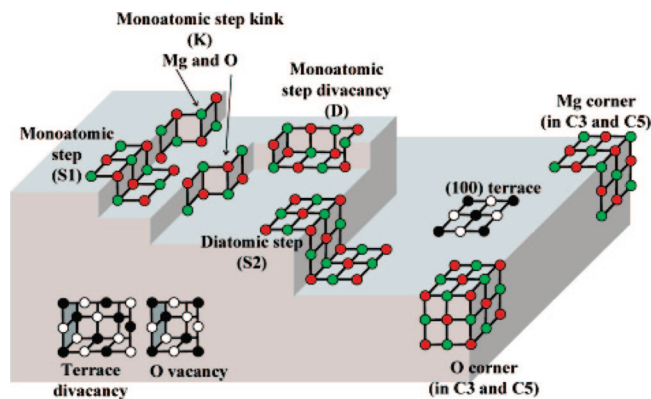
Figure 7. Model for surface sites in dry MgO (Reprinted with permission from ref 115. Copyright 2006 American Chemical Society).

spectra reported in Figure 6, recorded by Stankic et al.,[114] provide evidence of different surface sites on the CaO surface. The energy of the corresponding peaks decreases following the trend MgO > CaO > SrO > BaO. From this work, a very popular model for the surface of alkaline earth oxides was proposed, from which the most modern one, proposed by Chizallet et al.,[115] reproduced in Figure 7, is derived. The application of these techniques to other families of metal oxides is more difficult. In particular, in the case of transition metal oxides, other kinds of transitions, such as d $\rightarrow$ d and intermetallic CT transitions, may occur, together with bulk CT transitions, sometimes making the picture very complicated.

Optical spectroscopic measurements have also been at the origin of the concept of optical basicity, generally denoted by the symbol Λ, mostly due to Duffy.[116] This model has its origin in the nephelauxetic parametrization proposed by

Table 7. Some Industrial Applications of Solid Bases as Catalysts (Refs 5, 6, 8, and 94–106)

	catalyst	product	reactants	conditions	notes
aldol-type conversions	NaOH–SiO$_2$	acrolein CH$_2$=CH–CHO	CH$_3$CHO + HCHO	300–320 °C	Degussa
	CaO–BaO mixed oxide	2,2,4-trimethylpentane-1,3-diolmonoiso-butyrate	isobutyraldehyde	110 °C	Chisso
	MgO–SiO$_2$	1,3-butadiene	ethanol	370–390 °C	
	4% Na$_2$O/SiO$_2$, 4% Cs$_2$O/SiO$_2$	crotonic condensation products	2-butanone (methyl ethyl ketone, MEK)	325–400 °C	
	(Pt)–MgO–Al$_2$O$_3$ (calcined hydrotalcite)	mesityl oxide or methyl isobutyl ketone	acetone	120–250 °C condensation, dehydration, hydrogenation	Eastman
	anionic resin Amberlite IRA400	pseudoionone	citral + acetone	55 °C	Rohm and Haas
Guerbet condensation	Cs$_2$/SiO$_2$	methyl methacrylate	methylpropionate + formaldehye		Lucite alpha
	MgO–K$_2$CO$_3$–Cu	2-butyloctanol	1-hexanol + H$_2$	100–250 °C	Phillips
C-alkylation of methylaromatics with olefins	K/Al$_2$O$_3$, K/MgO, Cs/carbon	isobutylbenzene	toluene + propylene	100–250 °C	
olefin position isomerization	K/CaO, Na/Na$_2$CO$_3$	5-tolyl-2-pentene	ortho-xylene + 1,3-butadiene	140 °C	AMOCO and Teijin
	Na/NaOH/Al$_2$O$_3$	5-ethylidenebicyclo-[2.2.1]-hept-2-ene (EBH)	5-vinylbicyclo-[2.2.1]-hept-2-ene (VBH)	−30 °C	Sumitomo
transesterification/esterification	ZnAl$_2$O$_4$	biodiesel (methyl esters of fatty acids)	fats + methanol	200–250 °C	IFP
	anionic resins	biodiesel (methyl esters of fatty acids)	free fatty acids + methanol	30–100 °C	Rohm and Haas
dehydration/alkylation with alcohols	Cs/SiO$_2$ or Na/Al$_2$O$_3$	NMP	2-pyrrolidone with methanol	300–400 °C	Mitsubishi
	MgO	2,6-xylenol	phenol with methanol	400–450 °C	General Electric
	alkali/alkaline earth-promoted alumina or zirconia catalysts	methanethiol and ethylmercaptan	alcohol with H$_2$S	300–400 °C	Merck
epoxide ring-opening/oxyethylation	hydrotalcite	alcohol polyethoxylates	ethanol + ethylene oxide	150–180 °C	Henkel
dehydration	Na/ZrO$_2$	vinylcyclohexene	1-cyclohexylethanol	350 °C	Sumitomo
	Cs–P/SiO$_2$	ethyleneimine	ethanolamine	370 °C	Nippon Shokubai
ketonization	CaO–Al$_2$O$_3$	phenyl-1-propanone	benzoic acid with propionic acid	440–520 °C	Union Carbide
	ThO$_2$ or ZrO$_2$	2,4-dimethyl-3-pentanone	isobutyric acid	430 °C	BASF
NO$_x$ adsorption and reaction	Pt-Ba/Al$_2$O$_3$, Pt-KAl$_2$O$_3$	N$_2$ + CO$_x$	NO + hydrocarbons	200–400 °C	Toyota

Jørgensen with the application of ligand field theory.[117] According to Duffy, the basicity of an oxide material can be measured using red shifts in ultraviolet frequencies with respect to the value measured for cations in a very basic environment, taking crystalline calcium oxide as a reference. Simple molecular orbital theory shows that the ratio of the red shifts can be taken as a reasonable measure of basicity, especially in terms of the Lewis concept. This ratio (which, in effect, is the ratio of the orbital expansion "nephelauxetic" parameter, h, for the glass or the oxide to h for CaO) has been termed the "optical basicity". The orbital expansion parameter, h, for a ligand is related to its electron-donating ability. Some limits of the Λ theory have been discussed and bypassed by Lebouteiller and Courtine.[118] The data reported by these authors for binary oxides are in partial agreement with those reported later by Duffy[119] but are in better agreement with our own data arising from surface studies. An interesting feature of Λ is that it can be calculated for mixed and multicomponent oxides as the weighted average of the Λ's of the component oxides.

Λ is actually a bulk property but is quite directly correlated to surface basicity. In fact, Λ values are inversely correlated quite well with the O 1s binding energy as measured by XPS. In fact, the position of the O 1s binding energy XPS peak is correlated to the ionicity[120] (which is again a bulk property) but is also correlated to the surface basicity of metal oxides.[121] Actually, the separation of the surface components, due to surface oxide, hydroxide, and carbonate ions, from the bulk component of the O 1s XPS signal of metal oxides may not be easy.[122,123] On the other hand, both the optical basicity scale and the O 1s binding energy XPS scale are in rough agreement with the scale arising from surface characterization experiments (see below), with some exceptions. Bordes and Courtine[121] calculated Λ for several simple and mixed oxides and successfully correlated Λ values to the catalytic activity of many catalysts in several, mostly redox, reactions.

4.2.1.2. Surface Titration Methods. Titration methods,[32,124] i.e., the study of the interaction of indicator dyes with the solids from solutions, have been proposed as a technique for both qualitative and quantitative characterization of solid surfaces. The benzoic acid surface titration method, described by Tanabe et al.,[32] consists of titrating a solid acid suspended in benzene with benzoic acid using an indicator. This technique is widely applied in the fields of catalysis[41,95,97,101,102] and of colloids and soil sciences,[125] although it has many limitations in treating gas−solid phenomena, since the surface Hammett acidity function as defined by Tanabe has doubtful physical meaning and is, according to Corma,[97] intrinsically inappropriate and misleading.

4.2.1.3. Application of Molecular Probes for Basicity Characterization: Spectroscopic, Calorimetric, and Thermal Desorption Techniques. Several techniques allow the study of the surface acidity and basicity of solids at the gas−solid interface.[32,97,126,127] Most of them involve the use of molecular probes and allow the determination of the number of adsorbed probe molecules (such as adsorption gravimetry and volumetry), the differential and integral heat evolved during adsorption (adsorption microcalorimetry[128,129]), and the number of molecules that are desorbed with increasing temperature, thus allowing the calculation of the desorption energies (temperature programmed desorption[130]). If an acidic probe molecule which is very selective for basic sites is available, these techniques allow a characterization

of the amount of adsorbed species per unit surface area and/ or weight and the adsorption strength, and consequently, they allow measurement of the number of the adsorption sites of different quality. However, to have a more direct idea of what happens upon adsorption, spectroscopic techniques are necessary.

Among these characterization methods, IR spectroscopic techniques[108,131−134] are currently widely applied because of the moderate cost of FT-IR instruments and the well-established principles of the technique. The analysis of the IR spectrum of pressed disks of the pure catalyst powder (by using the transmission/absorption technique) or of the powder deposited as such (using the diffuse reflectance technique, DRIFTS) allows the detection of the spectra of adsorbed molecules and thus shows the reaction or the perturbation of the probes as a result of the interaction with the surface. Coupled with the simultaneous volumetric analysis of the extent of adsorption, IR techniques allow a quite complete quantitative/qualitative analysis of the adsorption phenomena.

However, in contrast to the acidity characterization with basic probes,[9] the use of "acidic" molecules to probe surface basicity is far less satisfactory. In fact, all "acidic" (or electrophilic) molecules (Table 8) also easily contain available nucleophilic (basic) atoms that can interact with surface acid sites. The use of hexafluoroisopropanol as a selective probe for basic sites was proposed several years ago to study surface basicity by microcalorimetry with good results[135,136] but with limited versatility. It is almost impossible to find simple molecules that actually only interact specifically with basic sites. Metal oxides that display significant surface basicity are always very ionic and also have, although weakly, some Lewis acidity. On the other hand, this may not be a limit: it is also the case that, in their practical application, acido-basicity rather than pure basicity is frequently the relevant property of metal oxides. The characterization of well-defined very weak Lewis acidity is, in our opinion, a good technique for basic surface characterization. For this reason, probes typically used for acidity characterization (such as carbon monoxide and pyridine) may be used for characterizing basic solids. Carbon monoxide is an excellent probe for weak Lewis acid sites.[137]
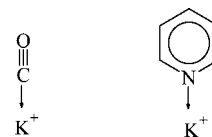
In Table 9 the values of the CO stretching frequency (wavenumbers) measured on different solids are summarized. This is shown, as an example, in Figure 8, where the spectra of CO adsorbed on Na/SiO$_2$ and on Ba/Al$_2$O$_3$ catalysts as well as on a heavily doped K/Al$_2$O$_3$ catalyst show intense low-frequency CO stretching bands. These are due to surface carbonyl species on weakly Lewis acidic Na$^+$, Ba^{2+}, and K$^+$ cations. For comparison, the frequencies for carbonyls on strongly acidic Al^{3+} surface sites of silica−alumina are also reported. Similarly, in Figure 9 the IR spectra of pyridine adsorbed on a heavily K-doped V$_2$O$_5$−Al$_2$O$_3$ oxidative dehydrogenation catalyst[138] and on the perovskite BaTiO$_3$ are reported. The most intense peaks of adsorbed pyridine (8a mode near 1590 cm^{-1} and 19b mode at 1440 cm^{-1}) are due to pyridine molecules coordinated to weakly acidic K$^+$ and Ba^{2+} ions. The spectrum of pyridine

Table 8. Molecular Probes Applied for Surface Basicity Characterization

compound	formula	reactivity	technique
carbon dioxide	CO_2	carbonates, bicarbonates, linear coordination on Lewis sites	IR, TPD, XPS, microcalorimetry
carbon monoxide	CO	formates, carbonite, polymeric anionic species, dioxycarbene	IR, ESR
carbon disulfide	CS_2	S_2CO^-, CO_3^{2-}, other species	IR
sulfur dioxide	SO_2	sulphites, disulphites, hydrogen sulphite, sulphates	IR, calorimetry
pyrrole	H_4C_4NH	H-bonding, pyrrolate anions, polymers	IR, ^{1}H NMR
carbonyl compounds	R—CO—H, R—CO—R	coordination on Lewis acid sites, enolization, enol condensation	IR, ^{1}H NMR
chloroform	H—CCl_3	H-bonding, coordination by chlorine on Lewis acid sites, hydrolysis	IR, ^{13}C NMR
acetonitrile	CH_3—CN	$^-CH_2$—CN anions, previous coordination by nitrogen on Lewis acid sites	IR
alcohols	R—OH	R—O^- anions, undissociative coordination, different H-bondings	IR
hexafluoroisopropanol	$(F_3C)_2CHOH$	dissociative adsorption, H-bonding	calorimetry, IR
thiols	R—SH	R—S^- anions, undissociative coordination, different H-bondings	IR
trimethylborate	$(CH_3O)_3B$	tetrahedral borate, dissociation	^{11}B NMR
borontrifluoride	BF_3	$F_3B \leftarrow O^{2-}$, dissociation	TPD
propyne	H_3C—C≡CH	H-bonding, π-bonding, dissociation	IR
ammonia	NH_3	H-bonding, dissociation to $^-NH_2$ anions, coordination by nitrogen on Lewis acid sites	IR
pyridine	H_5C_5N	$H_5C_4N^-$ anions, coordination by nitrogen on Lewis acid sites, dimerization	IR
nitromethane	CH_3NO_2	$H_2CNO_2^-$, CNO^- formed by decomposition	IR, ^{13}C NMR

Table 9. CO Stretching Frequencies of Carbon Monoxide Adsorbed as Monocarbonyl Species at Low Temperature on Closed Shell Cation Oxides (Experimental Data from This Laboratory^a

| catalyst	νCO (cm^{-1})
γ-Al_2O_3	2235, 2210, 2200−2180
TiO_2(anatase)	2226, 2208, 2182
Ca-MOR	2202
ZrO_2	2195, 2170
ZnO	2192, 2189
Ca-LTA	2187
Li-MOR	2185
Na-MOR	2177, 2164
Na-X	2174, 2165
Na-SiO_2	2174
Na-Y	2173
Na-FER	2173
ThO_2	2172
CeO_2	2168
K-LTA (ext surface)	2164
Na-LTA	2164
K-MOR	2162
CaO	2160, 2140
Ba—Al_2O_3	2159
MgO	2158, 2149
La_2O_3	2155
Cs-MOR	2155
K-Al_2O_3	2140
liquid	2138

^{a} See also ref 137.

adsorbed on γ-Al_2O_3, whose Al^{3+} surface sites are strongly Lewis acidic, shows the two bands at much higher frequencies.

