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Organic reactions catalyzed over solid acids

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1. Introduction

Several reviews have recently been published dealing with the use of solid acids as heterogenous catalysts for the preparation of specialty and fine chemicals [1–5]. The approach that has been commonly used in the previous reviews to organize such a large amount of information is based mainly in the type of organic reaction catalyzed by the solid acid. The interest in this burgeoning field is so large that, since the comprehensive Venuto's review on organic catalysis over zeolites four years ago [2], more than four hundred new references have appeared in the literature and the interest in this field is continuously increasing. Most of the references cited in the present review correspond to those articles published after 1992. Even though the reference list of this review is quite large, no attempt to cover exhaustively the articles published in this field has been made.

Herein, we have used a different methodology since we have focused on the strength requirements of the acid sites, their Brönsted or Lewis nature, and active location, to promote a particular transformation. According to the aim of this review, the selection has been based on the idea of establishing a relationship between the acid properties of the solids used as catalysts and the outcome of reaction. One point of major concern when preparing this review is that frequently there exist conflicting reports about the strength and nature of the acid sites intervening in the catalysis. These differences may arise from the use of different reaction conditions, but also from a poor characterization of the materials that have been employed.

Perhaps the main characteristic of solid acids, compared to liquid acids, is that solid acids encompass different populations of sites differing in their nature and strength [1]. Thus, it is possible to envision that whereas for some reactions all the sites, regardless of their strength and nature, may intervene in catalysis, for some other more demanding processes only the family of sites having the stronger acidity could be responsible for the activity of the entire material. It could even happen that the maximum acid strength of a particular solid could not be sufficient to promote a reaction. This leads to the conclusion that some solid acids can be more active in and selective to catalyzing a reaction type than others. In this sense, a consensus is beginning to be reached that the maximum strength of the sites that can be obtained using mesoporous aluminosilicates and zeolites in general does not allow them to be classified as superacid solids. In contrast, it is generally believed that some other solids like sulfated zirconia or supported heteropolyacids are superacids. It can, therefore, be expected that reactions where zeolites exhibit a low activity or are not active at all can be, however, performed in the presence of other materials.

Finally, it is clear that the acid strength requirements of an organic reaction are going to be strongly influenced by the presence of electron donor or with-

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drawing substituents on the functional group undergoing chemical transformation. In principle, electron donor groups will facilitate protonation by stabilizing the positively charged hydronated reaction intermediate, thus lowering the strength needed to promote the chemical transformation. The reverse applies for electron withdrawing substituents. This means that no generalizations about the acid requirements of a reaction can be made and that a careful consideration of the influence of the substituents on the chemical structure has to be done to extrapolate conclusions reached when using a parent compound.

2. Zeolites as solid acid catalysts

2.1. Reactions with low acid requirements

Non-acidic silanol groups are generally believed to be inactive catalytic sites when explaining the activity of zeolites. However, this assumption may change in view of the new findings in some reactions. Vapor-phase Beckmann rearrangement of ketoximes to lactams has been studied using acid zeolites as catalysts [6]. Coke has a negative influence on the activity of the catalyst, lowering the conversion and, subsequently, lactam selectivity also [6]. It has been proposed that coke formation takes place predominantly over the basic sites of the solid. In contrast to the rearrangement undergone by ketoximes, aldoximes give rise to nitriles under the same conditions [6].

Owing to its economic importance, cyclohexanone oxime rearrangement has attracted much attention [7]. Vapor-phase studies on a continuous flow fixed-bed reactor have shown that all the catalysts exhibit three phases: an initial period with high oxime conversion and coke build-up, a steady-state activity period featuring high selectivity to caprolactam and a final deactivation phase with a continuous slow lowering of oxime conversion and selectivity (Fig. 1) [8]. Because the presence of amines has no influence on the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, it has been claimed that the active sites for this reaction are not the acid centers, but most likely neutral silanol groups [9].

Analogous conclusions were reached by observing the influence of silica monolayer deposition covering the total surface of γ-Al_2O_3, ZrO_2 and TiO_2. Thus, formation of ε-caprolactam is enhanced by the deposition, whereas side reactions and catalyst deactivation are minimized (Fig. 2). Since pure SiO_2 is not able to promote this Beckmann rearrangement and the monolayer coverage was total (Table 1), it was proposed that the active sites are M–O–Si–OH silanol groups that should possess a very mild acidity [10].

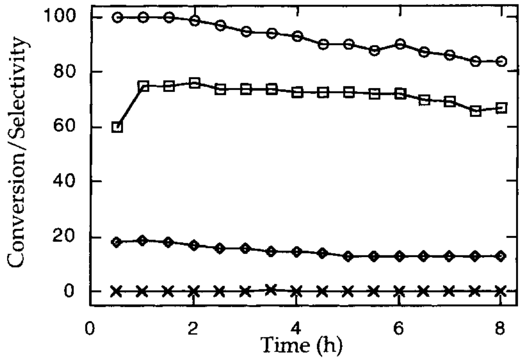


Fig. 1. Conversion of (○) cyclohexanone oxime, and selectivity to (□) ε-caprolactam, (◇) cyclohexanone and (×) 5-cyano-1-pentene over B_2O_3/Al_2O_3 at 300°C.

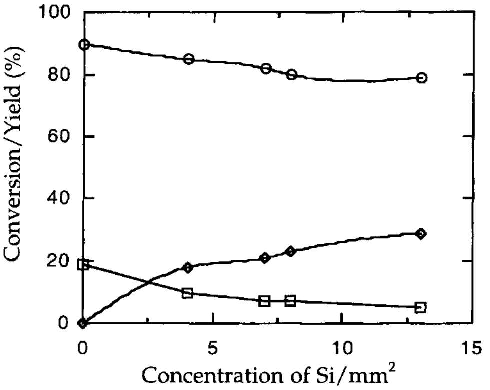


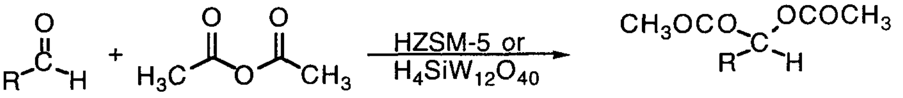
Fig. 2. Conversion of (○) cyclohexanone oxime, and yields of (□) cyclohexanone and (◇) ε-caprolactam against Si concentration on ZrO_2 after 1 h on-stream.

Similar low acid-strength requirements have been found when studying the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam over high silica ZSM-5 metallosilicates [11]. It was observed that the best catalyst for the process was the solid-containing indium in the framework, which corresponds to the lowest acid strength.

Table 1
Comparison of the activities of silica monolayers supported on various oxides for the cyclohexanone oxime rearrangement

Support	Surface concentration of Si	Rate per surface area	
	(atoms nm^{-2})	ε-caprolactam formation (10^{-5} mol h^{-1} m^{-2}), 623 K	isomerization from 1- to 2-C_4H_8 (10^{-10} mol m^{-2} h^{-1}), 393 K (*cis*/*trans*)
Al_2O_3	12.4	22.8	126 (1.1)
TiO_2	11.9	6.4	9.9 (1.2)
ZrO_2	8.0	27.3	1.5 (1.3)
SiO_2	—	1.4	0.1 (2.3)

Table 2
Initial rate and chemical yield for aldehyde diacetate formation over HZSM-5



Substrate	Initial rate (mol mg^{-1} min^{-1})	Yield (%)	Time required for final yield (h)
Benzaldehyde	2.6×10^{-6}	98.4	1.5
2-Methylbenzaldehyde	1.5×10^{-7}	43	24
4-Methylbenzaldehyde	5.0×10^{-7}	90.5	24
4-Nitrobenzaldehyde	1.2×10^{-6}	98.0	5.5
2-Nitrobenzaldehyde	6.0×10^{-8}	4.0	24
Hexanal	—	84.4	24
2-Ethylhexanal	—	64.4	24

With regard to the Beckmann rearrangement, it has to be said that the acid requirements found for the vapor phase have to be much higher when performing the reaction in solution at moderate temperatures [12]. Even oleum has been used to efficiently promote this rearrangement in the liquid phase at room temperature [13].

AlPO-11 is a very weakly acidic solid due to terminal hydroxyl groups or weak Lewis acid sites [14]. Accordingly, AlPO-11 does not promote methylation of toluene or *m*-xylene isomerization. However, this aluminophosphate molecular sieve has been found to be active for isobutanol dehydration.

2.2. *Reactions that require medium-strength acid sites*

Acetal formation and hydrolysis can be accomplished by a variety of heterogeneous catalysts possessing moderate acid strength, including modified silica gel [15], alumina [16] and clays [17]. Formation of acetals by reaction of carbonyl groups and alcohols or diols has been catalyzed by acid zeolites [18]. The use of benzene-1,2-dimethanol to protect aldehydes and ketones as 1,5-dihydro-2,4-benzodioxepines in the presence of an HY zeolite has been described [19]. Analogously, a facile conversion of aldehydes to the corresponding 1,1-diacetates catalyzed by HZSM-5 or tungstosilicic acid has been reported (Table 2) [20]. Liquid-phase trimerization of acetaldehyde to form trimeric *cis* and *trans* paraldehyde can be catalyzed by rare earth and partially proton-exchanged ZSM-5 [21]. Apparently, interconversion between the *cis* and *trans* isomers occurs through equilibration with monomeric acetaldehyde [21].

Although skeletal isomerization of *n*-alkanes is generally believed to be a highly acid-demanding reaction, a linear correlation has been found between the total rate of conversion of *n*-pentane and *Q*(1), which is the number of bridging ≡Si–(OH)–Al≡

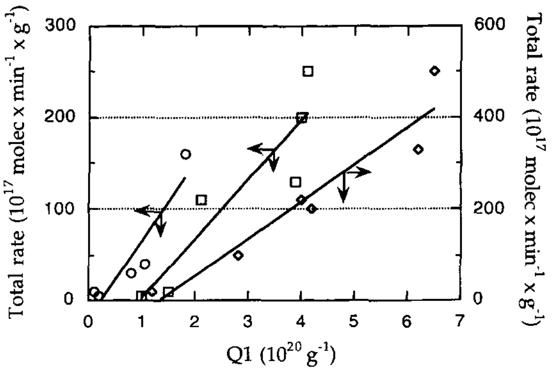


Fig. 3. Plot of total steady-state rate of *n*-pentane conversion vs. over (○) dealuminated HZSM-5, (□) H-mordenite and (◇) fluorinated USY.

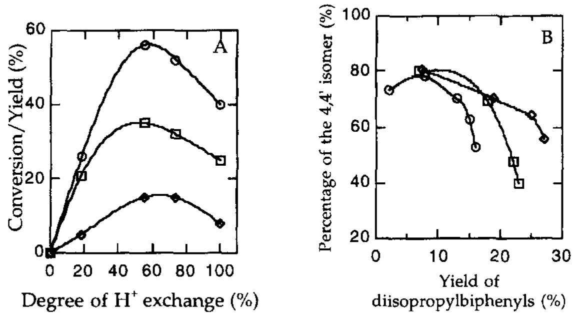


Fig. 4. (A) Relation between the catalytic activity of mordenite catalysts for biphenyl isopropylation and the level of proton exchange: (○) conversion; (□) yield of isopropylbiphenyls; and (◇) yield of diispropylbiphenyls. (B) Relation between the yield of diispropylbiphenyls and the fraction of 4,4′-diispropylbiphenyls in the isomers over mordenite catalysts. Exchange of Na^+ per H^+: (○) 100%; (□) 74%; and (◇) 55%.

groups having one Al in the next coordination shell of Si (Fig. 3) [22]. This leads to the conclusion that these sites are responsible for isomerization. However, they are not the strongest acid sites, since it is well established that the strength of a site increases as the number of Al on the next-neighbor sphere to Si diminishes, being those bridging ≡Si–(OH)–Al≡ with $Q(0)$ the strongest acid sites [1].

On a very different reaction, shape-selective diisopropylation of biphenyl and naphthalene over large-pore zeolites in the liquid phase has been recently reported [23–26]. Alkylation of biphenyl with propene to produce 4,4′-diisopropylbiphenyl has been investigated comparing SiO_2/Al_2O_3, Y faujasite, beta offretite, mordenite, ZSM-8 and ZSM-5 as catalysts [27]. Mordenite was found to be the most active and selective to 4,4′-diisopropylbiphenyl [28]. However, selectivity toward 4,4′ decreases with conversion due to its isomerization to thermodynamically more stable 3,4′-diisopropylbiphenyl [28]. Using partially Na^+-exchanged mordenites, the highest yield of 4,4′ isomer was obtained when 55% of the sodium cations of mordenite were exchanged with protons (Fig. 4). This partially exchanged mordenite suppresses subsequent isomerization of the primary product, while at the same time exhibits a complete propene selectivity toward alkylation. If more acidic (higher Na^+ to H^+ exchange) mordenite is used, other undesired processes such as propene oligomerization and product isomerization tend to be favored [29]. This reaction provides a nice example of how unnecessarily high acid strength can decrease the selectivity by promoting other competitive processes.

