

Solid acid catalysts

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Using qualitative and quantitative models, including both short and long range effects, progress has been made in understanding acidity in zeolites, but limitations that still exist in measuring that acidity by use of probe molecules. The benefits and limitations of enlarging zeolite pores by means of MCM-41 structures have been outlined. Major advances have been made in improving the catalytic activity of heteropolyacids and $\text{ZrO}_2/\text{SO}_4^{2-}$, as well as in tackling the mechanism through which $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyzes hydrocarbon reactions. Finally, new advances have also been made in the preparation and potential as acid catalysts of organic-inorganic composites (Zr phosphates and phosphonates, polysiloxane, nafion-silica).

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Abbreviations

EGS	energy gradient selectivity
HPA	heteropolyacids
HPW	12-tungstophosphoric acid
HSAB	hard soft acid base
MELS	molecularly engineered layered structures
MTBE	methyl-tert-butyl-ether
NNN	next nearest neighbours
RTDS	rapid thermal decomposition of precursors in solution
TPD	temperature programmed reduction

Introduction

Acids are the catalysts which are used the most in industry, including the fields of oil refining, petrochemicals and

chemicals. They are responsible for producing more than 1×10^8 mt/year of products. Among the first acid catalysts, the most commonly used were HF, H_2SO_4 , HClO_4 , and H_3PO_4 (in liquid form or supported on Keisgelguhr). Since 1940 the tendency has been to replace, when possible, those liquid acids by other solid acids, which present clear advantages with respect to the former. These advantages include along with their handling requirements, simplicity and versatility of process engineering, and catalyst regeneration, decreasing reactor and plant corrosion problems, and environmentally safe disposal. Most of the efforts have been directed towards the preparation of a solid thermally stable catalyst in which the acid sites have the required acidity (type and strength) to catalyze a given type of chemical reaction. A summary of the common industrially used solid acid catalysts is given in Figure 1 (GB McVicker, personal communication). In this paper, I will review the recent status of a series of environmentally friendly solid acids such as zeolites, heteropolyacids, sulfated metal oxides, and organic-inorganic composites which possess various acidities and will outline their characteristics, potentials and limitations.

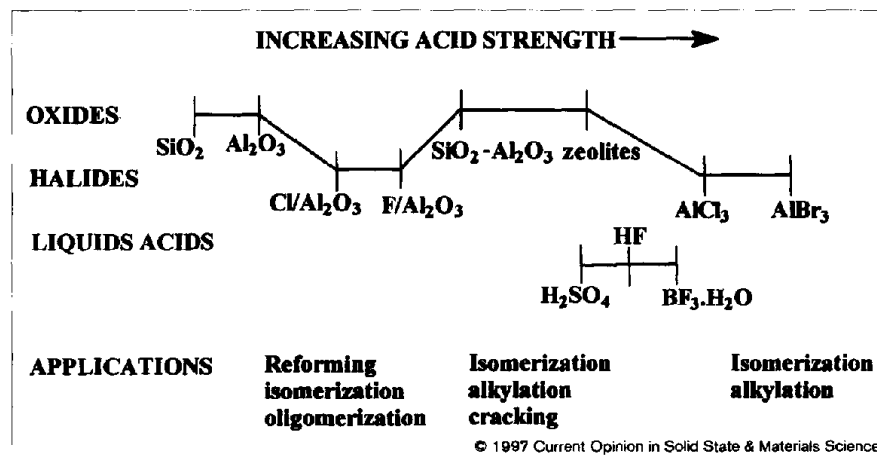
Zeolites

Among the different solid acids, amorphous silica-aluminas and zeolites have found wide application in oil refining, petrochemistry, chemistry, and in the production of fine chemicals. Their success is based on the ability to prepare samples with strong Brönsted acidity that can be controlled within a certain range, and which resist high reaction temperatures and catalyst regeneration conditions.

In a first approximation, the Brönsted acid function of amorphous silica-alumina and crystalline silica-aluminas, such as zeolites, is not very different and they were

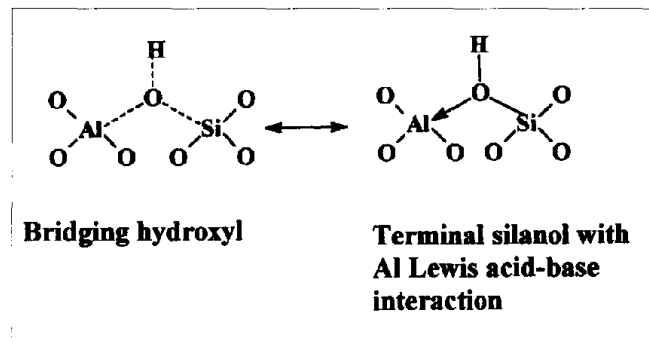
Figure 1

Relative acid strength of solid acids and their catalytic uses.



first described as an Si-OH group strongly influenced by a tricoordinated neighbouring Al^{3+} (see Fig. 2). This model was improved in the case of zeolites by taking into account that the oxygen supporting the acidic hydrogen was chemically bonded to Al^{3+} and Si^{4+} , making a real bridge between them. The actual situation is a resonance hybrid of the two structures described above [1].

Figure 2



Resonance hybrid of the Brønsted acidity in silica-alumina.

In the case of zeolites, the presence of a crystalline structure with well defined pores and cavities of molecular dimensions strongly affects the acidic and reactive properties of the material. A substantial change in the tetrahedral structure supporting the acidic group of a zeolite can be provoked, therefore, by substituting one proton that has a much higher electron affinity instead of the alkali cation that usually compensates for the zeolite's framework negative charge. In the case of crystalline silico-aluminates (zeolites), however, a global readjustment of the bond structure of the crystal occurs in order to prevent major local distortions in bonding. These long-range effects are much less important in the case of amorphous silicates, and the lack of symmetry energies allows amorphous materials to relax more extensively, resulting in a probably weaker acidity.

When compared with other solid acids, zeolites (and, more generally, zeotypes) possess certain peculiarities which make them a unique type of material. These are some of the properties: high surface areas; ability to control the number and strength of acid sites; high adsorption capacity, and important media (solvent) effects. The control of the molecular dimensions of the pores can result in shape selective effects and preactivation of the molecules inside the pores by strong dielectric fields and molecular confinement.

In a zeolite the total number of acid sites is controlled by the total number of framework aluminium ions present [framework]Al. At the same time the acid strength of

the zeolite will depend on the density of acid sites and consequently also on the Si:Al ratio. In this way, the strength of the acid site associated with a given Al depends on the number of Al in the next nearest neighbours (NNN), being the acidity maximum for that with zero Al in the next nearest neighbour position (ONNN). Therefore, in a given zeolite structure, all acid sites should be equivalent and exhibit maximum acidity when Al ions are completely isolated (ONNN). Semiquantitative theories such as the Al-NNN theory and topological density theory predict the limiting Si/Al ratios for isolated Al in zeolites.