To reveal the basicity of oxide catalysts, the reactivity toward the reactant molecules can also be studied. In Figure 10 the spectra of butyraldehyde adsorbed on silica are compared with that of the same molecule after adsorption on a Na/SiO_2 catalyst, which is used industrially for catalytic aldol condensation[41] (see below). The additional bands observed at 1652 and 1633 cm^{-1} on Na/SiO_2 are due to C=O and C=C stretching modes of the adsorbed aldol compound

and, thus, provide evidence of the presence and reactivity of basic sites associated with alkali ions.

4.2.1.4. Adsorption and the Thermal Desorption of CO_2 for the Characterization of the Basicity of Metal Oxide Surfaces. Carbon dioxide is actually a widely used probe for surface basicity characterization. Spectroscopic studies[139,140] show that carbon dioxide may adsorb both as an acid over basic sites and as a base over acidic sites. This is shown in Figure 11 for adsorption of CO_2 over the Na-LTA zeolite (Linde 4A).[141] When behaving as a base, CO_2 uses one of the lone pairs of its oxygen atoms, coordinating it to Lewis acid sites of ionic surfaces (Na$^+$ ions in this case). The upward shift to 2420−2340 cm^{-1} of the OCO asym-
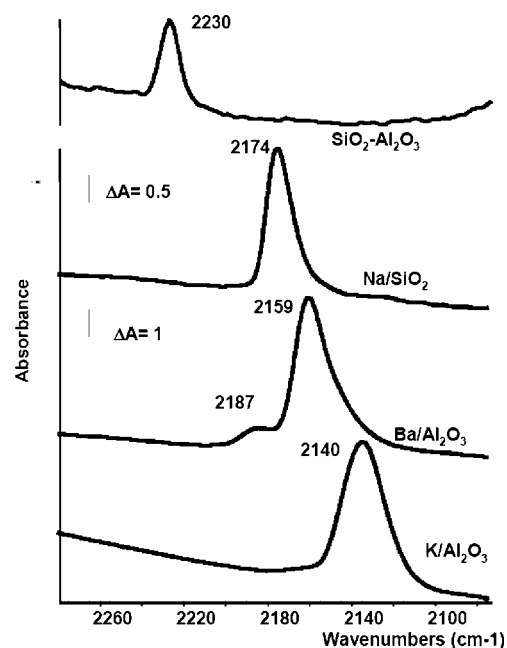
Figure 8. IR spectra of CO adsorbed at low temperature (ca. 150 K) on some solid catalysts (self-supporting pressed disks), after previous activation of the solids by outgassing at 773 K.
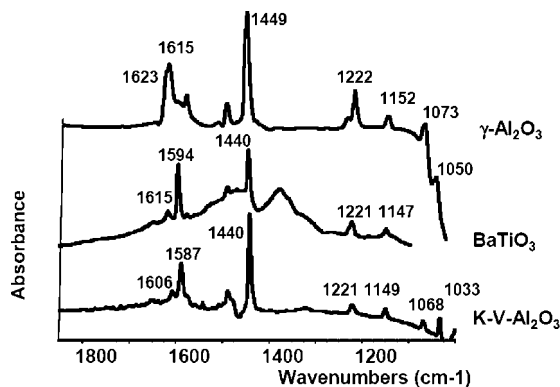
Figure 9. IR spectra of pyridine adsorbed on some solids (self-supporting pressed disks), after previous activation of the solids by outgassing at 773 K.
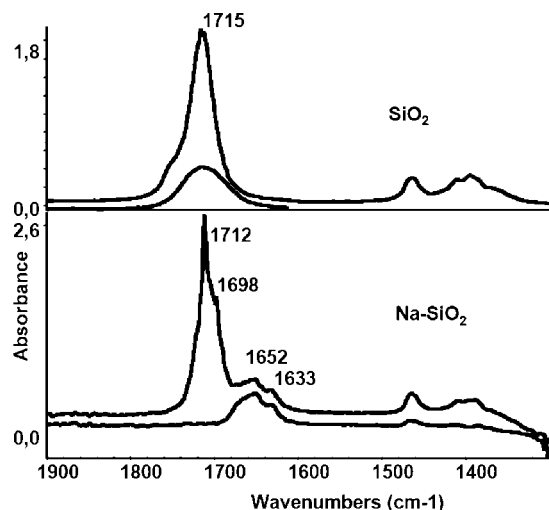

Figure 10. IR spectra of benzaldehyde adsorbed on silica and on Na-SiO$_2$ aldol condensation catalyst (self-supporting pressed disks), after previous activation of the solids by outgassing at 773 K.

metric stretching band is characteristic of this kind of adsorption. These weakly bonded species disappear from Na-LTA by simple outgassing at room temperature. When acting as an acid (or, better, as an elecrophile), CO$_2$ reacts with surface oxygen or hydroxide species, giving rise to carbonate or bicarbonate species. The free carbonate ion, as a result of its trigonal D_{3h} symmetry, has one characteristic strong infrared vibration (ν3; doubly degenerate asymmetric CO

stretching) found near 1415 cm^{-1} for bulk metal carbonates, together with two lower frequency IR active deformation modes. The lowering of the ion symmetry by coordination causes the splitting of this doubly degenerate ν3 vibration. In addition, the symmetric deformation mode ν1, normally only Raman active, is also activated in the IR. Different types of carbonate ions have been considered as possible surface species, as indicated by IR spectra. They can be represented by the simplified models shown in Figure 12. Type I (symmetrical) refers to a surface species whose spectroscopic features correspond to those of a noncoordinated ion. As discussed recently for the Ba/Al$_2$O$_3$ system,[142] planar trigonal carbonate species may actually form at the surface of basic materials so that their presence is not necessarily evidence of the formation of bulk carbonates. To distinguish bulk carbonates from surface trigonal carbonates, the intensity in the IR of the Raman active ν1 mode should be checked. In fact, in most cases, more than one carbonate ion is present in the smallest Bravais cell of bulk metal carbonate structures. Thus, coupling of their vibrational modes occurs. The coupling generates IR active vibrational modes arising from the Raman active and IR inactive ν1 mode. In contrast, for surface trigonal carbonates, this mode is usually detected in the IR, being made active by loss of symmetry, but is still extremely weak.

Monodentate, bridging, chelating (bidentate), and polydentate structures may also be formed at surfaces (Figure 12). The structures may be distinguished considering in parallel the stability of the structures (trigonal > polydentate > bidentate > chelating > monodentate) and the extent of their splitting of ν3 (bidentate $\geq$ chelating > monodentate $\geq$ polydentate > trigonal).[139] Some carbonate species, characterized by very large $\Delta\nu$3 and very low stability, are currently denoted as "covalent" or "organic like" but most likely are bent, very strongly perturbed CO$_2$ molecules.[140] Bicarbonate ions [HCO$_3$]$^-$ can also be formed by CO$_2$ adsorption or contamination. The species formed are characterized by νOH modes near 3620 cm^{-1}, by δOH modes near 1300−1200 cm^{-1}, and also by two νC=O modes at ∼1600 cm^{-1} and ∼1450 cm^{-1}.

Several different species are formed on Na-LTA zeolite (Figure 11) having different thermal stabilities, as is discussed elsewhere.[141] In Figure 13 the IR spectra of carbonates on different oxide surfaces are compared. The spectrum observed on Ca-LTA zeolite, with a very small ν3 splitting
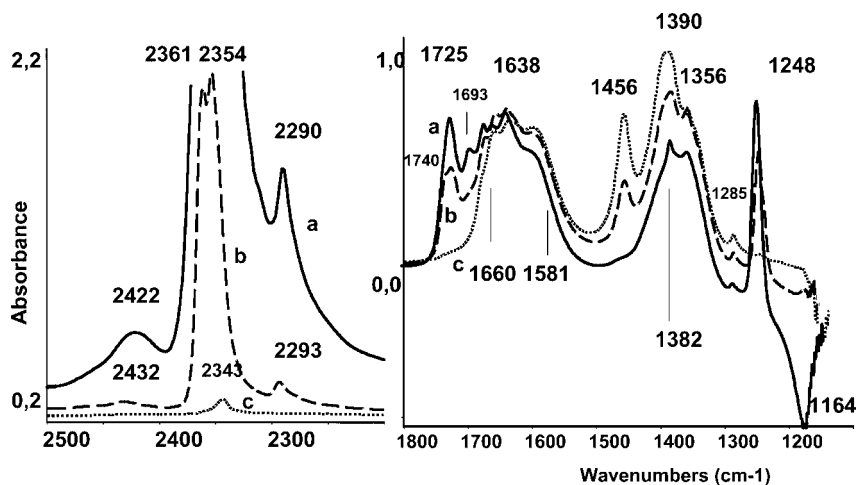

Figure 11. FT-IR spectra of the adsorbed species formed by contact of CO$_2$ gas with a 4A (Na-LTA) self-supporting pressed disk after activation, recorded in contact with the gas (a) and upon outgassing at rt for 2 min (b) or 10 min (c).
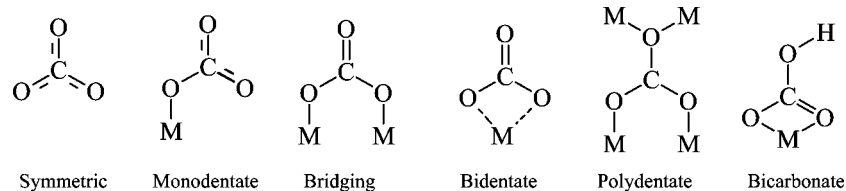
Figure 12. Structures of adsorbed carbonate species on metal oxides, as deduced by IR spectroscopy experiments.[139]
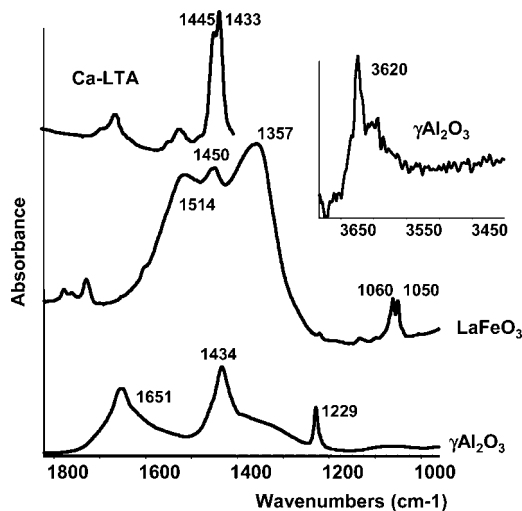

Figure 13. IR spectra of adsorbed carbonate species on some metal oxides (self-supporting pressed disks), after previous activation of the solids by outgassing at 773 K.

but a high stability of the species, is indicative of the formation of a strongly bonded nearly trigonal bulklike species formed on very strong basic sites. On the perovskite $LaFeO_3$, strongly bonded polydentate and nearly trigonal species are observed together. The spectrum observed after CO_2 adsorption on hydrated alumina is typical of weakly bonded bicarbonate ions.