Abounding on the idea of tuning up the acidity of the catalyst to the requirements of a reaction, it was found that cerium-exchanged sodium mordenite (Si/Al 50) is a superior catalyst than H-mordenite (Si/Al 50) for the 4,4′-diisopropylation of biphenyl using propene [30]. Moreover, while Ce,Na-mordenite does not catalyze the isomerization of the 4,4′ to the 3,4′ isomer at low propene partial pressure, it was found that this rearrangement occurs using the H^+-form of the mordenite of high Si/Al ratio [30].

A somewhat different approach, based on selective transalkylation, has been employed to prepare 4,4′-diethylbiphenyl in good yield (53%) and high isomeric ratio (86%) by reacting biphenyl with triethyl- or tetraethylbenzene over HY zeolite at moderate temperatures [31]. In contrast, no selectivity was observed for the direct ethylation of biphenyl with ethene over mordenite [31].

A kinetic study of toluene and benzene isopropylation with isopropyl alcohol on alumo- and ferrisilicate of MFI structure has shown that alkylation activity does not follow the acidity of the catalysts (both with regard to the number or the strength of bridging OH groups) [32]. The rate of the overall reaction seems to be controlled by the desorption/transport rate of relatively bulky cymenes or cumene. It was observed that MFI ferrisilicates possessing low-strength acid sites are the most convenient catalysts for achieving para-selectivity in the alkylation [32]. Liquid-phase toluene alkylation by 1-heptene at 90°C has been carried out in the presence of dealuminated Y zeolites [33]. Besides the expected heptyltoluene, other products derived from C=C double bond migration, heptene dimerization and diheptyltoluenes were also observed. A relationship between the apparent initial activity of the catalysts and their acidity was not observed [33]. For the selective synthesis of 2-methylnaphthalene over a series of acid MFI catalysts, a correlation between the number of sites of medium and high acid strength with the activity of the catalysts has been obtained [34]. For isomerization of 1-methylnaphthalene into 2-methylnaphthalene, it has been observed that the presence of methyltetralin as hydride donor increases the catalyst life by avoiding coke deposition on the acid sites [35].

A series of HNaY zeolites having different percentages of Na^+ content has been tested as catalyst for phenol alkylation with methanol (Fig. 5) [36]. The results obtained together with ammonia selective poisoning of strongest acid sites have shown that the product distribution is highly sensitive to the number and strength of the acid sites. Thus, O-methylation, to give anisole, requires lower acid strength compared to those involved in the C-alkylation leading to cresol [36]. Using γ-alumina as catalyst, the implication of acid/base pairs on the reaction of phenol and methanol has also been proposed [37].

Chemoselective Friedel–Crafts alkylations of benzene derivatives and furans by allyl, crotyl and cinnamyl alcohols have been reported over medium and large pore zeolites [38–40]. The C=C double bond of the allylic moiety remains unaltered and the predominant reaction products arise from the alkylation through the alcohol functionality (Scheme 1). This functional group selectivity contrasts with the H_2SO_4 catalysis in homogeneous phase, which lacks chemoselectivity. However, regioselectivity of the attack, using the parent allyl alcohol, is not complete for activated arenes and the alkylation occurs both, on the 1 and 3 positions of the allylic system [40]. Allyl alcohols are the alkylating reagents of choice since the corresponding chlorides generate HCl during the course of the reaction. HCl intervenes, modifying the reaction pattern [38]. In addition, by using a series of three partially exchanged HNaY zeolites in the cinnamyl alcohol alkylation, it was shown that all the acid sites, regardless of their strength, are active in catalyzing the formation of 1,3-diarylpropene, but the strongest acid sites (only present in the totally exchanged HY zeolite) promote a subsequent cyclization of the primary unsaturated cinnamylbenzene to arylindene or subsequent attack of a second arene molecule to form triarylpropane (Scheme 1) [39]. This results in a change in the selectivity of the process. Analogous alkylation of moderately activated benzenoid compounds with allylic alcohols to give 1-aryl-2-alkenes by attacking at the terminal position has been reported over acidic K-10 clay [41].

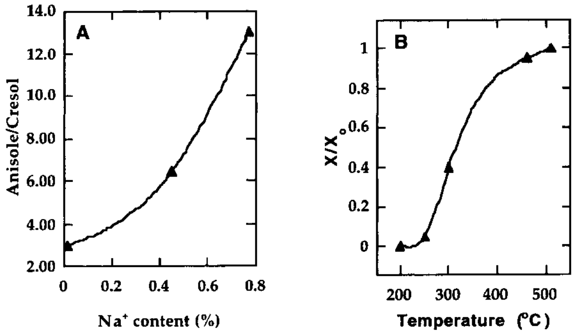
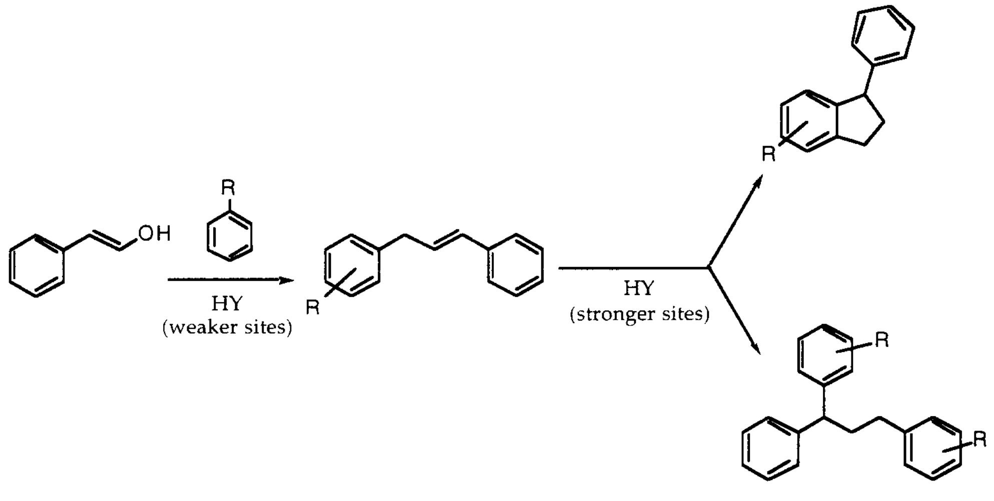


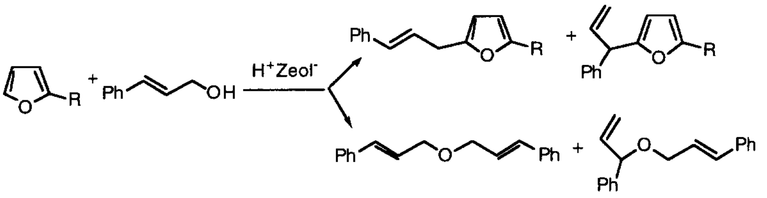
Fig. 5. (A) Evolution of anisole/cresol ratio as a function of the Na^+ content for HY zeolites ($t = 15$ min, conversion 10% obtained at different space velocities). (B) Ratio of the cresol conversion of poisoned-to-unpoisoned zeolite (X/X_0) vs. ammonia desorption temperature.

Besides benzene derivatives, 2-alkylfurans can also be chemoselectively alkylated by cinnamyl and crotyl alcohols in the liquid phase at moderate temperatures (Scheme 2) [40]. Formation of the corresponding symmetric ethers by dehydration of the allyl alcohols has been found to be a competitive reaction, especially at lower reaction temperatures [40]. The high reactivity of furans toward electrophiles allows the use of mild conditions for these alkylations, while their low aromaticity energy explains why conventional strong Brönsted or Lewis acids such as $AlCl_3$ or H_2SO_4 produce, in general, extensive polymerization and degradation of this heterocycle during Friedel–Crafts reactions [13].

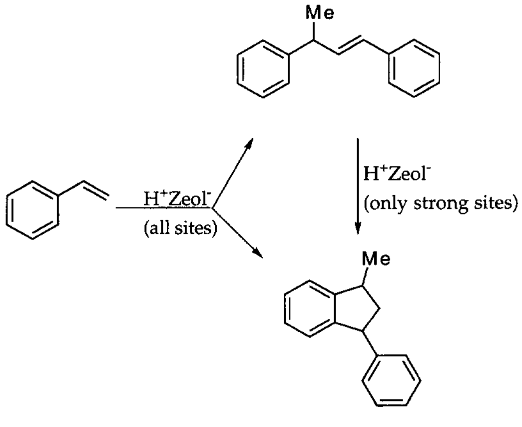
Oligomerization of styrene and its derivatives has been carried out using acid zeolites (Scheme 3) [42,43]. Besides trimers and tetramers, variable amounts of the cyclic and acyclic styrene dimers are formed depending on the conversion and the



Scheme 1.



Scheme 2.



Scheme 3.

percentage Na^+-to-H^+ exchange, Si/Al ratio, particle size and crystalline structure [42,44]. The average activity per acid site of zeolites was found to be of the same order of magnitude, but smaller than that measured for H_2SO_4. This fact could not be attributed to the acid strength demand of the dimerization, but more likely to diffusion restrictions imposed to the reactants and products through the zeolite micropores. In fact, it was established that all the acid sites, regardless of their strength, are active in promoting dimerization. In contrast, the consecutive cyclization of the primary open dimer with the structure of 1,3-diphenylbutene to the 1-methyl-3-phenylindan is exclusively catalyzed by the strongest acid sites of the zeolite (Fig. 6) [42]. As expected, substituents on the phenyl ring play an important role on styrene dimerizations. Thus, for vinylanisole, even NaY is able to promote the formation of 1,3-dianisyl-1-butene, the corresponding open dimer [45].

Besides alcohols, alkenes and alkyl halides, aromatic compounds also react with aldehydes and ketones [13]. This reaction is usually termed hydroxyalkylation, because the primary product after the incorporation of one aromatic nucleus in the C=O double bond is a benzylic alcohol. However, this primary product is more reactive under the reaction

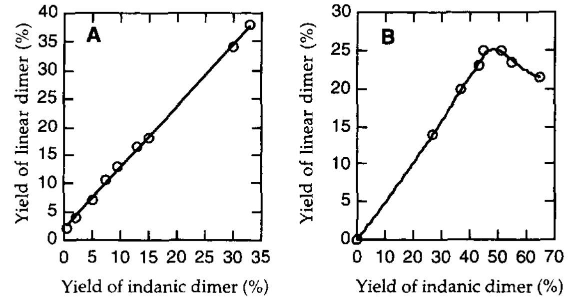


Fig. 6. Plots of the yields of the linear 1,3-diphenyl-1-butene vs. the cyclic 1-phenyl-3-methylindan. (A) For a HNaY at 50% of Na^+-to-H^+ exchange. (B) For a totally exchanged HY catalyst.

conditions than the starting carbonyl compound, and undergoes further transformation into *gem*-diarylalkanes. It has been reported that AlPO-5 shows a moderate activity for the condensation of phenol with formaldehyde leading to bisphenolmethanes although its performance was dependent on the method of preparation of the aluminophosphate [46]. This seems to be related to the presence of lattice defects in the material. However, if instead of activated phenol the parent benzene is used, the situation changes. An exponential relationship between the initial rate of diphenylmethane formation and the percentage of ion exchange in HNaY zeolites has been found for the condensation of formaldehyde with benzene [47]. Since the population of medium and strong acid sites increases exponentially with the percentage of H^+-to-Na^+ exchange, this lack of linearity has been taken as an evidence that only those moderate and strong acid sites can catalyze this hydroxyalkylation (Fig. 7) [47]. Using acetaldehyde as alkylating reactant of *ortho*-xylene, acetaldehyde aldolic condensation to crotonaldehyde was competitive with the hydroxyalkylation [48]. This autocondensation could be, however, minimized by using a semibatch reactor which is continuously fed with paraldehyde, thus ensuring that the *o*-xylene/acetaldehyde ratio is kept high during the whole reaction time. In this way, a high selectivity to 1,1-*bis*(3,4-dimethylphenyl)ethane was obtained while working at 140°C in the presence of Y or beta zeolites [48].