The importance of the effect of structural and compositional parameters on acidity and other zeolite properties has recently been studied by quantitative methods such as *ab initio* calculations and statistical mechanics calculations [2*]. The zeolitic proton has been studied in detail using quantum-chemical cluster calculations, and this methodology should be especially valuable for studying short-range effects. However, the cluster approach has two main disadvantages or limitations. The first one concerns the boundary effects due to the saturation of dangling bonds, since atoms having saturated dangling bonds are in a different environment than those in the crystal. The second limitation is that, owing to the finite size of the cluster, the calculations do not account properly for long-range electrostatic (coulomb) forces. These interactions are significant at very long distances, and they can determine important properties of the zeolites, such as the electrostatic potential and the electric field within the zeolite pores. Changes in the pores may affect the proton affinity of bridging hydroxyl groups. To solve this (second) problem attempts have been made to approximate long-range interactions within clusters with schemes which involve the embedding of a cluster in an array of point charges. A better account of the long-range coulomb interaction, however, is obtained by the recently developed periodic zeolite model [3,4]. For the calculations of the electronic structure and the energy of the periodically repeating structure Dovesi and co-workers [3,4] have developed a CRYSTAL program; however, it requires an important computational effort. This method has been shown to be particularly useful, not only in reproducing zeolite properties but also for studying the interaction of different molecules with the acid sites of the zeolite [3-7].

Models have also been developed which predict periodic structures by using lattice energy minimization and vibrational spectra using lattice dynamics. In this case the proper determination of potential functions used to describe the interactions between atoms is critical for carrying out adequate predictions. Very recently a very powerful shell model ion-pair potential for aluminosilicates has been derived by fitting its parameters to data obtained from quantum-chemical calculations on molecular models that represent typical subunits of zeolites [8]. The correct use of such potential describes accurately the long-range

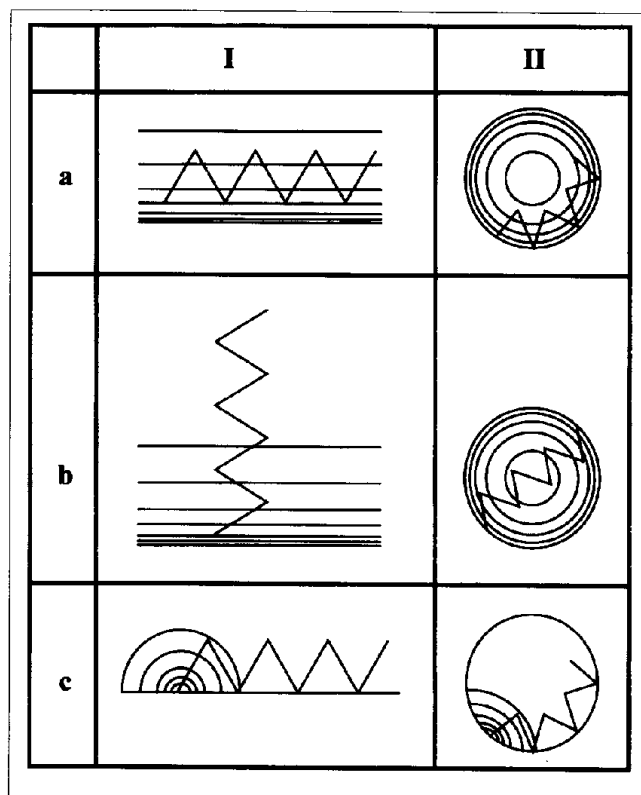
coulomb interactions and the polarizability of the oxygen anions.

When carrying out adsorption and reactivity studies of hydrocarbons at the acid sites of zeolites, a characteristic of paramount importance is the stabilization of certain adsorption states and transition state complexes by their interaction with neighbouring oxygens, as well as by the rest of the oxygens in the cages or channel. It has been shown that during the adsorption of methanol, as well as during the interaction of NH_3 and paraffins, the Lewis basic oxygen atoms in Brønsted acid zeolites can assist reactions that proceed via covalent transition states [2*,6–10], and then, the full zeolite channel or cavity becomes important during the initial interaction and also along the reaction coordinate. Along these directions long-range coulombic forces which can determine the electrostatic field, and its gradient, play a major role on adsorption and reactivity of hydrocarbons within the pores of zeolites [11,12]. This effect has been nicely shown for the cracking of paraffins on different zeolites: the $\text{C}_2:\text{C}_4$ and $\text{C}_3:\text{C}_4$ ratios can be used as an index of field gradient or energy gradient selectivity (EGS) [11,12], those fractions being larger when the field gradient is higher. In Figure 3 [11], it is schematically shown that the effect of the field gradient on the paraffin to be cracked could occur on both planar surfaces and cages. In addition, the effect of field gradients which weaken some alkane bonds depends on the charge density (i.e. Al content), the temperature, the zeolite structure, and the positive polarizing effect of cations.

When a given reactant molecule is confined in the cavity of a zeolite and the size of the molecule starts to match the size of the microscopic cavity, a change in the orbital energy level of the entrapped molecule occurs. This can be explained using the concept of electronic confinement [13*,14,15]. It is possible to see in Figure 4 that, as a consequence of the electronic confinement, the energy gap between π and π^* orbitals decreases and consequently the π bond becomes weaker than when unconfined. This will happen with any molecule with π electrons. The molecule should become more basic when confined and therefore more prone to react with the acid site of the zeolite [13*,14,15].

The concept of acid strength is quite useful to rationalize the ionic interactions occurring in zeolites. However, the fact that the bridged hydroxyl groups as well as the zeolite crystal have a strong covalent character, together with the observation that in many reactions occurring on the acid sites of the zeolite there is not a clear charge separation in the transition state [2*], makes necessary to discuss the acidity of zeolites not only from the point of view of their acid strength but also from the point of view of soft-hard acidities. When the hard-soft acid-base (HSAB) concept is applied to acid zeolites, it becomes obvious that the occurrence of reaction control by charges or orbitals