Although surface cations are also involved in the formation of surface carbonates, the basicity of the oxide is the dominating factor in their stabilization. Accordingly, adsorption microcalorimetry of adsorbed CO_2 allows some ranking of the basicity of metal oxides.[128,129,143] The results concerning thermal desorption of CO_2 from surface carbonate and bicarbonate species are, in the opinion of the present author, perhaps the best and easiest characterization of the surface basic sites on an oxide. The desorption may be followed

using temperaure programmed desorption (TPD, Figure 14) or thermogravimetry. It is also possible to follow the disappearance of the features of these species using IR spectroscopy: the higher the desorption temperature, the more basic is the adsorption site. For very basic materials, full desorption of surface carbonates needs treatment in the 500−800 °C range. The TPD patterns shown in Figure 14[144,145] provide evidence of how the CO_2-TPD technique also allows a quite detailed analysis of the basicity of different materials as well as of different preparations of the same material.[32,144−146]

The complete absence or very small extent of CO_2 adsorption observed on oxides of semimetals such as silica and on transition metal oxides in very high oxidation states (such as V_2O_5,[147] WO_3,[148] and oxidized chromia, which is covered by hexavalent chromate species[149]) points to the negligible basicity of the surface oxygen atoms in cases such as these, where the element−oxygen bond is highly covalent. According to this, IR spectroscopy of CO_2 adsorption may be used to test the surface coverage of ionic oxide carriers (such as alumina, titania, zirconia) when used as supports for more covalent surface active species such as $WO_3−TiO_2$,[150] $V_2O_5−WO_3−TiO_2$, and SCR-DeNOx catalysts[151] and $CuCl_2−Al_2O_3$ ethylene oxychlorination catalysts.[152] The full coverage of the support with a monolayer results in the complete disappearance of carbonate formation upon CO_2 adsorption, with total "poisoning" of the surface basicity.

4.2.1.5. Catalytic Probe Reactions. Catalytic test reactions represent a very important tool for acid−base characterization of solids.[32,97,153] Conversion of secondary alcohols such as isopropanol,[154,155] 2-butanol,[156,157] and cyclohexanol,[158] either to olefins or to ketones, is considered to be evidence of acidic and basic behavior, respectively. Similarly, the reaction of cyclopentanol in the presence of cyclohexanone to alkenes and hydrogen transfer products (Meerwein−Ponndorff−Oppenheimer reactions) is indicative of acid and
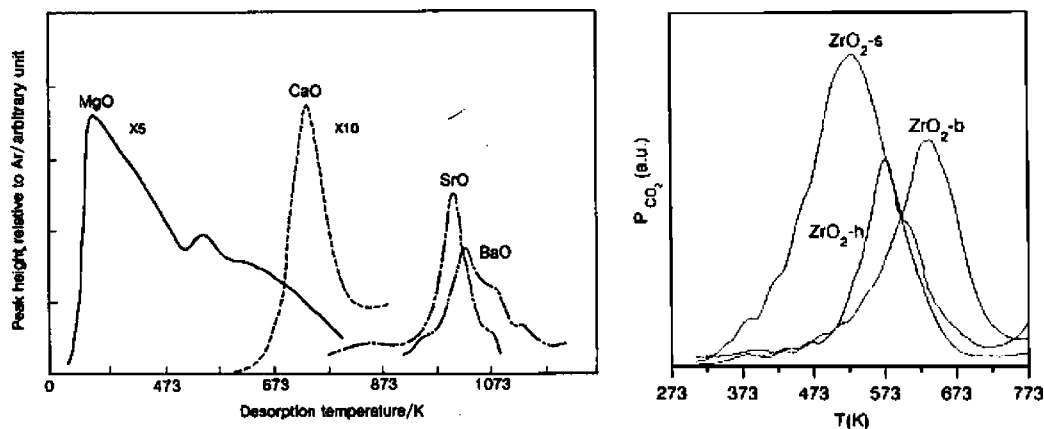

Figure 14. Temperature programmed desorption spectra of CO_2 from alkaline earth oxides (Reprinted with permission from ref 144. Copyright 1988 Elsevier) and from different zirconia preparations (Reprinted with permission from ref 145. Copyright 1998 American Chemical Society). ZrO_2-h is from The Harshaw Chemical Co. while ZrO_2-s and ZrO_2-b are homemade with and without silica stabilization, respectively.

basic character, respectively.[159] In fact, the adsorption of alcohols on oxide catalysts primarily involves the interaction of their oxygen atoms with the Lewis[160,161] or Brønsted[162] acid sites of the surface. The successive water elimination step is faster when this interaction is stronger. In contrast, on a surface having strong basic sites, an attack on the nearest C−H bond would occur, leading in the end to H_2 elimination. In this case, in the presence of a carbonyl compound, hydrogen transfer occurs.

The decomposition of the complex alcohol 2-methyl-3-butyn-2-ol (MBOH)[97,157,163−165] is very popular today. In fact, on acidic catalysts, it produces 2-methyl-but-1-en-3-yne by water elimination together with 3-methyl-but-2-enal by transposition, and on basic catalysts, it gives a mixture of acetone and acetylene, while, on amphoteric catalysts, it gives 3-methyl-3-hydroxy-2-butanone and 3-methylbut-3-en-2-one.

Skeletal and double bond isomerization of branched olefins such as methylenecyclohexane[158] are used to evaluate acidity and basicity, respectively. In fact, skeletal isomerization of olefins mainly implies isomerization of carbenium ions produced by protonation by Brønsted acid sites[166] while double bond isomerization can occur through formation of allyl species on acid−base pairs having the necessary basic character.[167] Position selective double bond isomerization of complex olefins under very mild conditions, such as the conversion of 4,4-dimethyl-1-pentene to 4,4-dimethyl-2-pentene (eq 19)[168]

$$(19)$$
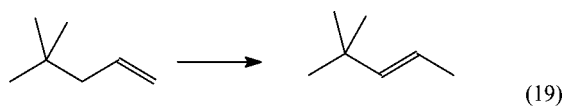
and of 5- vinylbicyclo[2.2.1]hept-2-ene to 5-ethylidenebicyclo[2.2.1]hept-2-ene (eq 20)[40]

$$(20)$$
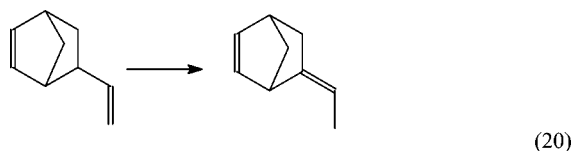
has been considered by several authors as an indication of superbasicity.

Reactions involving the formation of enolate species, such as, for example, the retroaldolization of diacetonealcohol,[154] the Knoevenagel condensation between benzaldehyde and carbonyl compounds with hydrogens in the α position,[97] acetonyl acetone cyclation, and isophorone isomerization,[97] are those most often applied in the characterization of medium basicity.

In a recent paper, Moreau et al.[169] used kinetic analysis of the isomerization of glucose into fructose to determine the basic strength of solid catalysts in water.

4.2.1.6. Theoretical Approaches. Several theoretical investigations on the nature of basic oxide surfaces as well as on the interaction between such surfaces and different molecules have been performed recently. Most of the work concerns MgO and other alkaline earth oxides.[170,171] The interaction of CO_2, SO_x, and NO_x over the (001) exposed faces or terraces of alkaline earth oxides has been the subject of several DFT studies.[172−176] It is largely accepted that most of the reactivity at MgO surfaces occurs at corners, kinks, and steps of the MgO (001) surface[177] (Figure 7). McKenna et al.[178] investigated the role of interfaces between MgO crystallites and concluded that delocalized holes can be
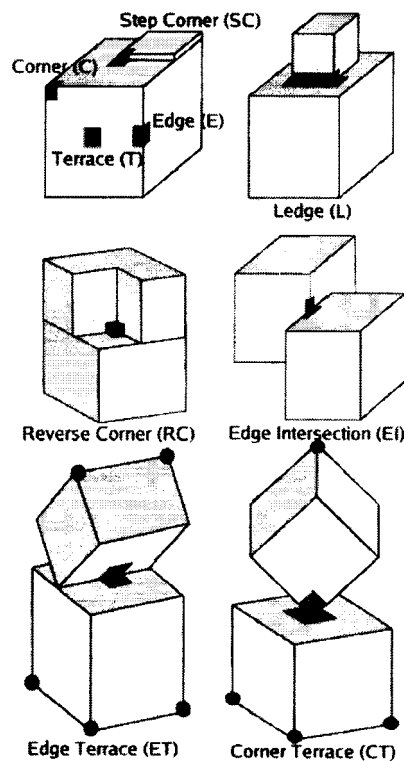

Figure 15. Features on the surface of MgO nanocrystallites and at interfaces between them. (Reprinted with permission from ref 178. Copyright 2007 American Chemical Society).

transiently trapped at a large number of places within a powder. In Figure 15, locations of such usually neglected sites at the contact between particles are shown. However, it is more favorable energetically for holes to trap on coordinatively unsaturated anions on the nanocrystallite surface, forming O^- species. Electrons are trapped at few interfaces but are readily trapped by surface kink and corner sites. According to Chizallet et al.,[115] the Lewis basicity and acidity of low coordination O^{2-} and Mg^{2+}, respectively, increase as their coordination number decreases (as is indeed expected[113]), which implies the same trend for the Brønsted basicity of the $Mg^{2+}-O^{2-}$ pair toward water. However, this trend can be changed if pairs leading to the formation of bridging OH groups are involved, typically on monatomic steps or in step divacancies where O_{2C}-H and O_{3C}-H (bridging and triply bridging hydroxy groups) are obtained, respectively, instead of the expected terminal O_{1C}-H. Kakkar et al.[179] investigated theoretically the enolization of carbonyl compounds over MgO clusters.

Several theoretical investigations have been performed recently related to applications of basic oxide surfaces. Among these, we can cite the adsorption of NO and NO_2 on BaO,[180,181] related to the application of Ba-based materials as NO_x traps and as adsorption and reduction catalysts (see below). Similarly, the adsorption of H_2S on MgO and ZnO has been investigated.[182]

Theoretical investigations on the adsorption of CO_2 on several basic oxides, such as La_2O_3,[183] MgO, and CaO[172,184] (associated with the development of CaO-based materials as CO_2 sorbents with a view to its sequestration from combustion gases; see below), and on cesium oxide clusters[185] have been completed recently. The results have been compared with those arising from infrared spectroscopy measurements. The IR spectra of CO_2 adsorbed on La_2O_3 at room temperature were similar to those of bulk $La_2(CO_3)_3$
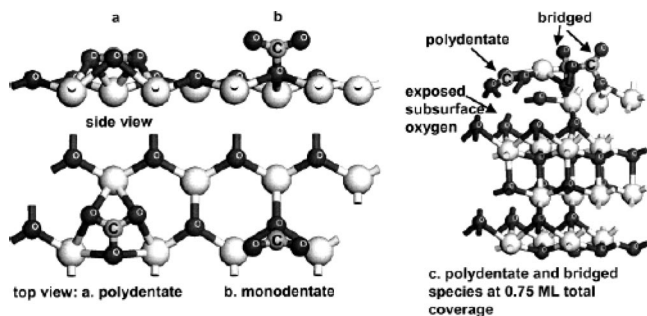
Figure 16. DFT models of carbonate species formed on CO_2 adsorption on $La_2O_3(001)$. Only top model layers are shown in parts a and b. (Reprinted with permission from ref 183. Copyright 2004 American Chemical Society).

and, accordingly, were assigned to the formation of polydentate and bulk carbonates. The structures of carbonates adsorbed on La_2O_3 as calculated by DFT[183] are shown in Figure 16. It seems worthy of remark that theoretical calculations most frequently result in structures and relative stabilities in good agreement with those deduced much earlier from experimental spectroscopy data. The study of Jensen et al.[184] showed that the HOMO energy level of surface oxide ions of MgO and CaO increases with decreasing coordination number. These results would indicate that CO_2 adsorbs as monodentate carbonate ions on edge sites and as bidentate carbonate on corner sites of MgO, while it would adsorb as monodentate carbonate ions both at edge and at corner sites of CaO. These data do not appear fully confirmed by experimental IR spectroscopic studies. These studies also allow the evaluation of the adsorption energy and the desorption temperature of CO_2 from alkali and alkaline earth

oxides, and they are in roughly good agreement with the experiments. Interestingly, the data of Tai et al.[185] show that, on an oxygen rich Cs oxide surface, no adsorption of CO_2 should occur. This provides evidence of the likely role of cations in the formation of surface carbonates, showing again that acidobasicity is needed more than pure basicity.

4.2.2. Composition Effect on the Surface Basicity of Metal Oxides: An Overview

As discussed elsewhere,[108,133] typical binary metal oxides (such as, e.g., magnesia, titania, zirconia, and alumina) are essentially ionic network structures (Table 10). Also, most ternary (mixed) oxides phases are ionic network structures (Table 11). The unit cells of some common structures are shown in Figure 17. Semimetal oxides, such as, e.g., silicas and germania, consist of essentially covalent network structures. The nonmetal oxides and the oxides of transition metals in very high oxidation states may be molecular in nature (i.e., nonframework), formed either by relatively small molecules (e.g., P_4O_{10}) or by macromolecular chains (e.g., CrO_3) or by layers (e.g., V_2O_5 and MoO_3).