It has been found that acetophenone reacts with activated aromatic solvents in the presence of Y, beta and omega zeolites giving hydroalkylation products [49]. Thus, acetophenone and toluene in the presence of large pore zeolites affords a complex mixture of 1,1-ditolylethanes, 1,3-diarylbutadienes and minor amounts of 1,1,1-triarylethanes, together with dypnone (Scheme 4). In contrast, the aldolic condensation of acetophenone to yield dypnone is the major pathway in benzene or carbon tetrachloride as solvents [49]. Although dypnone is also observed in the reaction of acetophenone with electron-rich arenes, it was found that aldolic condensation and hydroxyalkylation are independent processes. The influence of the particle size and the crystalline structure of the zeolite reveal that the conversion and selectivity is controlled by diffusion of reactants and products through the micropores. Accordingly, omega zeolite was found a very inefficient catalyst, while, at similar conversions, beta zeolite was much more selective to the less space demanding dypnone than Y zeolite [49].

In this context, one particular case when hydroxyalkylation of both aldehydes and ketones gives, in some cases, total conversion and complete selectivity toward bisarylalkanes is in the condensation of 2-alkylfurans (Scheme 5) [50]. HZSM-5 and H-mordenite were found to be less active than three-dimensional large pore Y and beta zeolites. Sulfuric acid was found to be less selective toward *gem*-difurylalkanes [50]. This fact may reflect again the negative influence

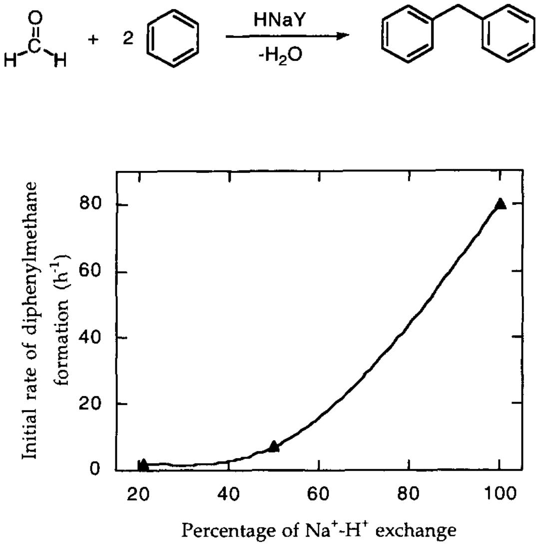
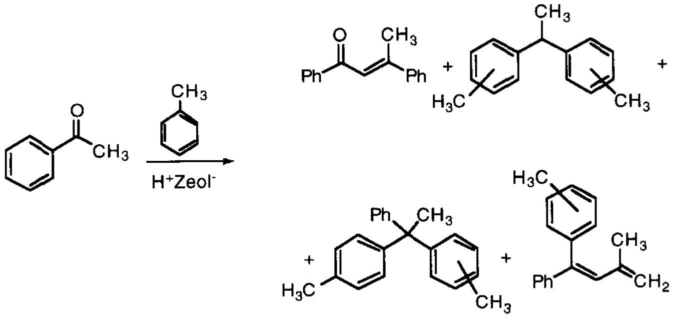
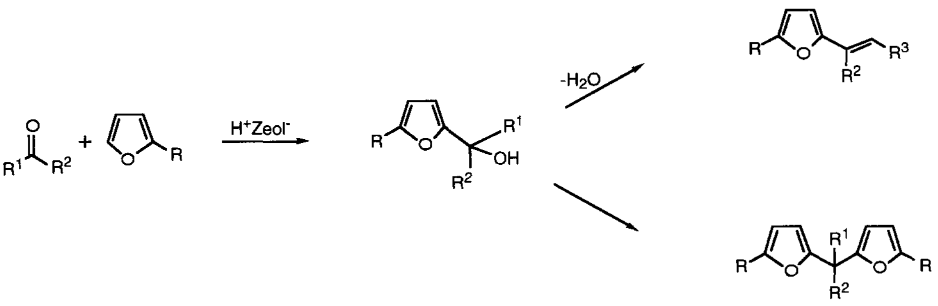


Fig. 7. Influence of the percentage of Na^+-to-H^+ ion exchange of HNaY catalyst on the initial reaction rate of diphenylmethane formation.



Scheme 4.



Scheme 5.

of strong Brönsted acids, due to extensive degradation and/or polymerization. An intramolecular condensation of ketones with aromatic rings leading to coumarins constitutes the last step of the Pechmann reaction. The synthesis of 7-hydroxycoumarins via esterification of 1,3-dihydroxybenzene with ethyl acetoacetate or with propenoic and propynoic acid and subsequent cyclization catalyzed by acid zeolites has been reported [51–53].

2.3. Reactions that require strong acid sites

Electrophilic additions of alcohols or water to C=C double bonds are catalyzed by acid sites. In order to study the influence of the acid strength of sites on the gas-phase formation of methyl *tert*-butyl ether from methanol and isobutene, a consistent series of partially ion-exchanged HY zeolites at the same exchange percentage with Li, Na and Rb were tested [54]. It was found that the initial activity for the formation of methyl *tert*-butyl ether at temperatures below 100°C was very similar, regardless of the nature of the accompanying alkali metal ion [54]. Assuming that the acid strength is modified by the alkali ion, the fact that these partially exchanged zeolites exhibit the same activity would suggest that no strong acid sites are required to catalyze this electrophilic addition. In contrast to the initial rates, the steady-state activities for methyl *tert*-butyl ether formation are strongly influenced by the different deactivation behavior [54]. Rb exchanged HY deactivates much more rapidly, probably by blockage of the micropores by isobutene oligomers.

In different reports, however, the catalytic activity of the zeolites for the gas-phase synthesis of methyl *tert*-butyl ether was found to increase with the acid strength [55]. An increase in the acidity of the HY zeolites produced by dealumination results in a significant enhancement in the intrinsic activity of the sites for methyl *tert*-butyl ether formation. The presence of extra-framework aluminum (EFAL) is an important parameter for determining the catalytic behavior of zeolites for this reaction [56]. In fact, the enhancement in the activity of methyl *tert*-butyl ether formation after treating a series of HY, H-Mordenite and HZSM-5 with ammonium fluoride or triflic acid has been ascribed to the formation of extra framework Al rather than to the effect of fluoride [57,58]. HZSM-5 seems to be the more suitable catalyst for high temperature (up to 175°C) formation of methyl *tert*-butyl ether, because it combines an excellent selectivity toward ether and a low deactivation [59].

Besides acid strength, other factors such as reactant-preferent adsorption or differences in surface polarities could be playing a significant role in the activity and selectivity of the catalysis. In this regard, it has been reported that zeolites exhibit better selectivities than the commercially used Amberlyst-15 resin for the gas-phase methylation of *i*-butene with methanol [60]. In order to explain this high selectivity, adsorption measurements were undertaken under the same conditions. It was found that while equal amounts of methanol and isobutene are adsorbed per acid site in Amberlyst-15, for zeolites up to 2.5 molecules of methanol and one of isobutene are adsorbed per acid site. This preferent adsorption of methanol in zeolites would suppress the formation of by-products arising from isobutene adsorption on acid sites such as dimerization and oligomerization [60]. Analogous results have been obtained for the ethylation of isobutene to form ethyl *tert*-butyl ether [61].

Addition of methanol to the C=C double bond of styrene catalyzed by pentasil zeolites has also been reported. It was found that the activity of modified pentasils correlates well with the acidity of the solid [62].

A study of the hydration of propene over acid zeolites has shown that the catalytic activities of H-mordenite and USY depend on their effective Brönsted acidity, defined as the concentration of acid sites multiplied by their acid strength (Fig. 8) [63]. For HZSM-5, the rate of hydration is influenced by intracrystalline diffusion and by the strength of reactant adsorption [63,64]. Thus, the increase observed in the apparent activation energies of propene hydration and methanol addition along with the aluminum content of HZSM-5 is due to an increase in the heats of adsorption of these polar reactants [64]. In the case of the 1-butene hydration over natural H-clinoptilolite, it was found that the active sites are really hydroxonium ions that react with 'gas-phase' 1-butene [65]. Increase in the percentage of water in the feed negatively influences the formation of butanol by generating inactive polyhydrated hydroxonium ions [65]. Liquid-phase hydration of cyclohexene has been carried out using highly silicious ZSM-5 and ZSM-11 as highly active and selective catalysts [66]. Large-scale production of isopropanol by catalytic propene hydration over modified industrial beta zeolite has been reported [67].

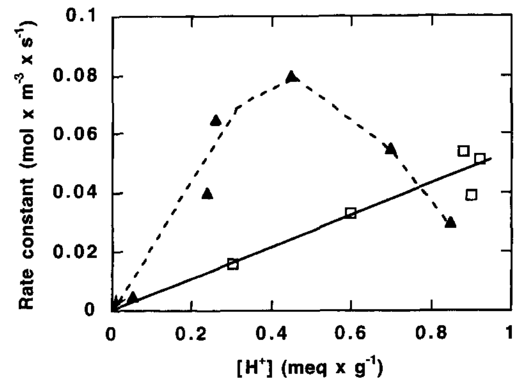
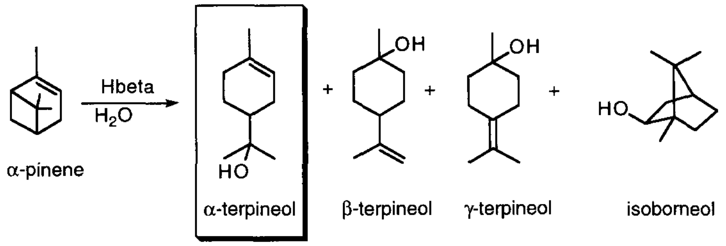


Fig. 8. Propene hydration rate constant vs. the concentration of Brönsted acid sites for (□) H-mordenite and (▲) HZSM-5.

Hydration of acetylene to form acetaldehyde has been found to occur at 180°C on the Cd^{2+} forms of LTA, X, Y, erionite, chabazite, mordenite, ZSM-5 and clinoptilolite but not in the H^+, Na^+, $La3^+$ or Co^{2+} forms of Y zeolite [68]. Hydration of α-pinene over beta zeolite affords as the main product the monocyclic alcohol α-terpineol (48%) although formation of bicyclic monoterpenes as by-products is higher over the beta zeolite than when using sulfuric acid as catalyst (Scheme 6) [69].

A review covering the various processes including acid-catalyzed reactions undergone by alcohols on zeolites and molecular sieves has been recently published [70]. Dehydration of aliphatic alcohols to the corresponding alkenes has been subjected to extensive studies [71–75]. Accompanying the intramolecular dehydration, giving alkenes, is the intermolecular dehydration leading to ethers, though the acid requirements for these two competitive reactions appear to be quite different. Ethers, in turn, can intervene as reaction intermediates in the final alkene formation.

Formation of ethers by intermolecular dehydration of alcohols can be so favorable that even the Na^+-form of bentonites can catalyze this reaction [76] or in the selective dehydration of 1-phenylethanol to diphenethyl ether over Ti pillared clays [77]. However,



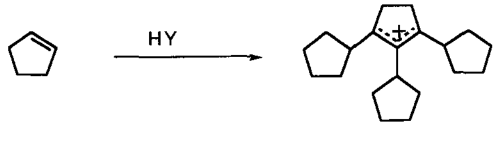
Scheme 6.

the activity of these clays increases with the Brönsted acidity of the catalyst [76]. Modified acidic aluminotitanosilicalite (Al)TS-1 also catalyzes ether formation from alcohols [78]. For other etherification reactions, such as glycosidation of D-glucose with *n*-butanol [79] and diethylene glycol conversion into 1,4-dioxane [80], a correlation between the activity and efficiency of the catalyst with the density of strongest acidic sites has been found. A mechanistic study has revealed that etherification of alcohols over acid zeolites follows a reaction pathway compatible with a typical SN2 mechanism with a total inversion of configuration and retention of the heavier alcohol oxygen [81]. Alternative SN1 mechanism involving the intermediacy of carbenium ions plays only a minor role in the formation of methyl *tert*-butyl ether from methanol and *tert*-butanol [81].

Dehydration may be so sensitive to the acid strength that a method for the evaluation of the acidity of zeolites at high temperatures emulating the real reaction conditions, termed catalytic titrimetry, has been developed based on the effect of amines on the rate of dehydration of isopropyl alcohol [82].