Figure 3



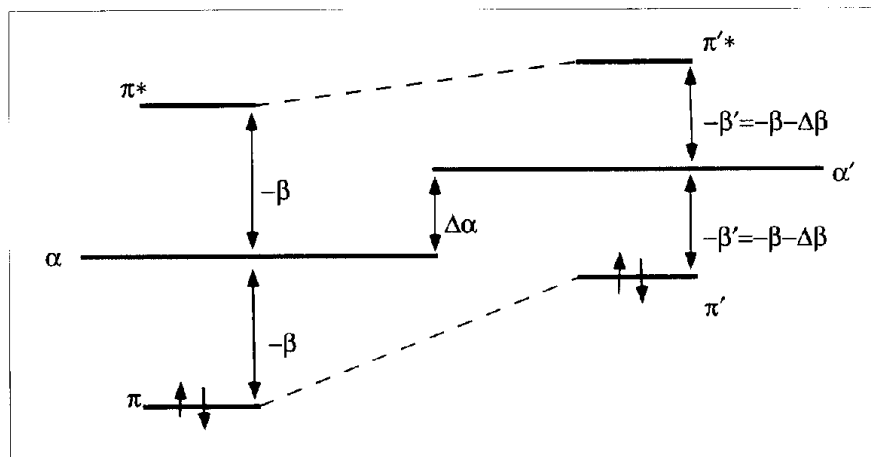
Scheme of a molecule (zigzag line) adsorbed on a flat surface (I) or in a cavity (II) with (a,b): homogeneous distribution of charges, that is, a rather homogeneous field (low energy gradient through the molecule when it is adsorbed in a cavity). (c) Discrete source of high field (curved lines) resulting from a heterogeneous distribution of charges (high energy gradient). Reproduced with permission from [11].

depends on the hardness or softness of the zeolite [16], the HSAB principle being more efficient in explaining zeolite reactivity when the interactions are covalent. Theoretical calculations show that the acid softness of zeolites increases as all of the following increase: the framework Si:Al ratio, the electronegativity of T atoms, and the T-O-T angle. These results are in good agreement with the experimental reactivity observed in the case of an orbital-controlled reaction such as the alkylation of toluene by methanol [16].

While we are clearly progressing in an understanding of the nature of acidity and catalytic reactivity in zeolites, we are not reaching a general consensus on the characterization of their acidity by basic probe molecules. It is now clear that the Hammett acidity function, and therefore, Hammett indicators cannot be applied to solid acids, and the H_0 values found do not accurately reflect the acid strength of such solids [17*]. When TPD of bases such as NH_3 , pyridine, methylpyridines, and so on, is carried out on solid acids, one has to be very careful in controlling the sample size, catalyst particle size, choice of carrier gas, flow rate, heating rate and so

Figure 4

Qualitative description of the π orbital energy spectrum for the ethylene molecule. On the left-hand side the spectrum of the unconfined molecule is depicted and on the right-hand side, the spectrum of the confined molecule. α is the coulomb integral and β is the resonance integral for the unconfined system, and α' and β' are the resonance integrals for the confined system. Reproduced with permission from [15].



forth as the appearance of the peak in one or another temperature can strongly depend on these parameters [18^{*}]. It appears from such work that TPD of amines, such as ethyl-, propyl- and butylamine may be more appropriate to measure the density of Brönsted sites. In order to measure acid strength, calorimetric studies of adsorbed pyridine have been carried out. It is claimed, however, that calorimetry cannot provide an acid strength distribution, as constant enthalpies of adsorption do not imply identical sites [18^{*}]. Recently, the formation of stable carbenium ions of increasing complexity has been used to rank the acidity of zeolites and to locate them in reference to other acids such as H_2SO_4 , AlCl_3 , SbF_5 , and so on [19]. All those acids are ranked based on the acid strengths of the carbenium ions and other electrophilic species sustained in those media. The authors claim that this method might be appropriate since the stabilization of transition states with electrophilic character is the objective of acid catalysis. It appears, however, that a method like this would not be able to separate the contribution of the intrinsic acidity and the solvation effects, which are so important in some acid media.

After all this, it seems at this point that still there are no truly useful probes for distinguishing materials with respect to acid strength, and one should rely on reactivity. I think that one can even question the adequacy of using basic probe molecules, especially in those cases in which the last objective is to correlate those observations with the catalytic activity for different hydrocarbon reactions. I keep asking myself, why use a reaction between a basic molecule (pyridine, NH_3 , amines etc.) and the acid zeolite to predict the reactivity of other, very different molecules in reactions, such as alcohol dehydration, double bond isomerization, chain isomerization, alkylations, cracking, and so forth? Since it is obvious that the acidity measured with a probe molecule will always correlate with the particular basic molecule used for characterization, how

will we be able to extrapolate those observations to reactivity and acid catalysis?

Nevertheless, the observed fact is that acid zeolites possessing a wide range of acidities and geometries can catalyze a wide range of reactions going from less demanding ones, such as *cis-trans* and double bond isomerization of olefins, to more demanding reactions such as cracking of paraffins and acylation of aromatics [20^{*}].

Mesoporous molecular sieves

It is true that zeolites have extremely interesting properties as acid catalysts and can be used as true molecular sieve catalysts; however, they are still limited in pore size, and can only deal with molecules smaller than 12 Å. Indeed, while advances have been made in the synthesis of ultralarge-pore zeolites and zeotypes [21,22], the materials obtained are still limited to use in processing large organic molecules useful in the refining of heavy feeds and in the production of chemical and fine chemical products. In this sense, new mesoporous molecular sieves with the pores periodically ordered have expanded the potential of zeolites [23^{**},24]. These materials can be made acidic by synthesizing them with tetrahedral Al and are a compromise between amorphous silica-alumina and zeolites. Indeed, similar to zeolites, they have a long-range order with well defined pores in the range of 20–100 Å, and like amorphous silica-alumina they do not present short-range order. Their acidity is weaker than that of zeolites and corresponds better to that of amorphous silica-alumina [25–27]. On the other hand, their large pores allow them to process heavy feeds and to be of interest for processes such as catalytic cracking and hydrocracking [25–27]. In the case of catalytic cracking it has been seen that acidic MCM-41 cannot resist the severe hydrothermal treatment occurring in the regenerator unit, and the porosity collapses [25–27]. The hydrothermal resistance can be improved by increasing the diameter of

the channel walls. An increase in the diameter of the walls from 7 to 20 Å has been claimed [28] and the hydrothermal stability of this material should be studied.

When my colleagues and I analyzed the acid characteristics of MCM-41 type materials [25–27], we thought that it would be possible to gain maximum benefit when using it for reactions that demanded weaker acidities and involved both large-size reactants and products. In this sense, we have focused our attention on the one hand on their use in mild hydrocracking [25–27], and on the other hand in their use as catalysts in the production of fine chemicals. For instance, they are particularly useful in the production of acetals which are of interest in the fragrance industry. In Table 1 the activity of acid zeolites with various crystal sizes, amorphous silica–aluminas and MCM-41 is given for the acetalization of aldehydes with different molecular sizes: heptanal, phenylheptanal, and diphenylheptanal [29]. The results clearly show that while for the smallest reactant, heptanal, the Beta zeolite is the most active catalyst, its activity strongly decreases when increasing the size of the reactant, while the activity of MCM-41 remains practically the same for all reactants and at a very good absolute level [29]. If this is important, what is even more important is the observation (Fig. 5) that the deactivation of the MCM-41 is much lower than that of a large pore tridirectional zeolite (HY). This effect is due to its milder acidity, that is, weaker adsorption of products, and faster diffusion of the bulky products formed.