Table 12 summarizes the typical features of the surface chemistry of pure oxide solids as related to their structural features. In the case of ionic or covalent network materials, the surface involves defects where oxide species and metal or nonmetal centers remain exposed and coordinatively unsaturated at the surface. These sites would be associated with a very high free energy and, consequently, would be very unstable. To stabilize the surface, reconstruction phenomena as well as reaction with molecules from the environment (e.g., water and CO_2) occur. This would limit
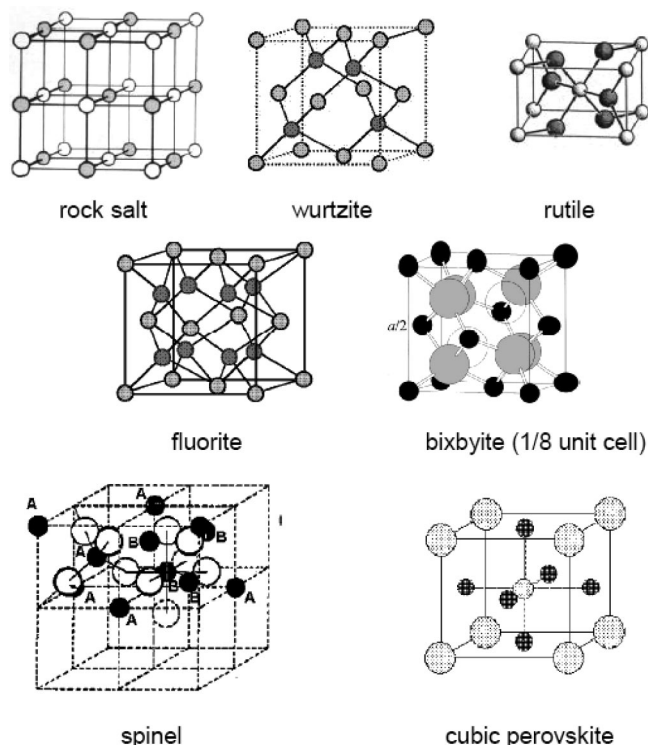
Table 10. Crystal Structures and Ion Coordinations in Stable Solid Simple Oxides

cation valence	type of structure	structure name	space group	Z	coordination cation	coordination oxide	examples
2	network	rock salt	$Fm3m$	4	6 (oct)	6 (oct)	MgO, CaO, SrO, BaO, MnO, FeO, CoO, NiO, CdO
		zinc blende	$F\bar{4}3m$	4	4 (tetr)	4 (tetr)	BeO (H)
		wurtzite	$P6_3mc$	2	4 (tetr)	4 (tetr)	BeO (L), ZnO
		tenorite	$C2/c$	4	4 (sq pl)	4 (tetr)	CuO
		cooperite	$P4_2/mmc$	2	4 (sq pl)	4 (tetr)	PdO, PtO
3	molecular/polymeric		$P3_1$	3	3 (trig)	1, 2	B_2O_3
	network	corundum	$R\bar{3}c$	6	6 (oct)	4	α-Al_2O_3, α-Cr_2O_3, α-Fe_2O_3, α-Ga_2O_3[a]
		tetragonal spinel	$I4_1/amd$	4	4 (tetr), 6 (oct)	3, 4	Mn_3O_4 (δ-Al_2O_3)
		ordered detective spinels	$C2/m$	4	4 (tetr), 6 (oct)	3, 4	θ-Al_2O_3, β-Ga_2O_3
			$P4_132$	8	4 (tetr), 6 (oct	3, 4	γ-Fe_2O_3
		"A"	$P\bar{3}m1$	1	7	6, 4	La_2O_3, Ce_2O_3, Pr_2O_3 (H), Nd_2O_3 (H)
		"B"	$C12/m1$	6	7	4, 5, 6	Pm_2O_3, Sm_2O_3, Eu_2O_3, Gb_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3,
		"C" bixbyite	$Ia\bar{3}$		6 (oct)	4	Pr_2O_3 (L), Nd_2O_3 (L), α-Mn_2O_3,
3, 2, 3		(detective) cubic spinel	$Fd3m$	8	4, 6	4	γ-Al_2O_3, η-Al_2O_3, γ-Ga_2O_3, Fe_3O_4, Co_3O_4
4		α-quartz	$P3_221$	3	4 (tetr)	2 (bent)	SiO_2, GeO_2[a]
		rutile	$P4_2/mnm$	2	6 (oct)	3	TiO_2, MnO_2, GeO_2, SnO_2, β-PbO_2
		anatase	$I41/amd$	4	6 (oct)	3	TiO_2[a]
		baddeleyite	$P2_1/c$	4	7	3, 4	ZrO_2 (L)
		tetragonal zirconia	$P4_2/nmc$	2	8	4	ZrO_2 (M)
		fluorite	$Fm3m$	4	8 (cub.)	4	ThO_2, CeO_2, HfO_2, ZrO_2 (H)
5	molecular		$R3c$	2	4	2, 2	rhombohedral P_4O_{10}
	layered	V_2O_5	$Pmmn$	2	5 (6)	1, 2, 3	V_2O_5, R-Nb_2O_5[a]
	network		$P2$	14	6, 4	2, 3	H-Nb_2O_5
6	molecular				4	1, 2	γ-SO_3 (S_3O_9)
	chain		$C2cm$	4	4		CrO_3
	layered		$Pbnm$	4	4-6	1, 2, 3	MoO_3
	network	ReO_3	$Pm3m$	4	6	2	ReO_3, WO_3 (distorted)

[a] Metastable phases. L, M, H = low, medium, high temperature form.

Table 11. Crystal Structures and Ion Coordination in Some Solid Mixed Oxides

structure name	formula	space group	Z	ion coordination			example
				cation A	cation B	oxide ion	
normal spinel	AB_2O_4	$Fd3m$	8	4	6	4	$MgAl_2O_4$, $CoAl_2O_4$, $ZnAl_2O_4$, $ZnFe_2O_4$, $ZnCr_2O_4$
inverted spinel	AB_2O_4	$Fd3m$	8	6	4, 6	4	$NiAl_2O_4$, $MgFe_2O_4$
ilmenite	ABO_3	$R\bar{3}$	6	6	6	4	$FeTiO_3$, $NiTiO_3$, $CoTiO_3$
lithium niobate	ABO_3	$R3c$	6	6	6	4	$LiNbO_3$ (H)
cubic perovskite	ABO_3	$Pm3m$	1	12	6	6	$SrTiO_3$, $SrZrO_3$, $BaZrO_3$
tetragonal perovskite	ABO_3	$P4mm$	1	12	6	6	$BaTiO_3$
orthorhombic perovskite	ABO_3	$Pnma$	4	6	6	4	$LaFeO_3$, $GdFeO_3$, $SrCeO_3$, $LaAlO_3$
rhombohedral perovskite	ABO_3	$R\bar{3}c$	2	6	6	4	$LiNbO_3$ (L), $LaMnO_3$
β alumina	$A_xB_{11}O_{16+x}$	$P6_3/mmc$	2	9	4, 6	4	$NaAl_{11}O_{17}$
olivine	A_2BO_4	$Pnma$	2	6	4	4	Mg_2SiO_4, Fe_2SiO_4
zircon	ABO_4	$I4_1/amd$	4	8	4	3	$ZrSiO_4$

Figure 17. Unit cells of some structures taken by metal oxides with a surface basic character; see also Tables 6 and 7.

the number of coordinatively unsaturated centers and cause the formation of new surface species such as the hydroxy groups and surface carbonates. However, on ionic oxides, unsaturated centers at the surface can remain or be generated by desorption of adsorbed water and CO_2 under heating. As a consequence of these phenomena, the surface of solid oxides can consist of surface coordinatively unsaturated cations (only on ionic surfaces), acting as Lewis acid sites, and of surface oxide and hydroxy species. Depending on the ionicity of the structure, oxide species can have from zero to very high basicity, while hydroxide species may be either acidic or basic.

Basic sites at the surface of solid oxides (well exposed oxide or hydroxide anions) can act as Brønsted basic sites by abstracting a proton from Brønsted acidic molecules. However, if this reaction occurs at the solid/vapor interface, it generates an anion that also needs to be adsorbed. In some way, consequently, Brønsted basicity needs the presence of Lewis acid sites to adsorb the conjugated base of the adsorbed acid molecule. Similarly, when the basic center adsorbs a Lewis acid (thus acting as a Lewis basic site),

nearby Lewis acid sites may be useful to stabilize the resulting anionic species (e.g., carbonates from CO_2).

According to our previous studies,[76,81] the dominant factors in governing the acidobasicity of metal oxides are the charge (C) and the ionic radius (r) of the cations, which may be combined in what could be called the "polarizing power", calculated either as C/r or as C/r^2. The larger the cation and the lower its charge, the less Lewis acidic it is, and in parallel the stronger is the basicity of the oxide anions. This is true for the bulk but is also reflected at the surface and is also true for surfaces of complex oxides such as a mixed oxide phase or, e.g., an oxide deposited over another material (such as another oxide, active carbon, or a polymer) acting as a carrier.

In Table 12 the conclusions arising from our IR studies[108,133,134] are compared with data arising from other techniques such as O 1s XPS binding energy (using the data collected by Dimitrov and Komatsu[120]), optical basicity values (from Leboutellier and Courtine[118]), data on the ionicity of the metal−oxygen bond, and CO_2 thermal desorption studies. Although the agreement is not perfect, the trends are quite parallel.

4.2.3. Strength, Amount, and Distribution of Surface Basic Sites on the Ideal Surface of a Solid

On solid materials, both the adsorption capacity and the catalytic activity (reaction rate) depend on the number of active sites (e.g., of basic sites having the appropriate strength to adsorb the molecules or to catalyze the reaction) present on the material as a whole. This means that the "density" of active sites (the number of sites per gram of the solid or per unit surface area) is an important parameter. On solids, the number and strength of the basic sites are quite independent parameters, and thus, they must be analyzed independently for a complete characterization of the surface. Additionally, several different families of basic sites may occur on the same solid surface, and their "distribution" (i.e., the density of sites for the different site families) must be characterized.

Additionally, both acidic and basic sites can be present in different positions (but frequently near each other) on the same solid surface and can work synergistically. This provides evidence for the significant complexity of acid−base characterization of solids.

Studies on basic oxides, in particular those concerning MgO,[164] which is apparently the most extensively investigated basic solid, have demonstrated the large effect of particle morphology on the basic behavior of surfaces. It is quite evident that the population of the most exposed, less coordinated sites occurring at corners, edges, and kinks is a key factor governing the number of surface basic sites on

Table 12. Summary of the Acid−Base Properties of Binary Metal Oxides

| element | oxidation state | cation size (radius, Å) | polarizing power range | | M−O bond nature | % ionicity[120] | acidity type | acidity strength | basicity, nucleophilicity | examples | XPS O 1s BE[120] (eV) | refs 118, 121 | T_{des} CO_2 (carbonates) |
			C/r	C/r^2									
semimetal	$\geq +5$	very small: ≤ 0.2	>25	<60	covalent molecular	<30	Brønsted	medium-strong	none	P_2O_5 (SO_3)	>533	0.33	no adsorption
semimetal	+3, +4	small: ≤ 0.4	>10	25−60	covalent network	<30	Brønsted	medium-weak	none	SiO_2, GeO_2 (B_2O_3)	531−533	0.48−0.54	no adsorption
metal	high: +5 to +7	small to medium: 0.3−0.7	>8	12−35	largely covalent network → layered → polymeric	>30	Brønsted Lewis	medium to strong	none	WO_3, MoO_3, CrO_3, Ta_2O_5, Nb_2O_5, V_2O_5	529−531	0.50−0.64	no adsorption
metal	medium: +3 to +4	small: 0.35−0.5	6−8	12−20	ionic network	>30	Lewis	strong	weak	γ-Al_2O_3, β-Ga_2O_3	529−531	0.65−0.77	<100 °C
metal	medium: +3 to +4	medium: 0.5−0.6	5−6	7−12	ionic network	>30	Lewis	medium	medium-weak	TiO_2, Fe_2O_3, Cr_2O_3	529−531	0.65−0.77	100−200 °C
metal	medium: +3 to +4	large: 0.7−1.2	3.5−5	2−7	ionic network	>30	Lewis	medium-weak	medium-strong	La_2O_3, SnO_2, ZrO_2, CeO_2, ThO_2	529−531	0.65−0.77	200−400 °C
metal	low: +1 to +2	large: 0.7−1.0	2−3.5		ionic network	>30	Lewis	medium to very weak	strong	MgO, CoO, NiO, CuO, ZnO, (Cu_2O)	527−530	0.78−12	400−500 °C
metal	low: +1 to +2	very large: >1.0	<2	<2	ionic network	>30	Lewis	medium to very weak	very strong	CaO, SrO, BaO, Na_2O, K_2O, Cs_2O	527−530	>1	>500 °C

solids, i.e. the density of sites per exposed surface area. On the other hand, particle size and porosity affect the extent of surface area per weight of the solids. Morphology, characterized by the surface area, the size and shape of the particles, and porosity, is mostly an effect of preparation and pretreatment procedures.