For the dehydration of 1-butanol over $AlPO_4$, the selectivity to butenes increases with the concentration of stronger acid sites, while an opposite trend was observed for dibutyl ether formation [83]. Analogous relationships between surface acidity and dehydration have been obtained for a series of secondary α-methyl alcohols over $AlPO_4$ catalysts [84]. Catalytic dehydration of partially exchanged neodymium X and Y faujasites increases after extensive γ-irradiation. This observation can be explained by an increase in the number of acid centers as a consequence of the partial structure destruction and the generation of tricoordinated Al atoms in the high-energy irradiation [85]. Vapor-phase dehydration of cyclohexanol to cyclohexene has been studied over H-(Al)ZSM-5 and H-(B)ZSM-5 by FTIR spectroscopy [86]. Other processes, such as skeletal isomerization, complex hydrogen transfers and aldol-type condensations (for cyclohexanone), take place along with the dehydration. Strong acid sites are active in this transformation of cyclohexanol, while the number of sites needed increases from the dehydration to hydrogen transfer reactions [86]. The presence of ammonia in the feed reduces the isomerization, especially the hydrogen transfer processes. An analogous FTIR study has been conducted for the vapor-phase dehydration of cyclohexanone to cyclohexadiene [87]. Some similarity between the results attained starting from cyclohexanone or cyclohexanol can be drawn except for the implication of aldol-type intermediates and the fact that ammonia co-feed stops the cyclohexanone reaction by forming the corresponding imine strongly held in the zeolite surfaces. Decomposition of the cyclohexanone imine at 450°C produces gaseous cyclohexadiene and ammonia [88].

In situ MAS ^{13}C-NMR studies have proved that dehydration of cyclohexanol and cyclopentanol gives rise to the formation of cyclopentenyl carbenium ions through a sequence that involves dehydration, double-bond migration, oligomerization, C_6 to C_5 ring equilibration and accumulation of cyclopentenyl ions (Scheme 7) [89]. In some experiments, up to one third of the carbocyclic material was positively charged.



Scheme 7.

The remarkable persistence of these carbenium ions, in high concentrations, in zeolites has been attributed to the acid strength of the zeolite and the stability of positively charged ions having a five-member ring structure [89]. The possibility to assign and detect carbenium ions by spectroscopic means allows to establish an alternative acidity scale based on the ability of zeolite to generate and stabilize these organic reaction intermediates. Likewise, it was observed that cyclopentene and cyclohexene behave in the same way generating cyclopentenyl cations [89].

Treatment of aqueous solutions of glucose (12 wt%) at 160°C in the presence of HY leads to a complete disappearance of the starting material, although a complex reaction mixture is obtained [90]. Several acid-catalyzed processes, including isomerization to fructose, partial dehydration to 5-hydroxymethylfurfural, cleavage to formic acid and 4-oxopentanoic acid and carbonization were found to occur [90]. The lower selectivity toward 5-hydroxymethylfurfural of the HY catalyzed glucose transformation, compared to the results attained in the homogeneous acid-catalyzed reaction, suggests molecular sieving effects in the former case [90]. In contrast, dehydration of fructose to 5-hydroxymethylfurfural at 165°C can be effected with remarkable selectivity (> 90%) over H-mordenites with low mesoporous volume (Fig. 9) [91]. This high selectivity of dehydration has been ascribed to a shape-selectivity effect of the mordenite [91]. Xylose, a pentose indigestible for most yeasts, can be isomerized in the presence of HY to xylulose, which can be fermented subsequently to ethanol [92]. It was found that zeolite catalyst is compatible with yeast fermentation pH [92].

By using the H^+-form of Y zeolite, loaded with one (*R*)-1,3-dithiane-1-oxide molecule per supercage, a chiral acid catalyst, able to discriminate between the two enantiomers of 2-butanol, was obtained [93]. The rate of dehydration of the pure (*S*)-2-butanol was found to be higher than the opposite enantiomer over the range of temperatures investigated (Fig. 10). Using computational molecular modeling, it was calculated that the binding energy for the *S* and *R* enantiomers were 64.7 and 48.3 kJ mol^{-1}, respectively. This difference in the adsorption of the two enantiomers is believed to be the origin of the enhanced reactivity of the (*S*)-enantiomer [93].

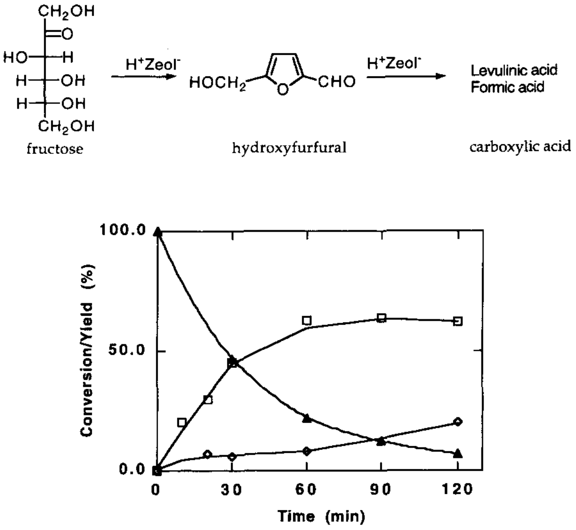


Fig. 9. Conversion of (▲) fructose and (□) yields of hydroxymethylfurfural, and combined carboxylic acids (◇) over H-mordenite (Si/Al 11) at 165°C using methyl isobutyl ketone/water (5/1) as solvent.

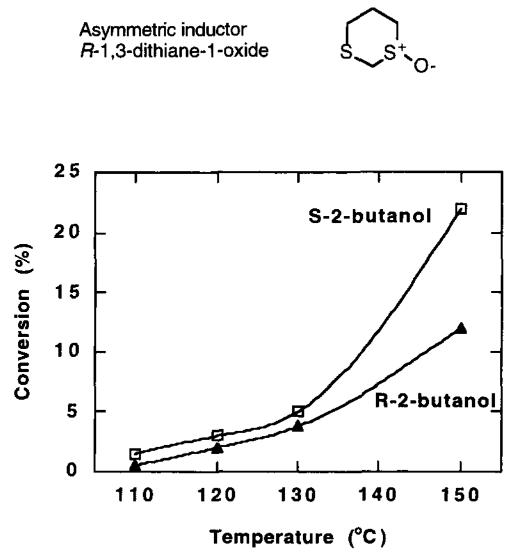


Fig. 10. Effect of the temperature on the conversion of (*R*)- and (*S*)-2-butanolover HY zeolite doped with one molecule of (*R*)-1,3-dithiane-1-oxide per supercage. Nitrogen used as diluent.

Skeletal isomerization of saturated and unsaturated hydrocarbons is a general transformation that can be conducted over acid zeolites [94–102] and other solid superacids [1]. For the isomerization of 1-butene over

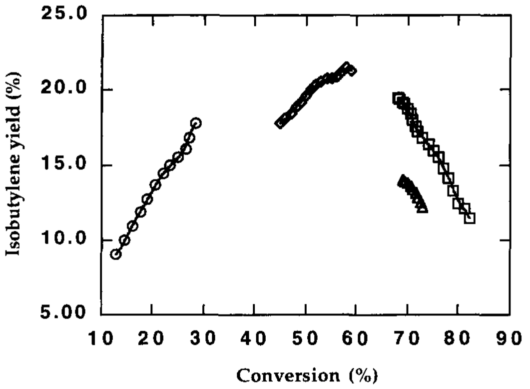
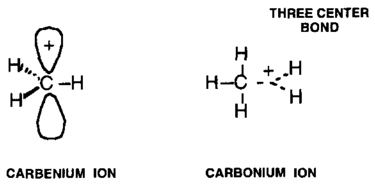


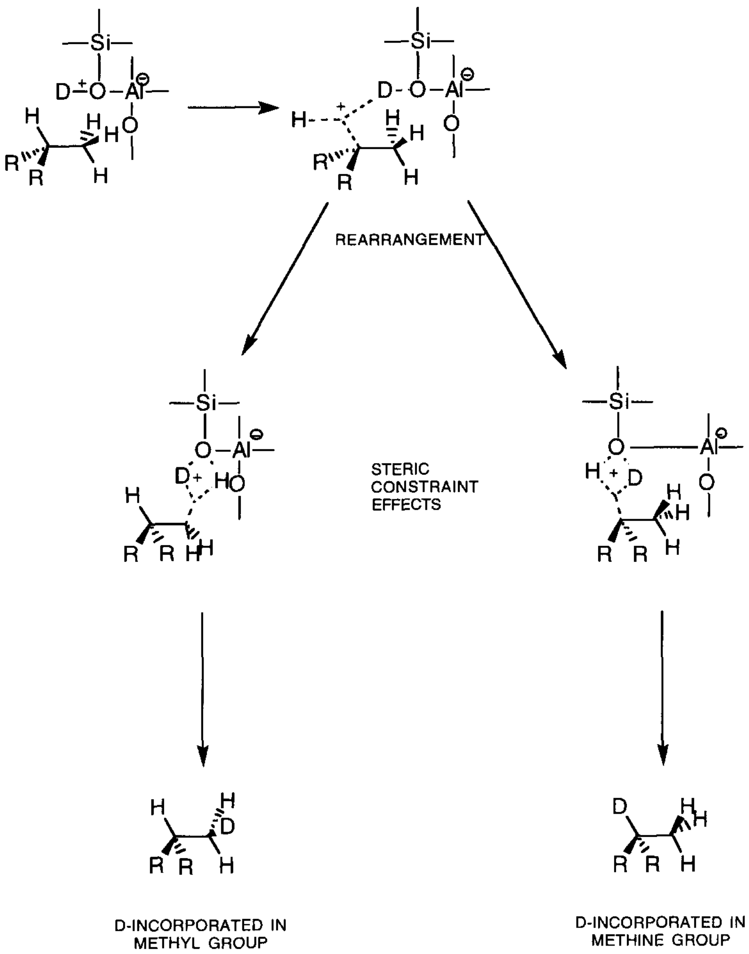
Fig. 11. Isomerization of 1-butene on a series of ZSM-5 and ZSM-11 catalysts: (○) [B]-ZSM-11 (B 0.23 wt%, aL 0.027 WT%); (◇) [B]-ZSM-11/Al_2O_3 (B 0.23 wt%, Al 0.033 wt%); (△) [Al]-ZSM-5 (B 0 wt%, Al 0.440 wt%); and (□) [B, Al]-ZSM-5 (B 0.35 wt%, Al 0.670 wt%).

ZSM-5 and ZSM-11, a synergistic effect between framework boron and aluminum tuning the acidity of the solid has been observed (Fig. 11) [103]. A study about the changes in activity and selectivity upon extended use of ferrierite for the *n*-butene isomerization has led to the conclusion that non-framework Al contributes to the formation of non-C_4 products and lowers the selectivity to isobutene [104]. Acid washings remove extra-framework Al from ferrierite giving a catalyst that exhibits excellent isobutene selectivity and catalytic activity [104]. Selectivity of the isomerization of 1-butene to isobutene over MCM-22 is strongly improved by increasing the Si/Al ratio of the zeolite [105]. This has been explained by a decrease in undesirable consecutive reactions when decreasing the density of Brönsted acid sites of the zeolite [105]. Novel aluminophosphate DAF-1 has been tested for the 1-butene to isobutene isomerization. It was found that although DAF-1 activity, selectivity and longevity are superior to other AlPOs for this reaction, its performance is worse than H^+-ferrierite and H^+-Theta-1 zeolites [106].



Scheme 8.