Table 1

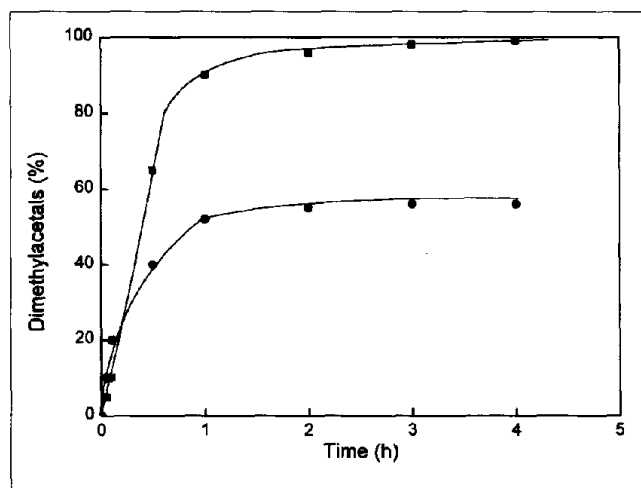
Influence of the catalyst pore size on the rate and % conversion in the acetalization reaction of heptanal (A), 2-phenylpropanal (B) and diphenylacetaldehyde (C).

Catalysts	Rate $r_0(\text{mol h}^{-1} \cdot \text{g}^{-1}) \cdot 10^3$			Conversion (%) ^a		
	A	B	C	A	B	C
1-MCM-41	2500	2480	2340	98	90	80
1-βH†	3300	2180	380	89	83	13
2-βH‡	3080	1340	180	94	55	8

^aTwo hour reaction time, †1-βH and ‡2-βH are Beta zeolites with crystallite sizes of 0.06 and 0.86 μm, respectively.

It thus becomes obvious that when one new material is discovered, there are two possible approaches to develop possible catalytic uses. One approach consists in starting from an interesting and relevant reaction, and if the material is not completely adequate, then one may try to modify it by further work on synthesis and postsynthesis treatments in order to improve its adequacy. There is, however, another approach which can lead to shorter term benefits, and this is to investigate first the characteristic of the material and then to look for the reaction and processes for which those characteristics are most appropriate. There is no doubt that there is still much scope for this second approach as far as the applications of MCM-41-type materials in acid catalysis are concerned.

Figure 5

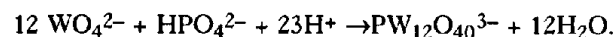


Acetalization of diphenylacetaldehyde with trimethyl orthoformate on MCM-41 ■ and HY ● catalysts. The percentage of dimethylacetals formed indicates the activity of each catalyst. Reproduced with permission from [29].

Even if there is great potential for catalyzing reactions with zeolites and mesoporous molecular sieves, there are still many reactions which require stronger acid sites than those present on these materials. It is thus necessary to develop stronger solid acid sites. Following this I will discuss heteropolyacids, ZrO₂-based solid acids, and organo–inorganic composites with strong acid properties.

Heteropolyacids

Heteropolycompounds involve a large class of coordination-type salts and free acids which are formed by the condensation of two or more different types of oxoanions, for instance:

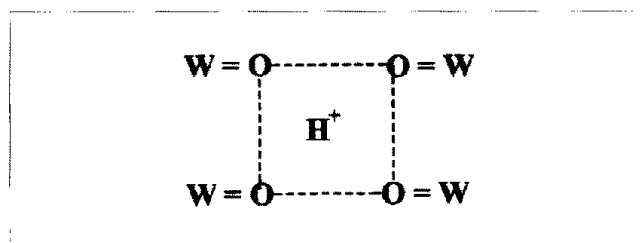


In these materials, the anion contains a central atom, typically Si or P, tetrahedrally coordinated to oxygens and surrounded by 2–18 oxygen-linked hexavalent peripheral atoms. These are usually Mo or W but can also be others, such as V, Nb, Ta, single or in combination. It is possible to prepare heteropolyanions with different structures such as the Keggin, Wells–Dawson, Anderson–Evans–Perloff, and so on. Most of the work has been carried out on the Keggin structure (XM₁₂O₄₀) because it is easy to prepare and reasonably stable. Among the different Keggin-type heteropolyacids (HPAs) that can be prepared, 12-tungstophosphoric acid (HPW) is the most widely studied for acid catalysis as it possesses the highest Brönsted acidity. In this case, the primary structure is formed by a central PO₄ tetrahedron surrounded by 12 WO₆ octahedra, which are arranged in four groups of three edge-shared octahedra of W₃O₁₃. These W₃O₁₃ units are linked by shared corners to each other and to the central PO₄ tetrahedron. Secondary structures are arranged when

the primary units are combined to form the solid. In the Keggin-type heteropolyanions, the secondary structure is formed by packing the polyanions into a bcc structure in which the protonated water dimer $(\text{H}_2\text{O})_2 \text{H}^+$ is connected to four anions by hydrogen bonding at the terminal oxygen atoms of the anions.

As a result of the large size of the polyanion having a low and delocalized surface charge density, the interaction between the polyanion and the compensating proton is weak and consequently their sites are strongly acidic (see Fig. 6) [30].

Figure 6



Weak interaction between the polyanion and compensating proton.

While the acid strength of HPAs is high, they have a limitation in their use in catalysis, and this is due to their low surface area in the solid state ($\leq 10 \text{ m}^2 \text{ g}^{-1}$), which corresponds to the external surface area of the crystal. When the reactants have a polar character, however, HPAs can take up polar molecules in amounts that correspond to more than 100 surface layer, and in this case their catalytic behaviour has been called 'bulk type catalysis' [31••]. Therefore, in the case of catalytic reactions involving polar molecules, they occur not only at the surface but also in the bulk solid of certain HPAs. The practical effect is that the catalytic system behaves like a highly concentrated solution, and this explains why these solids have been named pseudoliquids [31••]. Under the pseudoliquid conditions all acid sites are accessible to reactants, and the benefits of the system have been used commercially for reactions such as the hydration of propylene and n-butene, separation of isobutene, and polymerization of tetrahydrofuran [20•,31••].