Another factor greatly affecting the surface properties is the presence of impurities. Intentional doping or unwanted contamination of oxides with alkali ions (e.g., when residual from precipitating agents used in the preparation) neutralizes acid sites on solid acids and/or forms basic sites. Conversely, contamination with acidic components (e.g., such as CO_2 or SO_x adsorbed from the environment forming carbonates and sulphites or sulphates) decreases surface basicity and/or produces additional acidic sites on basic surfaces.

A further very determinative factor in the generation of surface basicity is the activation procedure. Extremely strong basic sites may only be generated by desorbing any adsorbed water (even from hydroxides) and carbon dioxide by high temperature treatment under vacuum or very inert atmosphere.

4.2.4. Basic Metal Oxide Families

4.2.4.1. Alkali Metal Oxides. The basic reactivity of oxides of alkali metals is so high that they are essentially unstable under common conditions, i.e. in the presence of water vapor, which is sufficient to convert them into the corresponding hydroxides, and in the presence of CO_2, which converts them into carbonates. Thus, bulk alkali metal oxides cannot normally be used as basic materials. However, alkali metal oxides can be supported or deposited over carriers, such as high surface area oxides (silica, alumina, titania, zirconia, magnesia, or zeolites) or activated carbons, by impregnation/calcinations or vapor deposition procedures. They are also frequently used as surface dopants on transition metal oxides and metal catalysts to introduce basicity or to reduce acidity. Potassium is frequently preferred to sodium, possibly because its definitely larger ionic size limits reaction with supports and the formation of bulk salts. The basicity also tends to increase with cationic size, so that Cs cation gives rise to extremely high basicity.

The strong basicity of these compounds is reflected not only in the stability of the surface carbonates but also in the very weak acidity of the alkali ions acting as Lewis acid sites. This is indicated by the IR spectroscopy of adsorbed ammonia and pyridine (e.g., for the systems K_2O-TiO_2[186] and K-V/Al_2O_3; see Figure 9) and of adsorbed CO (see Figure 8 for Na-SiO_2).

According to these considerations, alkali metal-doped oxides are among the most used solid catalysts in basic catalysis (Table 7), such as Na-SiO_2 for aldol-type condensations.[41,187] According to Kelly et al., 98% selectivity to 2-ethyhexenal can be obtained by condensation of n-butanal over Na/SiO_2 at 400 °C, as a step in the synthesis of 2-ethylhexanol, an important intermediate in the synthesis of lubricants and plasticizers

$$2 \quad \diagup\!\!\diagdown\!\!-CHO \longrightarrow \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\!\!=\!\!\diagdown\!-CHO \quad + \quad H_2O \tag{21}$$
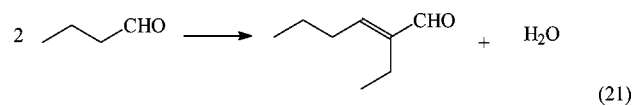
On the other hand, many industrial catalysts are doped, sometimes heavily, by alkali to reduce acidity or to produce basic functions. Among these we can cite the iron oxide based catalysts that are used in the dehydrogenation of
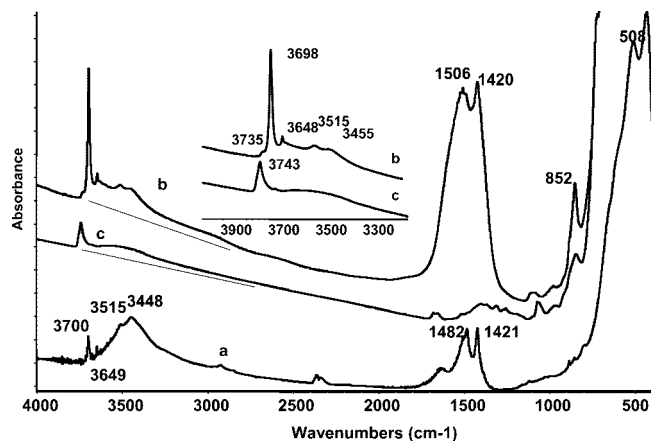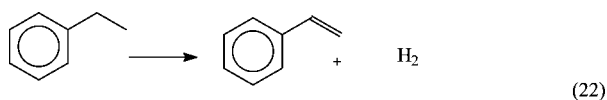
Figure 18. FT-IR spectra of a "MgO" commercial sample: KBr pressed disk (a); and pure powder pressed disk outgassed at 473 K (b) and at 873 K (c).

ethylbenzene to styrene and that may contain up to 13% of K_2O by weight with additional small amounts of MgO and CaO.[188,189]

(22)

4.2.4.2. Alkaline Earth Oxides. Beryllium oxide, BeO, in agreement with the small size of the Be^{2+} cation, has a quite acidic behavior[128,190] and crystallizes in the wurtzite structure with tetrahedral cation and anion coordination. All other alkaline earth oxides, whose cations are definitely larger in size, are among the strongest solid bases that may be stable as such under practical conditions. They crystallize in the rock salt type "periclase" structure, with octahedral coordination of both cation and anion. The increasing size of the cation results in an increased unit cell size as well as in an increased basicity. This is reflected, e.g., by the increased temperature for carbon dioxide desorption. On BaO, full desorption of carbonates is only obtained at 900 °C, as evident in the TPD spectrum reported in Figure 14, left side.

Actually, just as for alkali oxides, alkaline earth oxides are also so reactive that, when prepared as fine powders, they are generally at least partly converted into hydroxides and carbonates, or covered by carbonates upon exposure to ambient air. This is shown in Figure 18 for a commercial MgO sample. The skeletal spectrum recorded in a KBr disk, and also the spectrum of the pure powder recorded after outgassing at 473 K, show the typical OH stretching modes of brucite $Mg(OH)_2$ (3698 and 3648 cm^{-1}) as well as the split $\nu3$ modes of surface carbonate ions (1550−1400 cm^{-1}). The powder is converted into MgO but retains some surface carbonates upon outgassing at 600 °C. Under these conditions, the surface hydroxyl groups of MgO, responsible for the OH stretching band at 3743 cm^{-1}, appear. According to Bailly et al.,[164] surface hydroxy groups more than surface oxide anions may act as basic sites in catalyzing the conversion of MBOH. The behavior of CaO is similar, although even higher temperatures are needed to decompose the carbonates. The surface hydroxy groups of CaO absorbing at 3708 cm^{-1} appear after outgassing above 300 °C, when the surface is still largely carbonated.

Due to their strong basicity, alkali earth oxides cannot be covered by "monolayers" of other more covalent oxides, in contrast with what happens with ionic but less basic oxides,

such as zirconia, titania, and alumina. In fact, the surfaces of zirconia, titania, and alumina can be covered by "discontinuous monolayers" of vanadate, tungstate, and molybdate species,[191] actually constituted by monomeric mono-oxo species (i.e., pyramidal low coordination complexes with one short "double" bond), largely predominant at low coverages under dry conditions,[192] and polymeric species. On the contrary, with MgO, such surface species are not stable and penetrate into the bulk, pruducing tridimentional Mg vanadate,[193] tungstate, and molybdate. The same occurs with silica-doped materials, for which surface hydrogensilicate species predominate on titania,[194,195] alumina,[196] and zirconia while bulk silicates form with magnesia.[197]

The basicity of alkaline earth oxides increases with the cation atomic number, which is to say with increasing cation size and decreasing cation polarizing power, and with decreasing Madelung potential, which destabilizes the oxide anions.[170] In an interesting recent paper, Chiesa et al.[198] used the EPR spectrum of metallic ^{23}Na deposited on alkaline earth oxides to meaure their basicity.

MgO and CaO free from impurities are considered to be even superbasic, according to titration measurements in contact with water solution.[32] When fully cleaned by treating in vacuum at very high temperatures, highly exposed cations and anions are freed. This induces very complex chemistry, such as that producing $(CO_2)^{2-}$ "carbonite" species and $(C_3O_4)^{2-}$ trimeric species from carbon monoxide.[199] Such surfaces are also able to abstract protons from hydrocarbons, resulting in the formation of paramagnetic superoxide ions via a SIET (surface intermolecular electron transfer) mechanism, as detected by ESR spectroscopy.[200]

Alkaline earth oxides are the object of significant interest in the field of basic heterogeneous catalysis.[97] For MgO, different preparation methods give rise to particles characterized by different morphologies and consequently different surface basicity. The catalytic activity of MgO in the oxidative coupling of methane

$$2CH_4 + O_2 \rightarrow H_2C{=}CH_2 + 2H_2O \qquad (23)$$

was found to be enhanced by Ca and Na impurities, which also enhance its basicity.[201] Calcium oxide has been found to be an excellent catalyst for biodiesel production:[202] the performance is a little lower than that with NaOH solution, but, advantageously, CaO is a solid.

Because of their very high melting temperature (2852 °C for MgO, 2572 °C for CaO), bulk alkaline earth oxides of natural origin, such as magnesia produced by calcination of magnesite $(MgCO_3)$ and Mg,Ca mixed oxides produced by calcinations of dolomite $(MgCO_3{-}CaCO_3$ solid solution), find important application as basic refractory materials.[203]

The size of Mg^{2+} is sufficiently small to penetrate close-packed oxygen ions. For this reason, Mg ions can participate in the formation, for example, of mixed oxides such as spinels and ilmenites, whose oxygen packings are ccp and hcp, respectively. In relation to this, the deposition of Mg ions at the surface of normal carriers such as alumina may give poor stability because of the reaction producing Mg aluminate.

On the other hand, the size of the higher alkali earth cations is large enough not to allow their penetration into close-packed oxygen ions. Accordingly, Sr and Ba ions are involved in the formation of mixed oxides with less compact packing for oxide anions, such as perovskites and β-aluminas. Additionally, Sr and Ba ions may be supported on typical

**Table 13. Some Industrial Processes Using Basic Zeolites as Adsorbents[207,209]**

zeolite	separation processes
K-LTA or Linde 3A	ethanol/water (bioethanol fuel)
Na-LTA or Linde 4A	air, methane, natural gas, and nitrogen purification and dehydration
Ca-LTA (Linde 5A)	N_2/O_2 air separation
	H_2 purification from CH_4 and CO
NaA or NaX	alkane/alkene separation
NaX Faujasite (Linde 13X)	purification of C4 cuts from nitriles
	N_2/O_2 air separation
	benzene/cyclohexane
K,Ba-Y Faujasite	p-xylene/m-xylene

oxide carriers such as alumina and titania, forming quite stable basic materials. The alkali and alkali metal cations remain exposed at the surface, where their weak Lewis acidity (corresponding to the strong basicity of the oxide anions) is easily detectable by conventional probes, such as pyridine on SrO-TiO$_2$[204] and CaO-Al$_2$O$_3$[205] and CO on BaO-Al$_2$O$_3$ (Figure 8). Such surface layers adsorb carbon dioxide very strongly so that carbonate particles can form, as they do for example for catalytic materials belonging to the BaO-Al$_2$O$_3$ system,[142,206] which find application as traps for nitrogen oxides in the NSR (NO$_x$ Storage and Reduction) technology for purification of waste gases of diesel cars.

4.2.4.3. Alkali and Alkali Earth Zeolites. Zeolites are natural and synthetic framework silicoaluminates where charge balancing cations (usually alkali or alkali earth) are located in relatively large cavities formed by the $[Si_{1-x}Al_xO_2]^x$ negatively charged framework. These cavities are connected by channels that give rise to a variety of microporous structures which can be penetrated only by sufficiently small molecules, thus giving rise to the "molecular sieving" effect, which is very important in adsorption technologies,[207] as well as the "shape selectivity" effect, which is relevant mostly to the acid catalysis performed by the protonic forms of zeolites.[9,208,209] The cations are exchangeable; thus, zeolites may also act as cationic exchangers.

Although much work has been done on the catalytic activity of basic zeolites, it seems that, up to now, they still have no industrial application as catalysts.[210] On the contrary, several of them, in particular those denoted with the IZA (International Zeolite Association[211]) code LTA (Linde Type A) and the so-called X and Y zeolites, denoted with the code FAU, being isostructural with the natural zeolite Faujasite, have very important industrial applications as adsorbents, as reported in Table 13.