Based on the data of *n*-butane conversion over H-ZSM-5, it has been proposed that the transition state for this and related processes such as hydrogen–deuterium exchange, dehydrogenation and cracking proceed via pentacoordinated carbonium ions that are stabilized by the zeolite lattice, rather than true carbenium ions (Scheme 8) [107]. Analogous conclusions were reached for H–D exchange between deuterated zeolites and alkanes at 100°C [108]. Only alkanes having tertiary hydrogens could undergo deuterium exchange, giving monodeuterated alkanes. But deuterium is not specifically bonded to primary, secondary or tertiary carbons of the product. In more constrained zeolites, like ZSM-5, a high preference for the primary positions was found [108]. These findings are consistent with the attack of the zeolite acid site on the tertiary C–H bond forming a pentacoordinated carbonium ion which rearranges with deuterium migration to the more accessible primary or secondary positions, where steric effects on the interaction with the zeolite framework would be minimized (Scheme 9) [108]. Using perdeuteroisobutane and HNaY and H-mordenite, it was found that nine of the ten D atoms of the starting perdeuterated isobutane can be exchanged at lower temperatures, as the acidity of the zeolite increases [109]. Thus, using the the most acid Y sample of the series, the exchange takes place at 200°C, while no other skeletal transformations of isobutane were observed [109]. In this context, a comparative study has shown that the activity of HZSM-5 for the skeletal isomerization of *n*-butane at 300°C is higher than the activity of sulfated zirconia or the dicesium hydrogen phosphotungstate [110]. However, the selectivity to isobutane using HZSM-5 was lower than for the dicesium salt of the heteropolyacid [110]. Comparison of the performances of USY zeolite, amorphous SiO_2–Al_2O_3 and Amberlyst-15 for the H–D exchange of isopentane has revealed that only USY showed activity at 100°C [111]. However, this activity has not been attributed to differences in acid strength, but rather to steric effects associated to a confined reaction cavity. The corresponding olefins have been claimed to be true reaction intermediates in the H–D exchange [111,112]. Thus, the induction period that is observed in the exchange kinetics between isobutane and deuterated solid acids at temperatures below 100°C is suppressed when

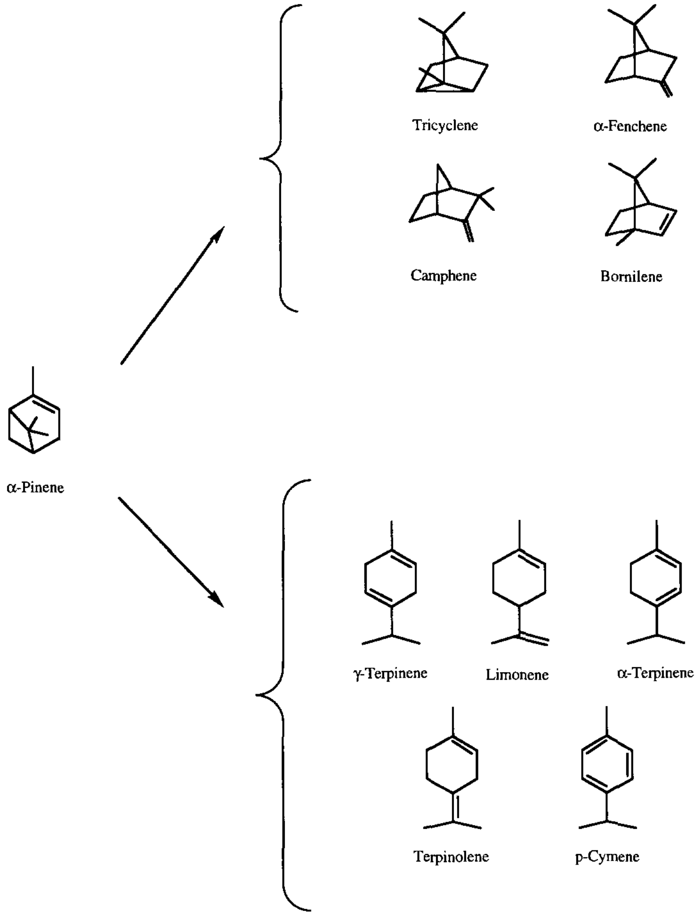


Scheme 9.

small amounts of isobutene are added to isobutane [112].

Aimed at the deeper understanding of the acidity of zeolites and the nature of the intermediates, ab initio quantum-chemistry calculations have been undertaken to predict reaction rates for the H–D exchange between deuterated methane and protonated zeolites [113]. These values compare reasonably well with those determined experimentally, thus showing the validity of the theoretical model [113].

Monoterpene interconversion can be catalyzed by acid zeolites [69]. Liquid-phase isomerization of α-pinene has been studied on a number of X and Y zeolites at 150°C (Scheme 10) [114]. The primary reaction products were camphene, tricyclene and p-menthadienes. Besides the Brönsted sites, it was found that extra-framework Al (EFAL) has a promoting effect on the catalytic activity. Selectivity toward camphene is also strongly affected by EFAL [114], increasing along the EFAL content of the catalyst. Vapor-phase isomerization of camphene has also been studied over H-ZSM-5 and HY [115]. The product distribution is extremely sensitive to the acid strength of the catalyst. Tricyclene is the predominant product over lower acidic strength while maximum amounts of monocyclics like terpinolene, terpinenes, p-menthene and p-cymene are formed over higher acidic solids [115]. Likewise, transformations of α-pinene, limonene and α-terpinene in the presence of USY, H-mordenite and HZSM-5 have been investigated and



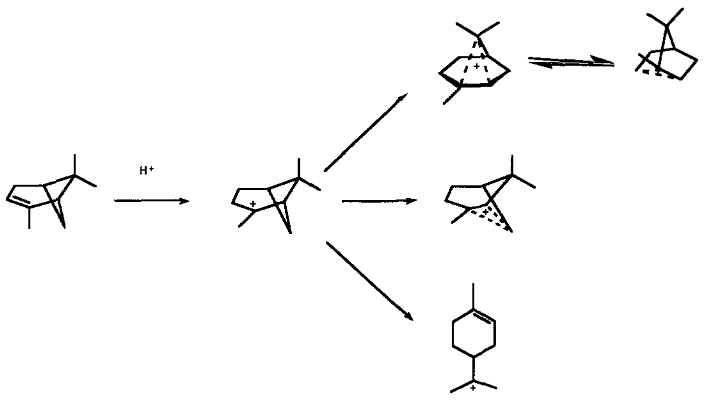
Scheme 10.

the results compared with those achieved using pillared clays [116]. Specific carbocation precursors are deduced from the product distribution (Scheme 11). Thus, bicyclic α-pinene, which was found to be the most reactive monoterpene in the series, rearranges through a norbornyl cation intermediate rather than fenchane derived carbocation. USY was the most active catalyst while some pillared clays show similar activity to HZSM-5 [116].

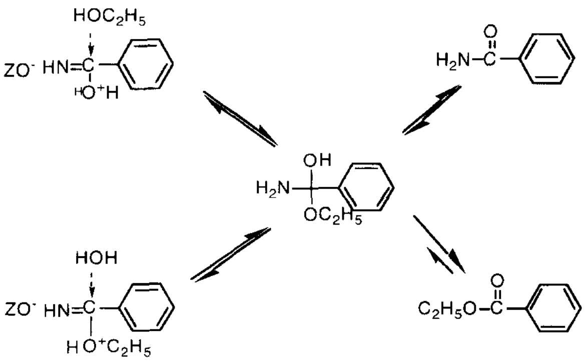
Kinetic studies of esterification of carboxylic acid with alcohols as well as their hydrolysis catalyzed by acid zeolites have been reported [117]. A selective synthesis of ethyl esters from aromatic nitriles using acid faujasites as catalysts has been reported (Scheme 12 and Table 3) [118]. Carboxylic acids can be esterified by alcohols in a batch reactor over acid zeolites following an experimental procedure analogous to that commonly employed in organic chemistry using liquid acids like H_2SO_4 [119,120]. Composite hydrophilic membranes consisting of KA, NaA, CaA and NaX zeolites and polyvinyl alcohol polymer were

Table 3
Initial rate of benzonitrile disappearance at 230°C over a series of catalysts with different number of strong acid sites (titrated by NH_3 TPD)

Zeolite	Si/Al	eq H^+ ($g^{-1} \times 10^3$)	$r_0 \times 10^6$ ($mol\, l^{-1}\, s^{-1}\, g^{-1}$)
Y	2.5	0.115	6.7
Y	15	0.160	77.0
Beta	15	0.292	13.0
Mordenite	9	0.452	26.0



Scheme 11.



Scheme 12.

found to be convenient heterogeneous catalysts for the esterification of acetic acid and ethanol because they combine the presence of active sites with the selective pervaporation–transport of alcohol–water mixtures [121]. From a preparative point of view, it has been found that esterification of glycerol with oleic acid to form selectively monoglycerides can be carried out over zeolites, although cationic exchange resin gives better results under mild experimental conditions [122].

N-alkylation of amines by alkenes or alcohols is another reaction type of economical importance that can be catalyzed by acid zeolites [123,124]. By combining adsorption studies of ammonia and methanol on a series of alkali-exchanged and Brönsted mordenites and erionites with kinetic analysis, it has been proposed that over alkali-exchanged molecular sieves the reaction proceeds via ammonolysis of chemisorbed methanol and over the Brönsted acid forms via methanolysis of chemisorbed ammonia [125]. Shape selective methylation of ammonia has been achieved using $SiCl_4$ modified acid mordenites [126]. The lack of formation of trimethylamine over mordenite has been justified because this product is too bulky to fit into mordenite channels [126]. Compared to mordenite, small pore H-chabazite as catalyst gives an enhanced yield of monomethylamine at higher partial pressures of ammonia, while formation of trimethylamine and dimethyl ether is extremely disfavored. It has been claimed that chabazite results are a case of transition state selectivity [127].

Other kinetic studies have suggested that the reactive species for the synthesis of methylamine from methanol and ammonia are adsorbed nitrogen bases [128]. According to this study, the presence of strong acid sites is required, but weak adsorption centers are also necessary to facilitate desorption of the final amine species from the stronger sites [128]. This is an interesting observation since it is in agreement with the fact that desorption of methylamines from strong Brönsted sites can be the rate determining step of the overall *N*-methylation [129]. Desorption of the resulting methylamine is also aided by competing adsorption of ammonia [129]. For the reaction of 2-methylpropene and ammonia, only Brönsted sites appear to be active [130,131]. Furthermore, the number and the strength of these Brönsted sites appear to be the factors controlling the efficiency of the solid toward the formation of *tert*-butylamine (Fig. 12) [132]. In agreement with these findings, H^+-exchanged ZSM-5 zeolite with a high Si/Al was found

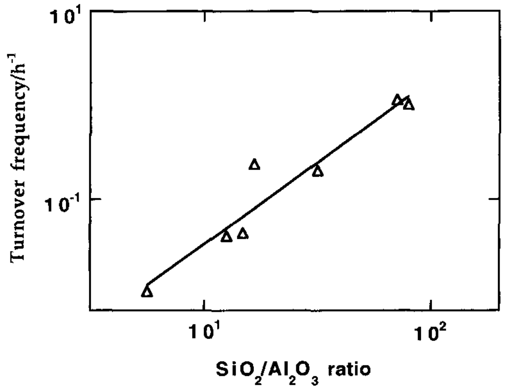


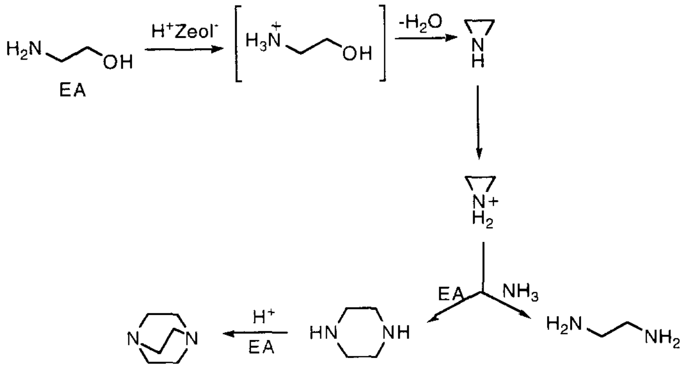
Fig. 12. Correlation between SiO_2/Al_2O_3 ratios and turnover frequencies defined as the amount of *tert*-butylamine formed per hour divided per the population of Brönsted acid sites.

to be the most efficient catalyst of the series [130,131]. Similar results have been reported for the alkylation of *n*-butylamine to *N*,*N*-dimethyl-*n*-butylamine with methanol. Thus, the alkylation rate turned out to be highly dependent on the strength of the acid sites [44]. Formation of C_6-imine by decomposition of 1-propanamine has been studied on MFI and its H^+, Ga, In and Cu forms [133,134]. H-mordenite has been found a highly selective catalyst for the reaction of ethanolamine with ammonia to form ethylenediamine (Scheme 13) [135–137]. Only minor amounts of ethyleneimine and piperazine were detected as byproducts. The results suggest that this reaction involves the stronger acid sites, the chemical intermediate being protonated ethyleneimine [135,136].