When nonpolar reactants are used, it becomes a priority to increase the surface area or even better to increase the number of accessible acid sites of the HPA. This is achieved in two different ways. The first one consists in preparing acid salts containing large cations such as K^+ , Rb^+ , Cs^+ , or NH_4^+ . These acid salts have large surface areas ($> 70 \text{ m}^2 \text{ g}^{-1}$) due to the packing of the small particles ($\leq 150 \text{ \AA}$) in which they are synthesized [32]. The final surface area is strongly dependent on the level of H^+ substitution by the large monovalent cation, as well as on

the nature of the cation. This can be seen in Table 2 for the case of H_{3-x}M_x PW acid salts, where M is Cs^+ , K^+ , or NH_4^+ [33,34]. It can be seen there that the samples contain both micropores and mesopores. The presence of micropores in the range of 7 \AA has been responsible for shape selective behaviour of $\text{Cs}_{2.2}\text{H}_{0.8}\text{PW}_{12}\text{O}_{40}$ for ester decomposition, dehydration of alcohols and the alkylation of aromatics [31••]. However, it is obvious that while the surface area increases with increasing H^+ substitution, the global acidity, that is the number of Brönsted acid sites, decreases. Therefore, a situation can be reached where the benefit achieved by increasing surface area (site accessibility) can be lost due to the strong neutralization of the acid sites by the monovalent cations. For this reason, a maximum in catalytic activity for surface-type reactions is usually observed for cation contents between 2 and 2.5, depending on the particular reaction and type of cation [32–34]. It is then more adequate to relate the catalytic activity of the acid salts with the surface acidity, calculated, in a first approximation, as the product of surface area times the number of remaining protons. Indeed, as shown in Figure 7, a similar trend is observed for surface acidity and activity for isobutane/butene alkylation [33,34]. Besides that, the nature of the countercation may also influence the acid strength distribution of the surface Brönsted sites in the acid salts [31••,33,34].

Table 2

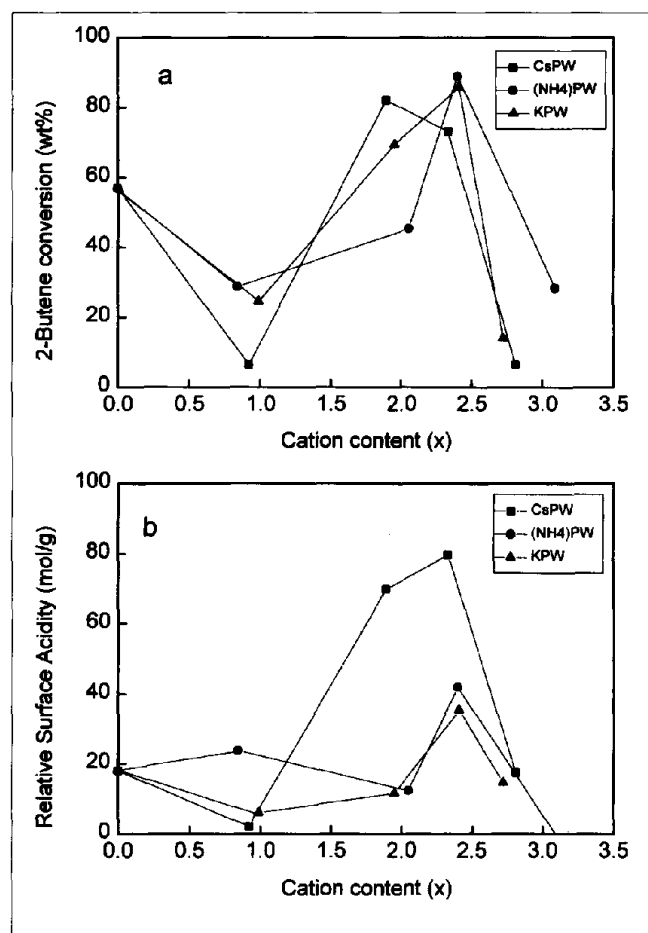
Chemical composition and textural properties of the ammonium, cesium and potassium salts of 12-tungstophosphoric acid prepared with different stoichiometries.

Sample	Cation/U.C.*	SBET (m^2g^{-1})	S_{micro} (m^2g^{-1})	Pore volume (cm^3g^{-1})
$(\text{NH}_4)_1\text{PW}$	0.84	11	6	0.0086
$(\text{NH}_4)_2\text{PW}$	2.05	13	4	0.0086
$(\text{NH}_4)_{2.5}\text{PW}$	2.40	70	51	0.0593
$(\text{NH}_4)_3\text{PW}$	3.09	69	50	0.0659
CS_1PW	0.92	1	-	0.0051
CS_2PW	1.89	63	46	0.0426
$\text{CS}_{2.5}\text{PW}$	2.33	119	43	0.0896
CS_3PW	2.81	92	33	0.0736
K_1PW	0.99	3	-	0.0067
K_2PW	1.95	11	-	0.0088
$\text{K}_{2.5}\text{PW}$	2.41	60	45	0.0508
K_3PW	2.72	52	44	0.0420

*U.C., unit cell.

There is a second procedure for increasing the surface area of the HPAs, and this consists in supporting them on a high surface area carrier. Suitable carriers should not have basic properties, otherwise the HPA will react with the surface and become deactivated. Best results have been obtained on silica, zirconia polymers and siliceous MCM-41 materials. When silica is used as the support, one optimum in the HPA content is observed for amounts above the monolayer. The optimum content

Figure 7

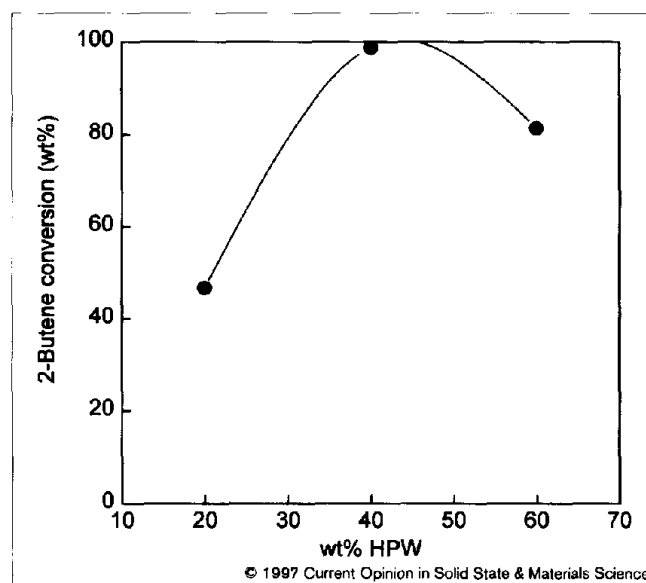


Initial 2-butene conversion during isobutane/butene alkylation (a) and relative surface acidity (b) of monovalent salts of 12-tungstophosphoric acid (HPW) as a function of cation content per keggin unit. Reproduced with permission from [33].

should be greater than that of the amount covering and directly interacting with the surface, but not so high that large crystallites of HPA are formed. Figure 8 presents the influence of the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ content on catalytic activity on silica. A maximum in activity for the alkylation of isobutane with butene is obtained in this case for ~30–40% wt acid content, which is slightly above that of the theoretical monolayer (A Corma, A Martínez, P Martínez, unpublished data). HPAs supported on silica also show interesting catalytic properties for fine chemicals synthesis [35,36]. HPA supported on clay has also shown to be an efficient catalyst for single-pot synthesis of methyl-*tert*-butyl ether from *t*-butyl alcohol and methanol [35,36].