In Figure 19 the elements of the crystal structure of NaX (13X or Na-FAU) and of NaA (4A or Na-LTA) zeolites in their dry form are shown. Alkali cation zeolites are formally
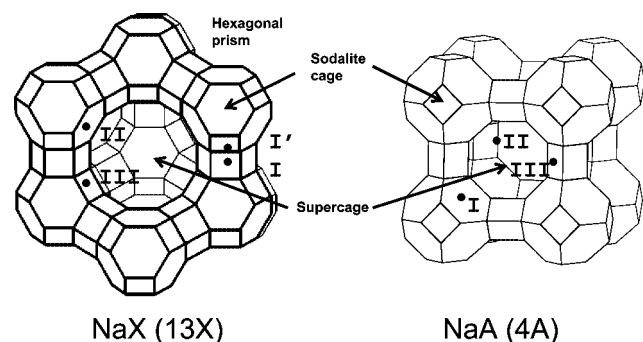
salts of strong acids, thus being essentially weak bases. Actually, in perfect cationic zeolites, free of extra-framework material, all oxygen atoms are exposed at the cavity surface and may act as basic sites. However, depending on their size, part of the cavities in some zeolites may be inaccessible to large and even small molecules. This occurs for the sodalite cages as well as for the prisms in the FAU and LTA structures (Figure 19), where the reactivity occurs in the so-called supercages. Spectroscopic studies show that the basicity of alkali zeolites is low, although reactivity of the oxygen atoms toward acidic probe molecules can sometimes be found, depending on the composition. For example, CO$_2$ is reported to form carbonate-like structures when adsorbed on Na- and Al-rich zeolites such as Na-X[212] and Na-LTA[141] (see Figure 11), but such structures do not form over Na- and Al-poor zeolites such as Na-ZSM-5.[213] Similarly, dissociative adsorption of H$_2$S can be found on Na-FAU.[214] In fact, for most zeolites the Si to Al framework ratio (8−100) is considerably larger than that for both LTA (Si/Al ratio usually 1) and FAU zeolites (where SI/Al is near 1 for X zeolites and near 2.5 for Y zeolites). Accordingly, the anionic charge of the framework is definitely larger for LTA and FAU cationic zeolites than for all others, as is also the concentration of Na$^+$ ions. Actually, in spite of the basicity of the framework, the behavior of stoichiometric cationic zeolites is dominated by the weak Lewis acidity of the alkali (and alkali earth) cavity cations, that are mostly involved in the adsorption of molecules such as CO$_2$ and CO but also true n-bases such as, e.g., ammonia or nitriles[215,216] and also weak π- bases such as olefins[217,218] and aromatic hydrocarbons. The internal cavity interactions in cationic zeolites may be complex, with the simultaneous participation of more Lewis acidic cations and perhaps also of the basic oxygen framework.[219]

On the other hand, cationic zeolites may be "overexchanged"; that is, more cations than those balancing the framework charge may be introduced. In this case, oxide particles are formed in the cavities. These particles, which under normal conditions may be carbonated and/or hydrated, may be very strongly basic if they belong, for example, to alkali oxides. This may be the case for commercial 5A zeolite (Ca,Na-LTA), where CaCO$_3$-like particles are usually present.[141,220] This is also the case for Cs oxide impregnated CsX zeolite, which is reported to be a very basic material.[221]

In recent years, some interest has been devoted to a new family of solids with zeolite-like structure, i.e. microporous titanosilicates such as ETS-4 (Engelhard Titanium Silicate No. 4, with formula Na$_9$Ti$_5$Si$_{12}$O$_{38}$(OH)·12H$_2$O) and ETS-10 (with formula (Na,K)$_2$TiSi$_5$O$_{13}$·4H$_2$O). Like for zeolites, ETS-4 has the interesting property of a possible tuning of the pore sizes.[222] The structure of this solid is shown in Figure 20.[223] These materials have the potential for adsorption[224,225] and separation of even very small molecules, for cation exchange, and for the extraction of heavy metals from water.[226]

4.2.4.4. Transition Metal, Rare Earth, and Higher Valency Oxides. As discussed elsewhere,[133] and above, typical metal oxides are essentially ionic network structures. This means that, in the bulk and on the surface, Lewis acidic cations and basic anions are present. The main factors determing the surface chemistry are the ionicity of the bond and the cation size. This is the case for transitional aluminas (γ-, η-, δ-, θ-Al$_2$O$_3$), for which the catalytic activity and adsorption behavior is undoubtedly related mostly to the

Figure 19. Unit cell structures of cationic zeolites useful as solid adsorbents, in their dry form.
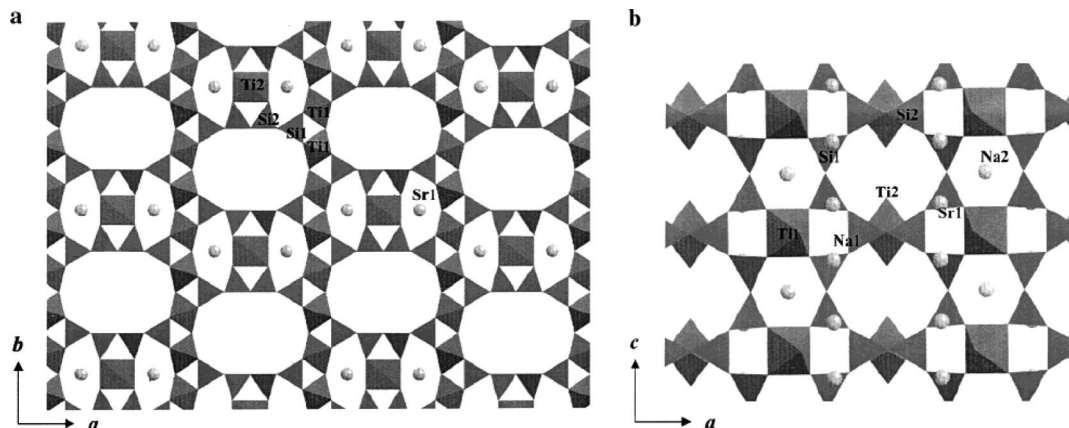
Figure 20. (a) View of the Na-ETS-4 framework down the [001] direction, showing open 12-membered rings caused by AA-type stacking of bridging units along the [001] direction. The ABAB-type stacking of the layers along the [100] direction is also illustrated. Sodium cations are shown occupying the Na1 sites adjacent to the bridging units. The titania chains containing octahedrally coordinated titanium propagate along the [010] direction. (b) View of the Na-ETS-4 framework down the [010] direction, showing the eight-membered silicate ring. Both sodium cation sites Na1 and Na2 (in the six-membered ring) are shown. Both the possible orientations of the five-coordinated Ti2 atom are shown in the figure. (Reprinted with permission from ref 223. Copyright 2001 American Chemical Society).

Lewis acidity associated with the coordinatively unsaturated small trivalent cations. However, the true particular sites of aluminas are very likely anion−cation couples which have very high activity and work synergistically as acid−base couples.[9] The basic counterpart may be oxide anions or hydroxyl species. A similar situation occurs for other metal oxides where acidity and basicity may be more or less predominant (see Table 8).

In fact, low valency transition metal oxides have medium-strong acid−base properties. Useful basicity is observed experimentally for divalent metal oxides such as wurtzite-type ZnO,[135,136] and tenorite CuO,[227] as well as for rock salt type CoO[228] and NiO.[229] The use of some of these materials as basic catalysts is however hampered by their reducibility to the corresponding metals. Weak basicity is observed for trivalent transition metal oxides such as iron oxide[230] and chromia.[149] In the latter case, the surface basicity strongly depends on the oxidation state, with the oxidized surface being less basic than the reduced one because of the presence of high valency chromate species. The basicity of ZnO and Fe_2O_3 is certainly involved in their reactivity toward H_2S, which allows their use for gas cleanup (see Table 2).

Scandia and, even more so, lanthanide oxides, such as La_2O_3 and Nd_2O_3, are stronger bases, in agreement with their larger cationic size. The significant basicity of rare earth sesquioxides made them the object of much investigation, in particular in relation to the development of catalysts for the oxidative coupling of methane.[156] The basicity of lanthana allows its use as a catalyst for several organic reactions including the synthesis of phytosterol esters[231] via transesterification.

Weak basicity coupled with medium Lewis acidity is also observed for the common titania polymorphs anatase and rutile,[232] while monoclinic and tetragonal zirconia[146] have a little more pronounced basicity. Among tetravalent metal oxides, CeO_2[233] has attracted much interest by its catalytic functions in the synthesis of organic compounds, which provide evidence of its relevant basicity. CeO_2−ZrO_2 mixed oxides form a cubic solid solution in the ceria-rich side,[234] which has a useful ability for NO_x absorption that is further increased by other rare earth doping.[235] Thoria is also reported to have strong basicity.[135] In fact thoria, zirconia, and ceria based materials already have industrial applications

(24)
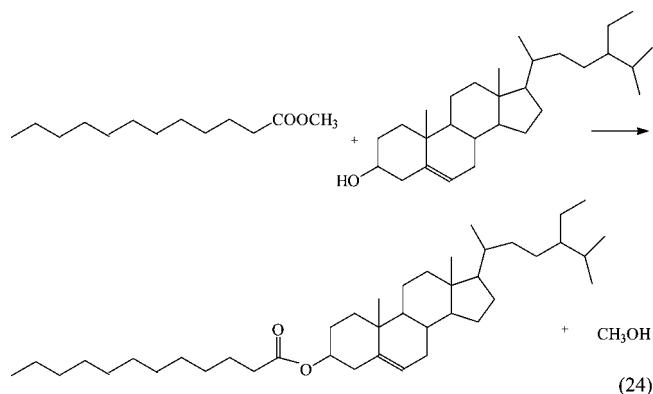
in some dehydration and ketonization reactions (Table 7), such as for the synthesis of diisopropyl ketone from isobutyric acid.

(25)
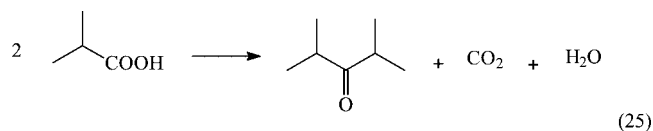
4.2.4.5. Hydrotalcites, Calcined Hydrotalcites, and Spinels. Hydrotalcite (HT, the layered double hydroxide, LDH, with formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) is a natural anionic clay having interesting basic properties. Its structure consists of brucite-like $[Mg_6Al_2(OH)_{16}]^{2+}$ layers with carbonate ions and water molecules in the interlayer region (Figure 21). It is a commercial synthesis product, is used in medicine as a stomach antacid, and serves also as an environmentally friendly, nontoxic, and heavy-metal-free filler to scavenge acid byproduct in halogenated polymers such as PVC. Hydrotalcite decomposes at 260−300 °C with the release of CO_2 and water and thus acts as a flame-retardant and smoke suppressant. The thermal decomposition of HT gives rise to a mixed oxide whose virtual composition is $5MgO \cdot MgAl_2O_4$, although these phases may give rise to mutual solid solubility, depending on the decomposition temperature. In fact, calcined HTs are intimate mixtures of rock-salt type and spinel-type solid solutions.

"Spinel" is the mineralogical name of magnesium aluminate, $MgAl_2O_4$, as well as of other isostructural mixed oxides
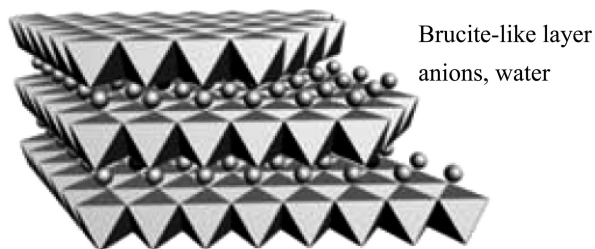
Figure 21. Structure of hydrotalcite.

of a trivalent and a bivalent ion. Stoichiometric $MgAl_2O_4$ is essentially a normal spinel phase with tetrahedrally coordinated Mg and octahedrally coordinated Al, and it is an important refractory material.[203] Due to partial inversion of the spinel structure, low-coordination Al cations typical of spinel-type aluminas can be detected at the surface and produce a small density of very strong Lewis acid sites.[136] The surface of nearly stoichiometric spinel materials shows a compromise between the basic character of rock-salt-type bivalent oxides and the more or less acidic character of the corresponding sesquioxides.[236–238] In the case of calcined hydrotalcites, excess Mg ions cause the predominance of the basic character of MgO. Doping with alkali may further increase the basicity of hydrotalcites.[239]

Several reviews have been reported recently concerning the application of Mg-Al HT or calcined HT as basic materials,[97,240–242] in particular in the field of fine organic chemistry. These materials, whose basic strength is somehow tunable,[243] are very popular as basic catalysts in academic research. On the other hand, they are also used industrially for aldol condensations[244] such as the synthesis of, for example, methyl isobutyl ketone, MIBK, by aldol condensation of acetone followed by dehydration and hydrogenation.[245] The full reaction may be performed in a single liquid phase reactor using Mg-Al hydrotalcite with 0.1% Pd:[246]

(26)
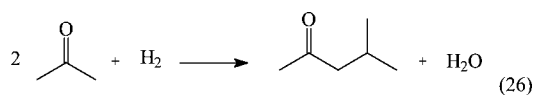
This single step process substitutes the older three step one, based on catalysis by caustic, acid catalyzed dehydration and hydrogenation:

(27)
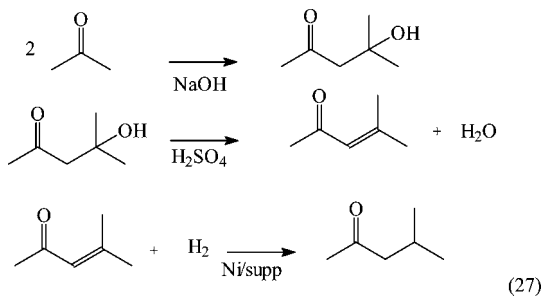
They also promote the oxyethylation of alcohols by ethylene oxide with the production of nonionic polyethoxylate surfactants:[247]

(28)
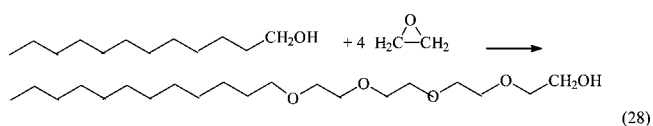
They have also been used as basic supports for noble metal catalysts[248] and for the abatement of SO_2 from waste gases. Magnesium aluminate spinels are widely applied as supports or components for nickel methane steam re-forming catalysts[249] just to limit surface acidity and, consequently, deactivation by coking.