Pentasil molecular sieves catalyze ammonia *tert*-butylation by methyl *tert*-butyl ether under supercritical conditions (> 300°C and > 19.3 MPa) in a batch reactor [138]. Byproducts include methylamines, isobutene and methanol. The use of methyl *tert*-butyl ether appears to be advantageous with regard to the direct amination of isobutene. Using alkali-exchanged beta and EMT zeolites as catalysts, alkylation of aniline by methanol occurs predominantly at the nitrogen [139]. Selectivity of the *N*-alkylation in the vapor-phase reaction of aniline with isopropanol over Y and ZSM-5 zeolites decreases as the contact time or the reaction temperature increases [140]. The main C-alkylation product of this process is the *ortho* isomer.

Friedel–Crafts alkylation [141–153]/dealkylation [147,154–158]/disproportionation [30,159–163]/isomerization [155,156,164] are among the reaction types that have been most thoroughly studied under a wide variety of reagents, zeolites and conditions.

A review covering the various aspects of shape selective catalysis over zeolites and molecular sieves, including primary and secondary acid-catalyzed shape selectivity, has been recently published [165]. Concerning the shape selectivity of methylation of toluene to *p*-xylene over ZSM-5, novel studies have proposed that this effect takes place only when the rate of xylene isomerization exceeds that of the direct alkylation [166,167]. All three – *ortho*, *meta* and *para* – would be primary products, but due to the different rates of transport, the bulkier isomers would be accumulated in the pores [166]. Moreover, based on the lack of influence of a high concentration of adsorbed mole-



Scheme 13.

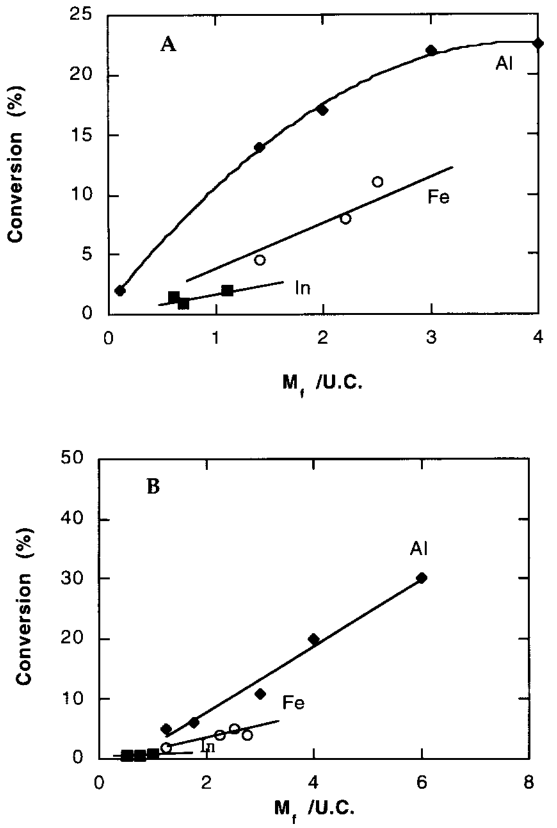


Fig. 13. (A) Influence of the framework heteroatoms on toluene conversion in its alkylation with ethene after 15 min time on-stream. WHSV 10.0 h^{-1} and temperature 620 K, toluene/ethene molar ratio 3.8. (B) Dependence of the conversion in toulene disproportionation on the number of framework heteroatoms after 15 min time on-stream. WHSV 2.7 h^{-1}, and temperature 770 K.

cules or coke precursors on the product distribution, it was suggested that transition-state selectivity does not play a major role in the product selectivities [167]. Using a series of isomorphically substituted MFI zeolites, it has been observed that the activity for the toluene disproportionation or alkylation with ethene is proportional to the concentration of framework bridging Si–OH–M and increases going from In to Fe to Al (Fig. 13) [168]. This is in agreement with an increase in the acid strength of the sites, showing that the strongest acid sites are those responsible for the catalysis. This study has been attempted to apply to the toluene alkylation with isopropanol but the outcome of the reaction is, then, controlled by diffusion

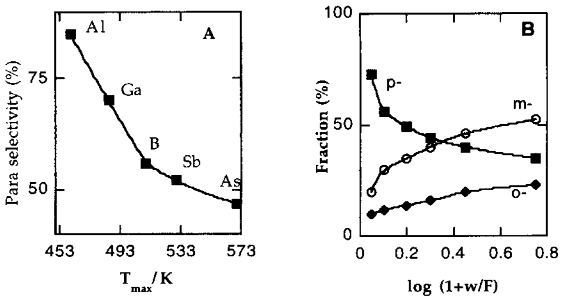


Fig. 14. (A) Correlation between *para* selectivity in the alkylation of toluene by methanol and strength of acid sites (T_{max}); (B) Effect of contact time (w/F) on the distribution of xylene isomers produced in the methylation of toluene over HZSM-5.

and a direct correlation between acidity and conversion could not be obtained.

Other studies on the methylation of toluene over MFI metallosilicates have led to somewhat different conclusions. It was found that the primary product is only the *para* isomer, because formation of the *ortho* is inhibited by transition-state selectivity [169]. By controlling the strength of the acid sites through changing the nature of the trivalent ion introduced into the zeolite framework, it was observed that weak sites still catalyze the alkylation, but the subsequent isomerization of the primary *para* isomer is disfavored (Fig. 14) [169]. This interpretation has also been corroborated by comparing the relation between the *para* selectivity in toluene methylation and the isomerization activity in *para*-xylene conversion (Fig. 15) [170]. When isomerization of *para*-xylene is prevented, selectivity in the toluene methylation is the highest [170]. Therefore, it can be concluded that one of the major factors to control the *para* selectivity is the strength of the acid sites. The presence of strong acid sites decreases the *para* selectivity by promoting undesirable subsequent isomerization of the primary *para*-xylene.

In this context, it is worth noting that the acid strength requirements for the isomerization of *ortho*- and *meta*-xylenes have been found to be higher than for the isomerization of the *para* isomer [171]. Thus, by using a pulse microreactor–chromatograph technique applied to the xylene isomerization over HZSM-5 as well as MgO- and CaO-modified HZSM-5, it has been observed that isomerization of *para*-xylene can

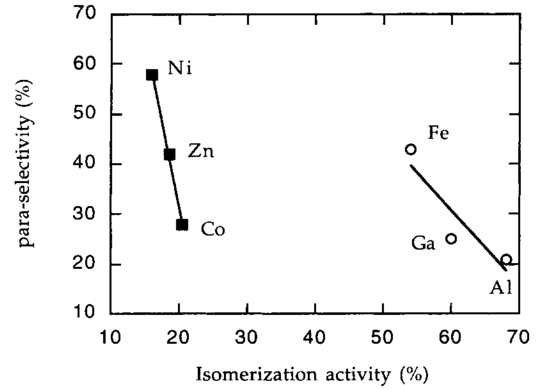


Fig. 15. Relation between *para*-selectivity in toluene methylation and isomerisation activity in *para*-xylene conversion using various MFI metallosilicates as catalysts.

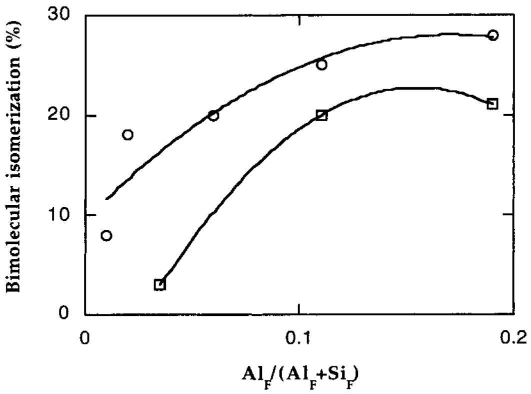


Fig. 16. Contribution of the bimolecular pathway to *meta*-xylene isomerization as a function of the Al T atom fraction over dealuminated HY zeolites: (○) according to the kinetic model based on $r_0 = (k_1 K_{a1p}/(1 + K_{a1p}) + [k_2(K_{a2p})^2]/(1 + K_{a2p})^2$; and (□) according to experimental values obtained using deuterated xylene.

occur also in acid sites of moderate strength, while the *ortho* and *meta* isomers need strong acid sites [171].

The uni- vs. bimolecular contribution to the overall isomerization of xylenes on pentasils zeolites still continues to attract much attention [172]. The selectivity of *m*-xylene isomerization over HZSM-5 is explained by restrictions to the transition state leading to the *ortho* isomer [166]. Using deuterated *m*-xylene as reactant, it has been found that more than 20% of the *p*- and *o*-xylene formed are generated via a bimolecular mechanism (Fig. 16). The relative proportion of uni- to bimolecular mechanism depends on the zeolite composition upon dealumination (Fig. 16) [173]. Although the relationship between the turnover number for the unimolecular contribution to the overall transformation fits with the topological model, the recognition of a bimolecular mechanism for the isomerization may limit its application as a test reaction to disclose the topology of microporous catalysts with unknown lattice structure [173]. A study on the effect of mordenite dealumination on the *m*-xylene isomerization and *n*-heptane cracking has shown that the stability of the catalyst increases upon Al removal [174]. *m*-Xylene isomerization, together with the hydroisomerization of *n*-decane has been used as test reaction to characterize the void structure of MCM-22 [175,176] before its structure was not definitely unveiled by X-ray diffraction studies. In agreement with the topology of MCM-22 uncovered later, the data were compatible with two non-interconnected micropore systems of 10 and 12 oxygen rings, the strongest acid sites being located in the former.

Vapor-phase methylation of phenol over copper aluminum hydrotalcites (Cu/Al ratio 3) affords as the major products *o*-cresol and 2,5-xylenol [177]. This selectivity was ascribed to the higher acidity of this catalyst compared to the rest of hydrotalcites that were tested.

Encapsulation of 12-tungstophosphoric acid inside the supercage of Y faujasite has been accomplished by the ship-in-a-bottle synthesis [178]. This heteropolyacid embedded within the zeolite voids has been found to produce a large increase in the activity of the zeolite for the isomerization and disproportionation of *m*-xylene (Fig. 17) [178].

For the methylation of ethylbenzene at 400°C under atmospheric pressure, a comparative study of the performance of HY, HMor and HZSM-5 has led to the conclusion that HY is the most convenient catalyst because it combines a high initial activity (although lower than HZSM-5) and a long deactivation time (although shorter than H-mordenite) [179].

A study for the ethylation of ethylbenzene over beta-, ZSM-5 zeolites as well as amorphous aluminosilicate under typical industrial reaction conditions (180–260°C, 35 bar, 5 h^{-1} WHSV of ethylbenzene) has led to the conclusion that the pore sizes of the solids do not play a significant role directing the selectivity toward a particular diethylbenzene [180].

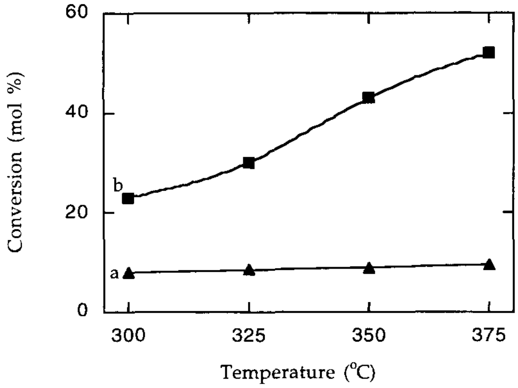


Fig. 17. Overall conversion of *meta*-xylene (mol%) on (a) acid Y zeolite and (b) PW_{12} heteropolyacid encapsulated inside Y zeolite. Conversions were measured in a pulse microreactor.

Table 4
Comparison of the performances of zeolite Beta, USY, and phosphoric acid (PA) for benzene alkylation with propene

	Beta Si/Al 14	USY Si/Al 3	PA
Product wt%	0.3	0.3	1.1
Toluene, ethylbenzene	193.0	477.0	200.0
n-Propylbenzene	94.3	89.9	95.1
Cumene	175.0	848.0	400.0
Phenyl-(C_4) (ppm)	82.0	530.0	400.0
Phenyl-(C_5) (ppm)	4.5	8.8	3.2
Diisopropylbenzenes	0.0	159.0	200.0
Triisopropylbenzenes (ppm)	0.3	0.4	0.2
Selectivity (%)			
[C9]/[C6]	95.7	92.5	97.0
[C9]/[C3]	91.8	85.7	91.8
[IPBs]/[C3]	98.3	98.2	96.4

Instead, the diethylbenzene distribution seems to be governed by thermodynamic or kinetic factors rather than shape-selective constraints [180]. In contrast to these results, it has been also reported that modified HZSM-5, as well as gallosilicate and antimonosilicate, exhibit a perfect *para* selectivity for the alkylation of ethylbenzene with ethanol [181]. Beta zeolites for the liquid phase ethylation and propylation of benzene have been found to perform more actively and selectively than Y zeolite or the conventional 'solid phosphoric acid' (Table 4) [182]. Decreasing the framework, Al content produces a decrease in both conversion and selectivity in ethylbenzene or cumene. Moreover, the catalytic activity of beta zeolite in the liquid phase is limited by intraparticle diffusion as evidenced by the lower activity as the particle size increase [182].