ZrO_2 and sulfated ZrO_2 have also been used as supports for HPAs. In this way, Pt promoted $\text{Al}_{0.83}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ on ZrO_2 gives excellent activity and selectivity for C_7^+ alkane isomerization [P1,P2], and it is a better catalyst than the pure acid supported on either ZrO_2 or SiO_2 . In the case of

Figure 8



Influence of acid content on initial conversion during isobutane/butene alkylation on HPW supported on silica.

sulfated ZrO_2 a synergetic interaction between the support and the HPA has been claimed to explain the good activity and selectivity for isobutane/butene alkylation [P1,P2].

Activated carbons are also adequate supports for HPA since the acidity of the heteropoly compounds is preserved [P3]. In the case of microporous carbons the HPA will be deposited on the external surface. However, in any support, if liquid phase processes are used, leaching of the supported HPA can be a serious problem [37]. Conjugated polymers such as polyacetylene, polypyrrole and polyaniline have been used as HPA supports. In the case of polyacetylene the HPA can be introduced on the surface of the polymer, while retaining its acidity [38]. However, unless a very special behaviour could be achieved, this will not be able to compete with other less expensive inorganic supports.

Finally, it is not surprising that the high surface area pure silica MCM-41 type materials have also been used as supports for HPAs. These materials should, in principle, allow for high loadings of HPA. In the original Mobil patents [P4–P6] it was claimed that HPAs on silica MCM-41 were active and selective catalysts for isobutane/butene alkylation, aromatic alkylation with long chain alkyl groups, and C_4 – C_9 alkane isomerization. The high surface area of these tubular mesoporous materials allowed high dispersions of HPA and the Keggin anion structure was preserved up to a loading of 50% wt. The benefits of the high dispersion were seen for the alkylation of *tert*-butyl phenol with isobutene [30]. This was nevertheless a surprising result as, taking into account the size of the HPA units one might expect that plugging

of the pores might occur, decreasing the accessibility of the reactants to some crystallites of HPA, if they were also located in the channels.

The major problem arising from the use of HPAs in acid catalysis is their deactivation over time and the required regeneration. It is obvious that HPAs cannot be regenerated by combustion, since their stability does not go beyond $\sim 300^\circ\text{C}$. However, there are two ways to tackle the problem. One is to decrease the rate of decay by using, when possible, bifunctional catalysts in the presence of H_2 and/or to work under supercritical conditions for which the prepolymer-polymer type of products responsible for deactivation could be washed out. The other possibility deals with the regeneration of the catalyst. For example, since at low reaction temperatures one should not obtain coke products and polymer species should predominate, it should also be possible to remove the poisonous products by washing with adequate solvent under the optimum conditions, or by mild hydrogenation.

Sulfated metal oxides

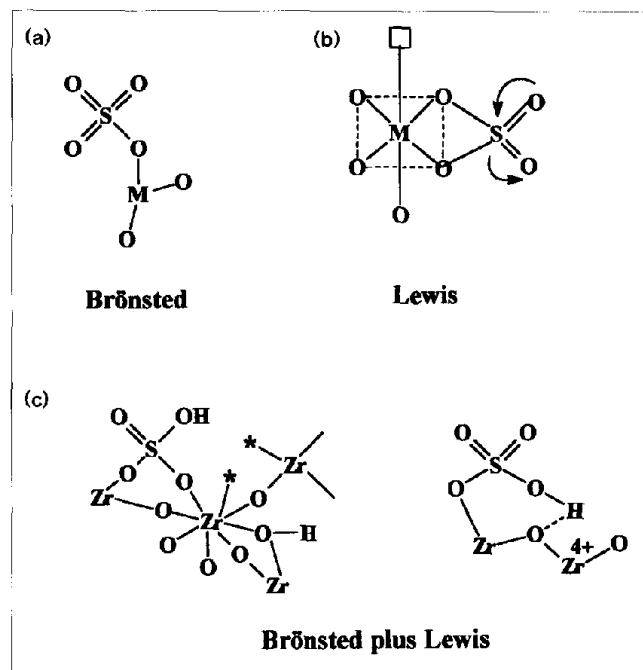
In the early eighties, it was found that when some transition metal oxides such as ZrO_2 , TiO_2 , SnO_2 , Fe_2O_3 , and HfO_2 were sulfated with either sulfuric acid or ammonium sulfate and were subsequently calcined, a remarkable increase in the surface acidity and in the catalytic activity for carbenium ion reactions occurred [39].

Concerning the nature of the acid sites involved, it is a general consensus that properly activated sulfated metal oxides contain both Brønsted and Lewis acid sites. Discrepancies can be found on the predominant role played by a particular site or even by the coupled Brønsted plus Lewis sites with respect to the final activity showed by these materials [40–46]. As an example, for models showing the possibilities of sulfated zirconia acting as a Brønsted acid (Kustov *et al.* [46]), Lewis acid (Pinna *et al.* [43]), and Brønsted plus Lewis acid (Adeeva *et al.* [47*]), see Figure 9.

Sulfated metal oxides were claimed to be superacidic on the basis of the following observations. Their acid strength measured by the Hammett indicators method goes up to $\text{H}_0 \leq -16.4$. Adsorbed benzene, which is a very weak base, desorbs at very high temperatures in TPD experiments. These materials are able to isomerize *n*-butane at temperatures below 100°C .

On these bases it was accepted that, indeed, a new type of solid superacids was obtained and this opened new perspectives in the use of friendly solid catalysts for carrying out, reactions involving very strong acid sites under mild conditions. However, when research on this subject had progressed it became necessary to question the superacidity of sulfated metal oxides on the basis of the following observations. The use of H_0 values for