Hydrotalcite-type LDHs can be prepared using bivalent cations whose hydroxides have brucite-type structures (such as Mg, Ni, Co, Zn) and several trivalent anions (Al, Fe, Cr). Thus, systems such as Ni–Al, Co–Al, Ni–Mg–Al, Ni–Zn–Al, Cu–Zn–Al, and Cu–Mg–Al form a hydrotalcite-type LDH that, after calcination, yields mixed phase oxides (oxide + spinel) which have basicity and additional very well dispersed reducible metal functions. Zn–Al hydrotalcites and their decomposition products also show useful basic properties in accord with the basic properties of both ZnO and $ZnAl_2O_4$.[135,136] In fact, Zn–Al hydrotalcites have been patented for industrial oxyethylation.[247] Zn–Al hydrotalcite calcined at moderate temperatures forms poorly crystalline Zn oxides that adsorb alcohols to give highly ionic alkoxide species.[250] Zinc aluminate has been patented as an optimal catalyst for light olefins double bond position isomerization (Phillips[251]) and has also been used recently in an interesting application as the catalyst for solid-catalyzed biodiesel synthesis by fat transesterification with the IFP process.[252] The use of a solid catalyst allows the distillation of methanol from the reaction medium, the separation of glycerine from biodiesel and fats, and the production of pure water and sodium-free glycerine. Zinc aluminate is either a component of or the support of Cu-based methanol synthesis catalysts[253,254] as well as methanol steam re-forming catalysts.[255–257]

$$CO + H_2 \leftrightarrows CH_3OH \qquad (29)$$

$$CH_3OH + H_2O \leftrightarrows CO_2 + 2H_2 \qquad (30)$$

Cu–Mg–Al mixed oxides arising from LDHs are good catalysts for the reduction of NO_x by ammonia,[258] and Ni–Al, Ni–Zn–Al, Ni–Co–Zn-Al, and Ni–Mg–Al mixed oxides obtained from LHDs are excellent catalysts for hydrogen production through methane[259,260] and are among the most promising for (bio)ethanol steam re-forming[261–264]

$$C_2H_5OH + 3H_2O \leftrightarrows 2CO_2 + 6H_2 \qquad (31)$$

LDHs based on trivalent elements other than Al, such as Cr and Fe, may also be produced and give a mixture of oxides and Cr or Fe spinels, which have several interesting properties. Chromite spinels, such as $MgCr_2O_4$[265] and $CoCr_2O_4$,[266] are excellent combustion catalysts, while others, such as $CuCr_2O_4$ and $ZnCr_2O_4$, are good hydrogenation catalysts. $ZnCr_2O_4$ was the material of choice for the old high-temperature methanol synthesis process.[267] Magnesium chromite spinels are also basic refractory materials with excellent high-temperature slag-resistance properties. They are used as raw materials for the production of linings for steel furnace ladles.[203]

Ferrite spinels, besides having very important magnetic properties, act as selective oxidative dehydrogenation catalysts in the conversion of butene to butadiene.[268]
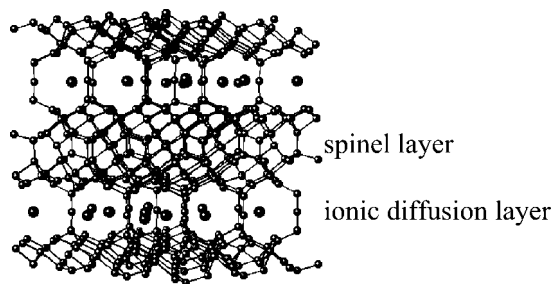

(32)

spinel layer

ionic diffusion layer
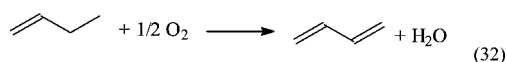
Figure 22. Structure of β-alumina.

Basicity may be useful in avoiding oligomerization of the diene product. $ZnFe_2O_4$ is also used as a regenerable absorbant for H_2S.[269] Just as with aluminates and chromites, ferrite spinels also allow large deviations from the AB_2O_4 stoichiometry, both with forms that have excess bivalent element and forms that have excess trivalent elements as well as with substitutions of the divalent and the trivalent metals forming solid solutions.[270,271] Bivalent-excess ferrites, such as $Mg_{1+x}Fe_2O_{4+x}$, are strongly basic materials.[272]

4.2.4.6. Perovskites. Perovskite-type phases form when small cations and large cations combine in a mixed oxide with the formula ABO_3. This can involve either a large bivalent cation and a small tetravalent cation or just two trivalent cations of very different size. The cubic structure of perovskite, which is the mineralogical name given to calcium titanate, $CaTiO_3$, is sometimes deformed to give different tetragonal, orthorhombic, and rhombohedral phases. Spectroscopic studies show that the surface is largely dominated by the large cations, which results in very basic oxide anions being at the surface of perovskites, as is the case for $BaTiO_3$,[273] $SrTiO_3$,[204] and several La perovskites.[274] Evidence of this is provided by the very weak Lewis acidity of the surface cations as probed by pyridine (see Figure 9 for $BaTiO_3$). Perovskites have been the object of much interest. Their properties have been summarized by Fierro and co-workers in a book[275] and a review.[276] These materials are thermodynamically very stable phases with several important electronic and optical properties. Among practical applications are the use of LSM (i.e., lanthanum strontium manganite $La_{1-x}Sr_xMnO_3$) and similar manganite perovskites as total oxidation catalysts[277,278] and also as a component of solid oxide fuel cell cathodes.[279]

4.2.4.7. β-Aluminas. The β-aluminas and similar structures are generated when a large cation (such as Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, or La^{3+}) is mixed with a large excess of a small trivalent cation, typically Al^{3+}. The structure (Figure 22) is composed of slabs of the trivalent metal oxide (mostly alumina), with a spinel-type structure and a ccp oxygen array, separated by layers of the very large cation along with a few oxygen ions to balance the charge. Ionic conductivity occurs along these layers. These materials have very high thermal stability and retain a large surface area (i.e., >20 m^2/g) even at a temperature of 1473 K.[280] In this case, as is also found for Ba-β-alumina[206] and La-β-alumina, the surface only exposes the large low valency cations, well detectable by adsorbing bases and very basic oxygen species that adsorb CO_2 in the form of carbonates. The decomposition temperature of surface carbonates on Ba-β-alumina ($BaAl_{12}O_{19}$) has been followed by IR under outgassing: $BaAl_{12}O_{19}$ appears to be far more basic than pure alumina and most pure oxides other than the pure alkaline earth oxides.

In spite of this high basicity, no application of this property seems to have been developed. β-Aluminas are industrially applied mostly in fields related to their ionic conduction, such as in secondary battery, fuel cell, thermoelectric converter, and sensor technologies. Their excellent thermal stability makes hexaaluminates useful as supports or components of high temperature methane and natural gas combustion catalysts[277,281] in gas-turbine applications involving temperatures up to 1773 K. Recently, they have been proposed as catalysts for abatement of N_2O through thermal decomposition. This exothermic reaction is performed at high temperature, both in the end-of-pipe configurations of the nitric acid and cyclohexanone oxidation processes (700 °C) and for the alternative application in the ammonia oxidation burner (1073−1173 K, wet oxidizing atmosphere).[282]

4.2.4.8. Basic Silicate Clays. Alkali and alkali earth metal orthosilicates, such as olivine (Mg_2SiO_4) and lithium silicates (Li_4SiO_4) and zirconates,[283] besides being important refractories, are applied in high temperature catalytic applications, such as biomass gasification,[284] tar removal catalysis,[285] and high temperature CO_2 adsorption.[286]

Smectite clays, such as montmorillonites (bentonites) and saponites, are sheet silicates in which a layer of octahedrally coordinated cations is sandwiched between two tetrahedral phyllosilicate layers. To complete the coordination of the cations, hydroxy groups are also present in the layers, with the theoretical formula for each layer being $Al_2Si_4O_{10}(OH)_2$. In the case of montmorillonites (bentonites), Mg substitutes for Al in the octahedral layers, and hydrated alkali or alkali-earth cations in the interlayer space compensate for the charge defect. In saponites, additional Al for Si substitution occurs in the tetrahedral sheets. Although the presence of alkali and alkali earth ions in their structure can give rise to some basicity, surface characterization studies of untreated montmorillonite and saponite provide evidence for predominant weak acidity for the surface of these materials.[9,287] The basicity can be increased significantly by chemical treatment, such as by exchange with Cs^+ ions.[288] Pillaring with basic materials is also possible.

Sepiolite, a hydrated magnesium silicate with the ideal formula $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 \cdot 8H_2O$, is characterized by a chainlike structure producing needle-like particles, instead of the platelike particles typical of phyllosilicate clays. Most of the world production of this clay comes from deposits of sedimentary origin located near Madrid, Spain. Sepiolite is an excellent material for cat and pet litters because of its lightweight, high liquid absorption and odor control characteristics.[289]

4.3. Other Solids Displaying Basicity

4.3.1. Metal Nitrides, Sulphides, Carbides, Phosphides, Halides

Because of the smaller electrophilicity of nitrogen, phosphorus, carbon, and halogens other than fluorine as compared to oxygen, bonds of these elements with metals and semimetals have lower ionic character, and consequently, the corresponding binary compounds (nitrides, sulphides, phosphides, carbides, and halides excepting fluorides) are expected to show lower basicity than oxides. The strong electronegativity of fluorine is a reason for the application of KF/Al_2O_3 as a strongly basic catalytic material.[97,102] 48% KF on alumina is a very versatile

commercial basic catalyst for organic synthesis.[290] Other supported alkali metal fluorides, such as CsF/α-Al₂O₃, have been found to display good basic catalytic activity.[291,292]

Transition metal sulphides are widely used in industry as catalysts for hydrodesulphurization and hydrotreating of hydrocarbon flows. Although traditional catalysts are alumina-supported Co−Mo, Ni−Mo, or Ni−W catalysts, the corresponding bulk unsupported sulphides, as well as other transition metal sulphides (such as the pure or mixed sulphides of V, Fe, Rh, Ru, Cr, Cu, ...), have been studied. The new and more efficient HDS catalysts which can reach the limit of 10 ppm in diesel fuel are likely to be mixtures of these sulphides.[293] These materials are thought to have Lewis acid sites able to interact with the sulfur atoms of (di)benzothiophenes, but to our knowledge, no information is available about useful surface basicity. Studies on the basicity of ZnS did not report any significant basicity.[32] On the other hand, we note that sulfur compounds are in general weaker bases than the corresponding oxygen compounds because of both the lower electronegativity of sulfur with respect to oxygen and also the lower ionicity of its bond with metals.

The medium-weak basicity of silicon nitride[294] and oxynitride,[295,296] as well as of aluminum nitride[193,297] and boron nitride[298,299] was recognized several years ago. These solids expose, at their surface, hydroxy groups and nitrogen atoms such as NH and/or NH₂ groups. In recent years, several other nitride, oxynitride, and phopsho-oxy-nitride materials such as VAlONs, AlPONs, ZrPONs, and AlGaPONs have been developed, particularly by Grange and co-workers,[300] and proposed as possible basic catalysts.