Isopropylation of *meta*-diisopropylbenzene over the acid form of molecular sieves has been proposed as a new test reaction to characterize the effective size of the voids in large pore molecular sieves by measuring the weight ratio of 1,3,5- to 1,2,4-triisopropylbenzene formed [183]. This ratio is shown to increase along the effective void size of the microporous catalyst.

In contrast to conventional acid catalysis that exclusively affords 3-picoline, C-methylation of pyridine on HY, HZSM-5, mordenite and beta zeolite in the gas phase leads to the formation of 2-, 3- and 4-picolines [184]. This fact is quite remarkable, taking into account that pyridine is a heterocycle reluctant to undergo aromatic electrophilic substitutions which, in any event, are directed to the 3-position due to the intense deactivating influence of nitrogen.

Using beta zeolites whose Si/Al ratios range from 50 to 320, it has been found that while the overall selectivity to diisopropylnaphthalene isomers decreases upon dealumination, the yield of the target 2,6-diisopropylnaphthalene exhibits the opposite trend [185]. Up to a maximum of 80% of the total diisopropylnaphthalene fraction can correspond to 2,6-diisopropylnaphthalene [185]. However, a different situation appears to occur using mordenite as catalyst [186]. Thus, an increase in the activity and selectivity toward 2,6-diisopropylnaphthalene and 4,4′-diisopropylbiphenyl has been observed on dealumination (Table 5) [186]. The increase in selectivity toward the 2,6 isomer of diisopropylnaphthalene has been attributed to a decrease of acid sites at the external surface [186]. It has been observed that the presence of water (up to 0.8 wt% on the catalyst) during the isopropylation of naphthalene has a beneficial effect on the β,β selectivity leading to 2,6- and 2,7-diisopropylnaphthalenes [187]. Accordingly, it has been claimed that formation of water, as co-product, as the reaction progresses would justify why the β,β selectivities for naphthalene dialkylation using isopropanol as alkylating reagent are higher than those under the same experimental conditions employing propene [187]

Dealuminated HY zeolites, rather than ZSM-5 or ZSM-12, have been found to be the catalysts of choice

Table 5
Effect of Si/Al ratio of H-Mordenites on the isopropylation of naphthalene

Si/Al	Time	Yield (%) [a]			Isomer composition (%)			
	(min)	IPN	DIPN	PIPN	2	2,6	2,7	1,6
20	1800	39.8	31.6	9.3	67.1	28.5	17.0	11.1
30	720	48.9	31.1	3.5	66.6	37.9	16.2	11.6
40	450	49.7	28.2	2.4	69.9	44.8	17.8	10.2
46	660	48.6	29.1	1.9	73.3	51.5	20.1	9.4
60	330	46.7	32.8	0.8	86.9	60.8	22.5	9.1
176	300	44.9	34.1	0.2	92.2	59.3	29.4	9.2
220	60	39.4	41.1	0.5	55.4	63.5	27.1	8.1
256	180	35.9	43.8	0.9	87.2	64.6	25.7	8.0
440	60	36.6	43.3	0.2	88.6	65.1	26.0	8.0

[a] IPN, DIPN and PIPN correspond to isopropyl, diisopropyl and polyisopropylnaphthalenes, respectively.

for the production of linear 2-phenyldodecane (97% selectivity) by reaction of benzene with 1-dodecene [33,88].

Isomerization of *sec*-butylbenzene [188], cymene [189] and other alkylarenes has been studied in the presence of acid zeolites. The factors dominating the formation of *n*-propyltoluenes in the toluene alkylation with isopropanol are the zeolite restrictions to intracrystalline diffusion of reagents and products as well as the number and strength of the sites. Thus, the highest yield of the desired *p*-cymene was obtained using MFI molecular sieves having low numbers of bridging OH groups of a lower acid strength such as H-(Fe)ZSM-5 [189]. Dealkylation and disproportionation are always competitive reactions to the isomerization. For the gas-phase isomerization of dichloro- and difluorobenzenes in the presence of pentasil zeolites containing Al, Ga or Fe, a correlation between the acid properties of these zeolites and their ability to induce the isomerization has been found [190].

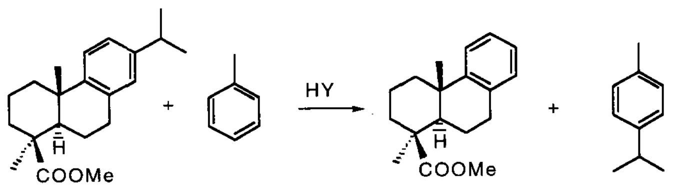
A comparative study of toluene disproportionation using pillared clays and HZSM-5 and HY zeolites has shown that the efficiency of the most active pillared clay prepared with chromium hydroxy oligomers as pillars is intermediate between that exhibited by HY and ZSM-5 zeolites [191].

The catalytic properties of Y zeolites, dealuminated by steam stabilization, for the transalkylation of toluene with trimethylbenzene have been studied in a pulse microreactor [192]. Using USY having a bulk Si/Al of five, transalkylation proceeds with better yields than disproportionation of trimethylbenzene [192].

Transalkylation from trimethylanilines (methyl groups on the aromatic ring) to aniline, giving dimethylanilines plus *p*-toluidine, has been carried out over faujasites [193]. In contrast to this intermolecular process, only intramolecular 1,2-methyl shift occurs using HZSM-5 [193]. This is in agreement with the smaller micropore dimension of the pentasil zeolite.

Transalkylation from methyl dehydroabietate to toluene as a solvent in the presence of HY zeolites has been successfully applied for the deisopropylation of dehydroabietate into methyl *trans*-podocarpa-8,11,13-trien-15-oate (Scheme 14 and Fig. 18). Contrary to what is observed with $AlCl_3$, no formation of the *cis* isomer takes place, although elimination of the methylcarboxylate group and cracking can occur in the zeolite catalyzed reaction at temperatures > 100°C [194].

Nitration of benzene derivatives by nitric acid and acyl nitrates has been carried out using acid zeolites as catalysts [195–199]. In the vapor-phase nitration of benzene with aqueous nitric acid, the activity and stability of the catalyst depends on the catalyst preparation procedure [200,201]. A stable catalyst was obtained by acid treatment of low Na^+ USY [200]. A simple procedure has been developed for the liquid phase nitration of benzene derivatives without any solvent, using equimolar mixtures of concentrated



Scheme 14.

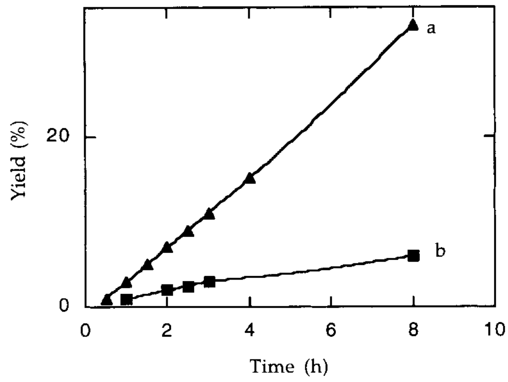
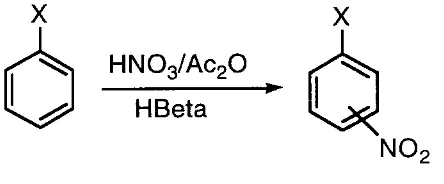


Fig. 18. Product distribution vs. time on the transalkylation of dehydroabietate and toluene over HY (framework Si/Al 16.5, extra-framework Al 3). (a) methyl dehydroabietate; and (b) product arising from elimination of the methyl carboxylate group.

nitric acid and acetic anhydride at 0–20°C in the presence of beta zeolite (Table 6) [202]. This nitration proceeds with quantitative chemical yield and the best *para* selectivity ever reported. The beta zeolite can be recycled several times and the only by-product formed is acetic acid [202].

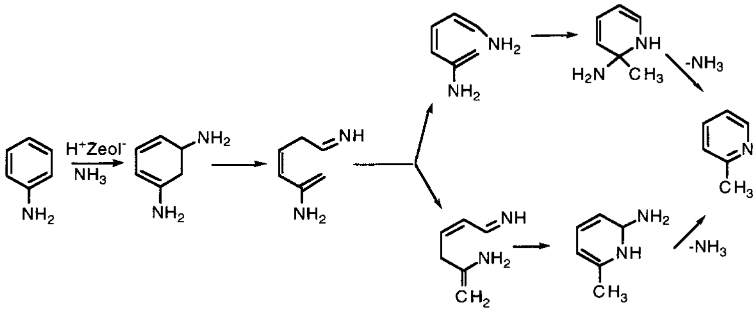
Table 6
Product distribution in the catalyzed nitration of mono substituted benzenes using stoichiometric amounts of acetic anhydride in the presence of H-Beta



X	Time	Yield	Product proportions (%)		
	(min)	(%)	*ortho*	*meta*	*para*
F	30	>99	6	0	94
Cl	30	>99	7	0	93
Br	5	>99	13	0	87
H	30	>99	—	—	—
Me	30	>99	18	3	79
Et	10	>99	15	3	82
i-Pr	30	>99	9	3	88
t-Bu	30	92	8	trace	92
Ph	30	70	trace	0	>99
NO_2	120	13	1	92	7

Rearrangement of arylamines to the corresponding *ortho*-methyl substituted aza aromatic heterocycles under high NH_3 pressures (10 MPa) and reaction temperatures (327°C) over zeolites has been investigated (Scheme 15) [203]. HZSM-5 was found to be the best catalyst of the series. Two alternative mechanisms – different from those proposed earlier – were suggested. Both of them start with the addition of NH_3 to the aromatic nucleus followed by ring opening giving a highly unsaturated intermediate, the nature of which is thought to be either alkyno-imine or enamino-imine. Regardless of the open intermediate, the subsequent ring closure and NH_3 elimination would lead to the final heterocycle [203].

Owing to the immediate economic importance, a large number of articles have appeared dealing with alkene alkylation with alkanes, in particular, isobutane butene alkylation. Alkylation of isobutane with 2-butene has been carried out in a series of well-characterized beta zeolites, differing in source of Si, framework Si/Al ratio, and the particle size [204,205]. It was found that the most active and selective catalyst (higher trimethylpentanes to dimethylhexanes ratio) was also the most stable catalyst. Stability of the beta zeolites with regard to dealumination during the activation steps increases with the Si/Al ratio and particle size. The same authors have reported that, for steam-dealuminated HY zeolites, a maximum of the 2-butene conversion is reached for samples with unit cell sizes between 2.435 and 2.450 nm, while the trimethylpentanes to dimethylhexanes ratio continuously increases along the faujasite unit cell size (Fig. 19) [206]. Concerning the mechanism of catalyst deactivation, it has been suggested that butene alkylation over USY suffers from slow hydride transfer relative to olefin addition. This gives rise to a rapid formation of C_{12} trimeric carbocations which have been suggested to be responsible for zeolite deactivation [207]. From the initial reaction-rate data, evidence has been obtained for a Brönsted acid mechanism [207]. Isobutane alkylation of 2-butene has also been studied in the presence of other protonic- and rare-earth-exchanged zeolites such as H-EMT, [208,209] CeY, [208,209] and novel MCM-22 [210,211]. It has been reported that H-EMT is a superior catalyst than dealuminated faujasites [209,212]. MCM-22 exhibits, at high olefin conversions, a very high initial cracking activity attri-



Scheme 15.