Figure 9



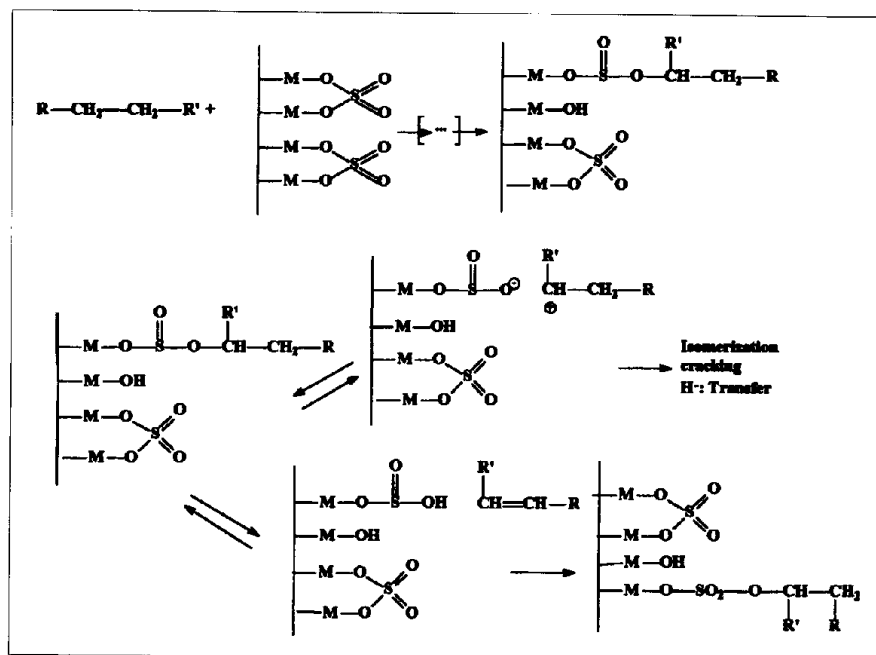
Acid sites on sulfated zirconia. (a) Brønsted, (b) Lewis and (c) Brønsted plus Lewis sites.

solids are meaningless [17**]. Benzene is not an adequate molecule to measure the acidity of sulfated metal oxides by TPD since it is oxidized on the surface [48,49]. Microcalorimetry and infra-red studies of NH_3 adsorption gave initial heats of $150\text{--}165\text{ kJ mol}^{-1}$ [50]. Proton NMR and acetonitrile adsorption show Brønsted sites weaker than those present in ZSM-5 [47*]. *n*-Butane isomerization occurs by a bimolecular mechanism [51], and on Brønsted sites with heats of NH_3 adsorption of $125\text{--}140\text{ kJ mol}^{-1}$. Alkylation of isobutane with butene also occurs on sites of medium strength [52,53]. Fe, MnSZr and NiSZr do not show enhanced acidity but work as a bifunctional catalyst for *n*-butane isomerization [47*,54].

The question remaining is this: why, if they are not superacids, can they catalyze reactions which are typically catalyzed by superacids? One answer to this question was given recently [17**] by studying the reaction of benzene on sulfated zirconia. The catalytic results were explained not by protonation and formation of benzenium ions as the initiating step, but by the one-electron oxidation of the substrate with the formation of cation radicals. The initiation is followed either by recombination of ion radical species leading to surface esters, or by the reaction of benzene present. The authors claim that the high one-electron oxidizing ability of sulfated metal oxides is the key to their enhanced activity in the conversion of saturated hydrocarbons. A mechanism which takes this into consideration has been presented by Genciu and Farcasiu [17**] (see Fig. 10).

Figure 10

Mechanism of benzene reaction on sulfated zirconia.



In this mechanism the one-electron oxidation followed by trapping of the cation radicals on the surface leads to sulfite surface esters which can either ionize generating carbocations, or eliminate to form alkenes, both species being able to carry out carbocation reactions. A mechanism of this type would be in agreement with the *n*-butane isomerization C¹³ mechanistic studies, which show that the reaction occurs via C₈ intermediates.

It is not surprising that in a material of this type the final catalytic properties can be strongly dependent on the preparation conditions. Indeed, sulfated metal oxides were initially prepared by a two step process which involved the mixing of a zirconium hydroxide with sulfuric acid or ammonium sulfate and then calcining the mixture to temperatures of 500–650°C. It has been shown that each one of the steps, that is, the formation of the zirconium hydroxide, sulfation and final calcination has to be optimized in order to produce an adequate catalyst [55,56]. Furthermore, this optimum can be different depending on the metal oxide to be sulfated. It appears [55,56] that one of the key points in preparing active catalysts by a two step procedure is the amount of tetragonal-phase zirconia in the sulfated zirconia. The catalytic activity is higher when the amount of the tetragonal phase is larger [55,56]. This tetragonal phase appears to be stabilized by the sulfate groups on the surface, and is responsible for the increase in surface area of the sulfated material. It is possible to control the amount of the tetragonal phase by an adequate control of the pH of precipitation of the zirconium hydroxide precursor. The reason for the above could be that the tetragonal phase has a higher content of nonbridging surface hydroxyl groups than the monoclinic

phase, and this seems to be a crucial factor for producing active materials (Ward and Ko [42]).

Other preparation methods have recently been developed. Sulfated metal oxides have been prepared by a sol-gel method [42,57,58], which involves the formation of a zirconium-sulfate co-gel by adding sulfuric acid to zirconium *n*-propoxide in isopropyl alcohol. This one step method appears to be simpler than the two step preparation procedures and allows a better control of the variables. It also allows the direct formation of bifunctional catalysts by the addition of chloroplatinic acid to the gel mixture. A new preparation method, named rapid thermal decomposition of precursors in solution (RTDS), which involves the use of hot pressurized water at hydrothermal conditions to force metal ion precursors to go into phases of oxyhydroxides and oxyhydrosulfates, has been used to produce sulfated zirconia with crystallite sizes below 100 Å [59].

From a practical point of view, sulfated metal oxides have some drawbacks. Besides possible problems in preparation, the maximum inconvenience lies in the fast deactivation of catalyst. The reasons for catalyst deactivation can be sulfate loss during the process or during catalyst regeneration, a crystalline phase transformation from the tetragonal to the monoclinic, and finally formation of coke during the process.

One can easily understand that sulfur is lost during catalytic processes such as hydroisomerization and hydrocracking in the presence of H₂, even more so when a metal component such as Pt is present and temperatures above

180°C are used [60,61]. It has been observed [62] that sulfur can also be lost in processes that do not involve added H₂, as well as during catalyst regeneration due to the relatively high temperatures and the possible presence of carbon monoxide.

In a recent paper [63], it was indicated that deactivation could occur by a crystal phase transformation during the process; however, the initial activity could be restored by heating the catalyst in the presence of O₂.

In any case, it appears quite clear that the presence of sulfate will always be a problem or at least a limitation for the practical use of this type of catalyst. Thus, instead of SO₄²⁻, tungstate has been used as a promoter of ZrO₂. This catalyst, with the addition of Pt, not only shows a reasonable activity for carrying out n-paraffin hydroisomerization reactions, but also strongly suppresses the cracking from increasing and therefore, increases the selectivity for branched products [64,65]. It is clear that more research should be done along the direction of substituting SO₄²⁻ in this type of catalyst.