Transition metal nitrides are well-known as excellent hydrotreating catalysts.[301] They have also drawn considerable interest in recent years for their potential use as a catalyst for other hydrogenation reactions. Using MBOH catalytic conversion as a reaction probe, Keller et al.[302] found significant surface acidity for W₂N, Mo₂N, and NbN catalysts: dehydration is thought to occur on Brønsted acid sites, whereas isomerization should occur on metal-oxo ones. Conversely, using CO₂-TPD and MBOH decomposition, McGee et al.[303] found useful basicity at the surface of W₂N and Mo₂N, with a basic site strength and density similar to those of ZnO but lower than those of MgO. However, for acetone aldol condensation, Bej and Thompson found higher activity for Mo₂N than for MgO.[304]

4.3.2. Solid Metal Hydroxides and Carbonates

Very basic metal oxides are actually carbonated and hydrated under ambient conditions, but not at high temperature. These materials, such as solid NaOH, Na₂CO₃, limestone, and limes, are used in a number of applications, as discussed above. Strong solid bases may be generated *in situ* from alkaline and alkaline-earth metal carbonates by adding a small amount of acetic acid at reflux in toluene under water-free conditions,[305] and this could even result in superbasicity, probably from decomposition of the carbonates to oxides. When used at the gas−solid interface (e.g., as catalysts), the real structure of the material (oxide, hydroxide, carbonate) depends on conditions. Alkali carbonates are frequently used as supports for alkali metallic catalysts.[4,32,101]

On the other hand, sodium and potassium hydroxides and also calcium oxide and carbonate have important applications in metallurgy and glass production technologies as "pure"

solids for the reactive melting of refractory metal oxides such as, e.g., silica and zirconia, to produce melt salts.[7]

4.3.3. Activated Carbons and Impregnated Activated Carbons

Activated carbons (ACs)[306] are produced by pyrolysis of various carbonaceous materials such as coal, polymers, vegetables, etc. They are very high surface area materials (>1000 m²/g) and very active in adsorption both at the liquid−solid and at the gas−solid interfaces. Whether the AC surfaces in contact with water act as weak acids or weak bases strongly depends on the pH. At low pH, the basic surface sites (i.e., ketonic groups or alcoholic groups) are protonated while, at high pH, carboxylic acid groups are dissociated. In coal-derived ACs, in addition to the ambient pH, the nature of any inorganic matter inclusions may also play a role in determining the acid−base behavior of their surface. ACs are frequently impregnated by, for example, alkali oxides or carbonates to increase adsorption of acidic compounds and thus act as strongly basic materials. ACs may also be used as supports for catalysts, e.g. for noble metal hydrogenation catalysts.

ACs are widely used as adsorbants for both wastewater and waste gas purification. For example, they are the optimal technique for the removal of phenol[307] and phenolics[308] from water. Activated carbon, usually wide-pore carbon with a large total pore volume, and carbon molecular sieves are widely used to abate H₂S from both waste[309] and fuel gases,[310,311] although they are quite delicate and only have an accepatble lifetime under small loadings. Activated carbons are in principle regenerable by mild heating during purging with inert gases such as steam or nitrogen. However, the regeneration is usually partial, and some authors consider them as not regenerable when applied to H₂S. Nonimpregnated ACs are better than base-impregnated ACs to purify siloxane-contaminated biogases, but here again, only partial regeneration can be obtained, in this case because of the polycondensation of siloxanes in the adsorbents.[312]

4.3.4. Anionic Exchange Resins

Ion exchange resins were introduced in the 1960s and today are widely applied as adsorbents and catalysts in the chemical industry.[313−315] The most used materials are functionalized macroreticular polystyrene-based ion-exchange resins with 20% divinylbenzene (DVB), like the materials of the Amberlyst family produced by Rohm and Haas.[316] Other polymers, such as acrylic−DVB copolymers as well as cellulosics, are also used. Basic anion exchangers are mostly characterized by the presence of the trimethylammonium functional group bonded to the aromatic rings and counterbalanced by anions such as the hydroxide anion. These materials are active as catalysts in, for example, methanol carbonylation to methyl formate and the Knoevenagel and aldol condensations.[32,315,316] Resins with different compositions are also used as absorbents, e.g. in wastewater purification[316] and heavy metal separation in metallurgy, such as in the preparation of uranium nuclear fuels[317] and in the treatment of spent nuclear fuels. They are also sometimes used as supports for heterogeneous catalysts. One of the limits of these materials is their limited temperature applicability range (usually <150 °C).
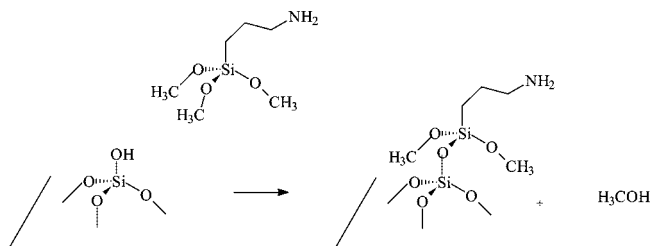
Figure 23. Structure of the surface species formed by grafting trialkoxy-silyl-propyl amine on silica.

4.3.5. Organic Bases Grafted on Microporous or Mesoporous Metal Oxides and Other Organoinorganic Solids

The surface acidobasicity of silica-based oxides may be modified by grafting functionalized oraganosilicon compounds. Trialkoxy-silyl derivatives carrying organic functions react with surface silanol groups[318−320] to give materials carrying, for example, amine or thioalcohol groups at the surface (see Figure 23). Similar properties may be obtained with several kinds of organic−inorganic hybrid materials prepared in different ways.[321] Mesoporous materials such as aminopropyl-modified HMS[322] and aminopropyl-functionalized SBA-15[323] were prepared and can show basicity[324] and activity in basic catalysis as first shown by Macquarrie.[325] These solid materials, carrying basicity similar to that of amines, may also be used to further anchor basic organic molecules. In any case, they must be used under mild conditions to avoid decomposition of the organic moieties.

4.3.6. Supported or Solid Alkali and Alkali Earth Metals or Organometallics

As seen above, alkali and alkali earth metals, as well as their organometallics, are extremely strong bases and nucleophiles and act as catalysts or as initiators in anionic chain reactions such as, e.g., anionic polymerizations. These reactions are done in dry organic solvents or in liquid ammonia, where alkali metals dissolve and ionize. Alkali metals can be deposited on solid surfaces such as alkaline earth oxides,[198,168] producing solid materials which have high reactivity and can be considered to be superbasic. Electrons released from the alkali metal atoms are assumed to be entrapped in the oxygen vacancies. Very high reactivity has been reported for alkali metals supported on carbon materials,[326] on alumina,[327] and on alkali carbonates,[101] as well as for KNH_2 and $RbNH_2$ species supported on alumina.[97,102] Alkali metal clusters can also be grown in the cavities of zeolites.[328] These materials are largely used, e.g., as initiator/catalysts in hydrocarbon conversions.[4] Sumitomo has developed superbasic catalysts based on $(NaOH)_x/Na_y/\gamma\text{-}Al_2O_3$ with $x = 5-15\%$ wt/wt and $y = 3.8\%$, which allow the alkylation of benzylic positions of alkylaromatics with olefins and olefin double bond isomerization at temperatures as low as -30 °C.[329] An important example of this chemistry is the production of isobutylbenzene, an intermediate for the synthesis of ibuprofen (a useful antiinflammatory agent) by side alkylation of toluene with propene.[330]
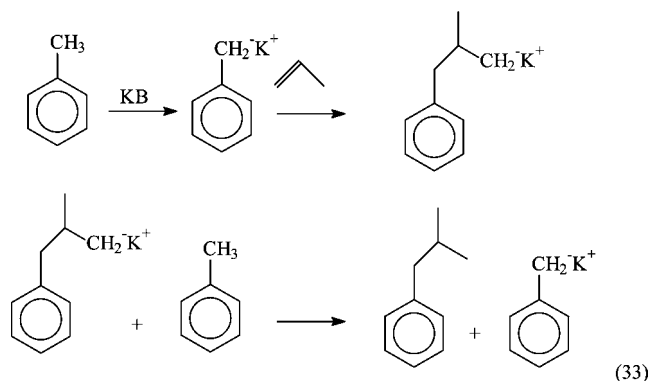
(33)

5. Comparative Discussion: Safety and Environmental Issues and Process Options

The data summarized above allow comparisons of the use of liquid versus solid bases in practical industrial and laboratory applications. It is evident that the use of most liquid bases entails a number of problems.

Aqueous hydroxide solutions present relevant safety problems when there is a spill or uncontrolled release. In fact, skin contact of solutions with pH > 11 results in saponification of fats and solubilization of proteins, thus producing severe burns with deep ulceration. Hydroxide aerosol can be a severe irritant of the eyes and mucous membranes. Concentrated caustic solutions also cause corrosion, which requires the use of special Ni-alloys to prevent cracking and failures in vessels and tanks.

If released to the environment, caustic solutions are pollutants just because of their basicity. The disposal of used caustic solutions requires previous neutralization by mineral acids, with regeneration being a possible but expensive treatment.

Most molecular bases have significant volatility and release toxic vapors. This is the case for ammonia and amines. On the other hand, bases characterized by low volatility may also present safety problems related to their toxicity in the liquid phase. The release to the environment of these bases is dangerous, and disposal is also problematic. Corrosion problems are also reported for liquid bases such as, e.g., ethanolamines.

Fewer problems arise from manipulation of weak inorganic basic solutions and slurries, such as limestone, limes, sodium carbonates, and potassium carbonates, although these compounds also may corrode metals and be toxic and dangerous.

It is evident that the manipulation of most inorganic solids, such as clays and base metal oxides, is by far less dangerous and problematic. Interestingly, to generate strong basicity from most of these materials, "activation" procedures, such as heating in dry and CO_2-free atmospheres, are needed, while to poison the strong basicity, exposure to the environment is sufficient. Water vapor and carbon dioxide poison surface basicity, which makes manipulation of these solids in the environment safe. Most inorganic solid bases are not deliquescent, so that corrosion problems are almost nonexistent, but additional problems do come from the presence of heavy metal elements in the oxides, which makes manipulation unsafe and disposal problematic in this case.

The use of solids instead of liquids in catalysis and ab-/adsorption may have several process advantages. In fact, fixed beds of solids do not need to be separated from liquid and gaseous streams, which usually allows simpler process operations, since complex separation procedures are avoided.

On the other hand, caustic solutions used as basic catalysts and absorbents are frequently actually not separated or regenerated but simply neutralized to produce waste salt solutions. As discussed by, for example, Kelly and King,[41,187] the use of solid basic catalysts allows wastes to be greatly reduced.

Some inorganic solids also have the advantage that in one way or another their basicity is finely tunable with composition, both in terms of the density of sites and in terms of strength. This may be done, for example, by varying the loading and the alkali cations (for example, Cs versus K or Na) supported on carriers or by doping with other materials. In other cases, basicity tuning may also be accomplished by varying pretreatment conditions, such as in the case of hydrotalcites[243] and their calcination products. Finally, several solid bases, according to their refractory character, may be applied at high temperature for use as catalysts and adsorbents. This is essentially not possible with liquid bases because of their volatilization and decomposition. High temperatures facilitate high reaction rates and sometimes avoid the need for preliminary cooling of gaseous streams, such as in the case of hot gas purification processes.

An intermediate situation occurs with organic solids such as ion exchange resins, with carbon materials, and with inorganic solids carrying grafted organic bases. These decompose at high temperatures, but their manipulation is quite safe, and also their disposal can be not so problematic. More problems occur for active carbons impregnated with heavy metal compounds.

6. Conclusions

Chemical compounds characterized by basic behavior have a useful role in all fields of chemistry. Although the fundamentals of basicity in solution have been well established for decades, it seems that several developments have recently occurred in the field. For example, theoretical studies have been performed in recent years to model the real state of chemical species in solution. In spite of this, it seems that the real state of the hydroxide anion in solutions has still not been fully established. New techniques have also been developed for the characterization of basicity in the gas phase (proton and cation affinities and basicities) and have also been used to rank bases in relation to their liquid phase behavior.

The field of liquid bases has been enlarged beginning in the 1990s with the preparation and characterization of new molecules characterized by extremely high basicity, i.e. superbases. The practical application of these compounds is apparently still limited but is increasing with the development of promising new processes.

The data reported here give a picture of the basicity of solid materials in relation to the more classical and well-known features of basicity in liquids. Although characterization of the basicity of solids is not an easy matter, we report here an attempt at systematization of basicity of solids (in particular, metal oxides) and a short summary of the best techniques to be used to characterize it. Our studies suggest that pure basicity on solids actually does not exist, but acid−base couples with predominant basicity are active in adsorption, catalysis, and surface reactivity.

The development and the use of solid bases may, in several cases, improve the chemical and environmental processes, from different points of view. In fact, while the use of liquid bases may result in significant corrosion and safety problems

(related to toxicity, volatility, and sometimes causticity), with the use of solid bases, these problems are almost nonexistent. The use of solid bases may also improve chemical processes in terms of performance. In fact, solid bases do not mix with liquid products, thus avoiding the need for difficult separation and purification steps. In some cases, e.g., biodiesel production, the quality of the product or byproducts may also be increased by solid catalysts. Finally, the use of solids may result in a reduction of corrosive and toxic wastes. Solid bases are also very useful in environmental chemistry for the abatement of air and water pollutants, sometimes allowing also the reuse of both the pollutant molecule and the basic adsorbent.

The use of solid bases in liquid phase reactions may cause some problems, in particular in multipurpose plants where it is possible to perform different reactions in the same reactor and plant. However, it seems not impossible to design multipurpose plants with solid catalysts too.

The basicity of solids may be tuned, in terms both of strength (from very weak to very strong) and of the abundance or density of sites. Solid bases may be applied to solid−gas systems as well as to solid−liquid systems, although in the latter case for some solids (e.g., alkalized oxides) leaching problems may occur. In practice, it seems that solid basicity gives rise to excellent flexibility. In practice, the field of basic heterogeneous catalysis is a quickly developing field. All these developments have a significant positive impact in the improvement of industrial processes in terms of the green chemistry approach.

7. References

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