Organic-inorganic composites as solid acids

Organic derivatives of zirconium phosphates and phosphonates

In the last decades a new class of layered materials with a general formula M(IV)(RXO₃)₂nS has been developed where M(IV) is Zr, Ti, Sn, Pb, Ge, Ce, Th and so on; X is P, As, or Sb; and R is H, OH or an organic group; and S is an intercalated molecule.

One of the properties of these materials is their ability to intercalate organic molecules, which can then react, forming covalent bonds with the POH groups in the layers. Among the different organic-inorganic composites one can prepare starting with the layered zirconium phosphates and phosphonates, the so called molecularly engineered layered structures (MELS) are of special catalytic interest.

Starting from Zr diphosphonates (ZrR[PO₄]₂) it is possible to obtain layered compounds with layers cross-linked

by diphosphonate groups with different interlayered distances (Fig. 11). In these materials, the replacement of some diphosphonates by small O₃P-H or O₃P-OH groups results in lamellar structures with great interlayer accessibility. It is known, that the pillared cross-linked mixed compounds obtained with biphenyl-phosphonic acid and phosphonic acid, Zr(O₃PC₁₂H₈PO₃)_{0.5}(O₃POH), have a basal spacing of d₀₀₁ = 13.6 Å and a specific surface area in the 200–350 m² g⁻¹ range with a bimodal pore distribution (pores of 6 and 48 Å) [66].

From the point of view of catalysis the interesting feature of these materials is the possibility of sulfonation of the aromatic rings, producing Brønsted acidity [67,68], which is active for reactions such as isobutane/butene alkylation, Friedel-Crafts alkylation, alcohol dehydration, methanol conversion to gasoline, hydrolysis of esters, and so on. Some drawbacks associated with these materials are diffusional restrictions for bulkier molecules, and reaction and regeneration temperature limitations.

Polysiloxane materials

In an analogous way as that mentioned above, alkylsulfonic groups can be bonded to a silica matrix forming an organic-inorganic polymer with acidic properties (HL Rotgerink, personal communication). They are obtained by condensation of organosilane monomers with the corresponding organic derivative in a sol-gel process (see Fig. 12).

The introduction of sulfonic acid in an inorganic matrix introduces into the composite a higher resistance to chemical attack and oxidative degradation. Also, in contrast with organic resins, the polysiloxane materials do not swell in organic media, as generally occurs with organic-inorganic composites. They are thermally more stable than their pure organic counterparts. In this case, polysiloxane can be used at reaction temperatures as high as 200°C. These catalysts show promise for acid-catalyzed reactions for the production of chemicals and fine chemicals. In this sense, it has been shown that they are active for the preparation

Figure 11

Effect of pillar length on interlayer spacing in pillared α-zirconium phosphate. Reproduced with permission from [66].

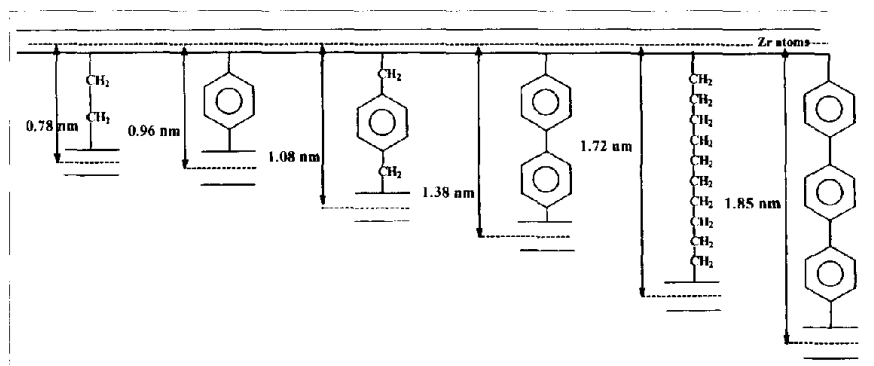
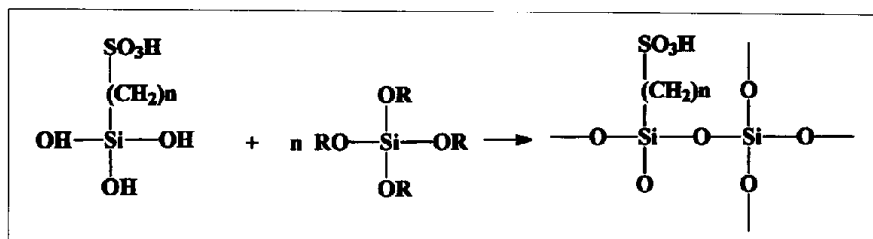


Figure 12

Sol-gel process of the condensation of an organosilane monomer with an organic derivative.



of bisphenol A by condensation of phenol and acetone (HL Rotgerink, personal communication).

Nafion-silica composites

Very recently researchers from DuPont have produced a high surface area nafion resin-silica nanocomposite with strong acid properties [69**]. It consists of small (20-6 nm diameter) nafion resin particles entrapped within a porous silica network. The resultant material has a BET surface area in the range 150-500 m²g⁻¹, the calculated effective surface area of the nafion particles is in the range of 50-153 m²g⁻¹, which is much higher than the surface areas of the normal polymer beads. A sol-gel method has been used to prepare the composite, and solutions of nafion resin are mixed with soluble silicon sources to form a gel, which is dried to a clear hard glass-like material. It is obvious that a material of this sort shows great promise as a catalyst for reactions catalyzed at lower temperatures such as alcohol dehydration, Friedel-Crafts aromatic alkylation and α -methyl-styrene dimerization. Most demanding reactions, such as nitration of benzene and acylation of *m*-xylene with benzoyl chloride, also occur on these organic-inorganic acid composites. In order to show the difference in reactivity with respect to nafion and Amberlyst-15 resins, the rate constant for benzene propylation to cumene at 60°C in liquid phase is given in Table 3.

Table 3

Reactivity for alkylation of benzene with propylene.

Catalyst	13% Nafion resin/SiO ₂	NR-50	Amberlyst-15
rate (mM (g cat.h))	1.98	0.30	0.61
rate (mM/(meq ⁺ H ⁺ .h))	16.50	0.34	0.14
acid capacity (meq ⁺ H ⁺ .g ⁻¹)	0.12	0.89	4.4

*meq, milliequivalent.

Conclusions

As a general conclusion, it is possible to say that a large variety of solid acid catalysts are now available. The acid strength of the sites can be varied over a wide range, and with the introduction of the nafion-silica composites superacidities can be achieved. However, it is not possible with any of the catalysts presented in

this review to possess at the same time very strong acidity, high surface area, high mechanical resistance, high thermal hydrothermal stability, and inexpensive catalyst production. Certainly, a compromise needs to be reached in each case. Nevertheless, there is a strong incentive to find solid acids which can replace the unfriendly H₂SO₄ and HF acids. The only limit to explore new potential materials is our imagination.

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