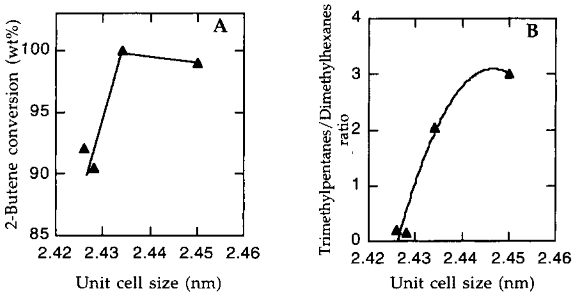


Fig. 19. (A) 2-Butene conversion obtained at 1 min time on-stream as a function of the unit cell size of USY samples; (B) Trimethylpentanes-to-dimethylhexanes ratio at 1 min time on-stream as a function of the unit cell size of USY catalysts.

butable to the presence of strong Brönsted acid sites as well as diffusional restrictions of bulky trimethylpentanes formed inside the cages but having problems to exit through the channels [211]. MCM-22 gives less trimethylpentanes than large pore zeolites (USY, beta, mordenite), but more than medium pore ZSM-5 at similar conversions of 2-butene [211]. Attempting isobutane alkylation using H-SAPO-37 as catalyst, it was found that butene dimerization giving C_8 olefins is the predominant process [213]. This has been attributed to a considerably lower relative concentration of strong acid sites of H-SAPO-37 compared to USY [213].

Oligomerization of terminal and internal long-chain linear olefins has been successfully achieved using large pore zeolites with high Si/Al ratio as catalysts [214]. Both reactant and product selectivity seem to operate in the oligomerization of C_{12} to C_{18} olefins. After hydrogenation of the resulting oligomers, synthetic lubricant stocks with excellent physical properties are produced [214]. On the other hand, oligomerization of propene, 1-decene and isobutene has been catalyzed over ZSM-5 and 2,6-di-*tert*-pyridine surface-deactivated ZSM-5 [215]. Oligomerization is faster and gives a higher percentage of C_{20} using unmodified ZSM-5. However, the structure of the C_{20}^{+} oligomers determined by ^{13}C-NMR is identical in both catalysts and corresponds to almost linear products, with a small amount of methyl substituents. The near-linear structure of the product starting with isobutene indicates that most of the methyl groups at the double bond, become part of the polymer chain [215]. This could be due to the steric constraints imposed by the channels of the medium pore zeolite. Polymerization of ethene to polyethene of high melting point and density has been achieved over Cr^{3+}-montmorillonite, while selective dimerization to butenes takes place over Ni^{2+}-montmorillonite [216].

Friedel–Crafts acylation of simple arenes by acyl chlorides is considered a more acid-demanding reaction than the analogous aromatic alkylation counterpart. This reaction type is usually carried out using strong Lewis acids like $AlCl_3$ and anhydrous $ZnCl_2$. The use of a recoverable, environment-friendly catalyst would be, therefore, highly valuable.

As we pointed out in the Section 1, the ability of aromatic nuclei to undergo acylation by acyl chlorides is going to be greatly enhanced by the presence of electron donating substituents [13]. It is, therefore, not surprising that Friedel–Crafts acylation of electron rich arenes using acyl chlorides can be effected in the liquid phase in the presence of zeolites. Using La^{3+}-exchanged Y zeolites, a relationship between the rare-earth cation content and the activity of the solid toward toluene acylation has been reported (Fig. 20)

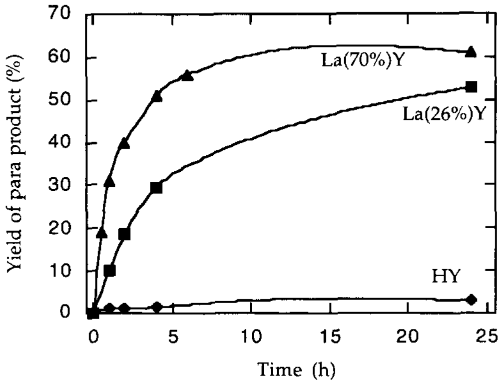


Fig. 20. Yield of *para*-4-methylpropiophenone in the reaction of propionyl chloride and toluene over lanthanum-exchanged NaY and HY zeolites.

[217,218]. The product yield increases in the following series: benzoyl < acetyl < propionylchloride. In addition, the reaction displays a remarkable *para* selectivity [217]. An almost linear relationship between the yield of resulting acetophenone and the Al content of the zeolite has been found for the acylation of anisole with acetyl chloride [218].

For the liquid phase benzoylation of benzene with benzoyl chloride, H-beta zeolite exhibits higher activity and selectivity than Y, REY, mordenite and ZSM-12 [219]. In addition, it was found that the yield of benzophenone over beta zeolites decreases with the isomorphic substitution of Al by Ga or Fe or with the increase of Si/Al ratio (Tables 7 and 8) [220]. This suggests that the optimum catalyst must possess a high density of strong acid sites [220]. Acylation of benzofuran by acetic anhydride in the liquid phase at 60°C over Y zeolites has been reported [221].

Table 7
Influence of the isomorphic substitution on the activity of beta zeolites for the benzoylation of benzene with benzoyl chloride

	Catalyst		
	H-(Al)Beta	H-(Ga)Beta	H-(Fe)Beta
SiO_2/M_2O_3	26.0	28.2	30.0
Reaction conditions			
Temperature (K)	353	353	353
Benzene/benzoyl chloride (mol/mol)	5	5	5
Catalyst/benzoyl chloride (wt/wt)	0.33	0.33	0.33
Time (h)	18	18	18
Product yield (wt%)			
Benzophenone	54.0	32.8	19.0

Table 8
Influence of the reaction temperature and Si/Al ratio of H-Beta on the reaction of benzoyl chloride with benzene

SiO_2/Al_2O_3 (molar ratio)	Reaction temperature (K)	Product yield (wt%)
26.0	313	2.1
26.0	333	16.2
26.0	353	54.0
41.5	353	24.6
60.0	353	8.9

Taking into account the fact that acyl halides are far more reactive than carboxylic acids, it can be anticipated that direct Friedel–Crafts acylation using carboxylic acids would be even more acid demanding than when starting from acyl chlorides. In addition, strong Brönsted – instead of Lewis – acids are commonly employed under conventional catalysis to effect these reactions using carboxylic acids. No liquid phase direct intermolecular acylation of simple benzene derivatives by carboxylic acids over acid zeolites has ever been reported. Nuclear aromatic acylation using carboxylic acids can be effected, however, in the vapor phase over acid zeolites [222]. An unexpected *ortho*-selectivity toward *o*-hydroxyacetophenone has been observed upon dealumination of the outer surface of the crystallites for the acylation of phenol by acetic acid on ZSM-5 zeolite. This effect has been attributed to the existence of two parallel pathways for the formation of the *o*- and *p*-hydroxyacetophenones [223]. Owing to entropic reasons, intramolecular acylations to form five- or six-membered rings are always favored with respect to analogous intermolecular processes. This would justify why intramolecular cyclization of 2-benzoylbenzoic acid over zeolites has been reported as a convenient preparation procedure of anthraquinones, which is an important intermediate for the large-scale synthesis of hydrogen peroxide [224]. Likewise, 4-phenylbutyric acid undergoes an intramolecular Friedel–Crafts acylation in the presence of H-beta using chlorobenzene as solvent [225]. However, intermolecular acylation of toluene or butylbenzene with 4-phenylbutyric does not occur

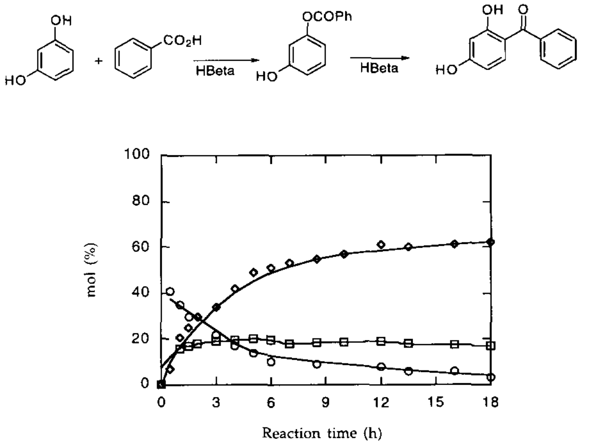


Fig. 21. Direct Fries reaction of resorcinol and benzoic acid in the presence of H-Beta in 4-chlorotoluene as solvent at reflux temperature: (○) resorcinol; (◇) 2,4-dihydroxybenzophenone; and (□) resorcinol monobenzoate.

over acid zeolites [225]. This has been justified by an unbalanced adsorption equilibrium between the two reactants on the surface of the catalyst.

Direct esterification of resorcinol with benzoic acid, followed by subsequent Fries rearrangement toward benzophenones in one-pot liquid phase operation has been examined with several catalysts (Fig. 21) [226,227]. The industrial chemical 2,4-dihydroxybenzophenone can be prepared in an 88% yield by a recycling procedure starting from benzoic acid and resorcinol in the presence of H-Beta using *n*-butylbenzene as solvent. Further insight into the Fries rearrangement was obtained by carrying out the reaction with a series of substituted phenols and various benzoic acids. The much faster rearrangement of resorcinyl 2-methylbenzoate (yield > 90%) compared to the sluggish reactivity of resorcinyl 2,6-dimethylbenzoate using H-beta as catalyst has been explained as a consequence of the discriminating pore dimensions of the beta zeolite [226].

Diels–Alder cycloadditions can be catalyzed by acid zeolites. A comprehensive study about the activity and the regioselectivity of the Diels–Alder reaction of isoprene with a series of seven dienophiles using large- and medium-pore zeolites, including ZSM-5, mordenite, and two different HY zeolites, has been reported [228]. Comparison of the results achieved with those using conventional Lewis catalysts ($AlCl_3$, $AlBr_3$, BF_3, $AsCl_5$, AsI_3, etc.) revealed that except for ZSM-5, the reactivity of the dienophiles and product regioselectivity is similar for both series of catalysts [228]. Optimization of the experimental conditions, with regard to yield and selectivity, was studied for the reaction of isoprene and 2-cyclohexanone using multivariate statistics [228]. High yields of *cis*-6-methyl-6,7-dehydro-1-octalone were obtained. It was observed that in conventional Lewis acid catalysis, this product is rapidly epimerized into the *trans* isomer [228].

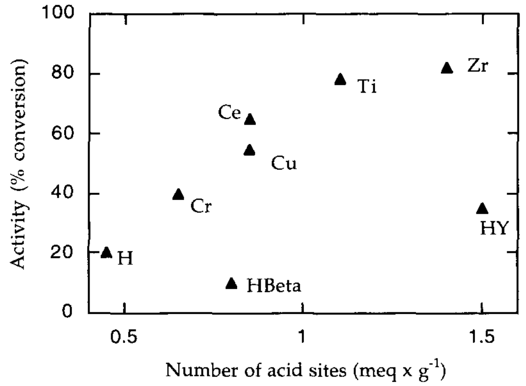


Fig. 22. Influence of the acidity on the activity of zeolites and clays for the cycloaddition of methyl acrylate and cyclopentadiene.

The performance of acid Y and beta zeolites for the Diels–Alder reaction of methyl and (-)-menthyl acrylates with cyclopentadiene has been found to be related to the number of acid sites and similar to that of different cation-exchanged clays (Fig. 22) [229]. This has led to the conclusion that concentration or confinement effects do not play a significant role in cycloaddition. However, the large size of the bulky cycloadducts having a pendant menthyl group and, being similar to the dimensions of a zeolite cage, has to be noted.

In this regard, for the reaction of dihydropyran with acrolein, high yields of cycloadducts were obtained over dealuminated HY (Si/Al 15) and H-beta (Si/Al 25) compared to H-mordenite (Si/Al 10). This has been ascribed to the smaller micropore dimensions of the last zeolite [230]. MNDO calculations of the frontier orbital interactions have supported the claim that Brönsted acid sites should be more efficient than the Lewis sites to promote catalyzed Diels–Alder reactions [230]. However, although Brönsted sites may enhance the efficiency of the active sites, these are traditionally considered as Lewis sites in nature in many organic chemistry textbooks [13].

2.4. *Influence of the external acid sites*

Alkylation of toluene with enhanced *para* selectivity has been accomplished by using a catalyst whose crystallite core is acidic ZSM-5, but the outermost layers of the zeolite grains are a non-acidic silicalite shell [144]. These structured zeolite particles were obtained by hydrothermal crystallization of silicalite in the presence of ZSM-5 seeds [144]. This result gives a quantitative estimation of the negative role that external surface acid sites play on the *para* shape selectivity.

Enhanced selectivity by a factor of two toward the *para*-cresol in the methylation of phenol by modification with P_2O_5 or MgO of pentasil zeolites has been reported [231]. This effect seems to be attributable also to a deactivation of external surface sites.

On the other hand, the external sites of H-mordenite, which do not deactivate as readily as the internal ones, are responsible for a non-selective 3,4′ plus 4,4′ alkylation of biphenyl [232]. By studying the liquid-phase isopropylation of biphenyl with propene using three mordenites of Si/Al ratio of 20, 30 and 40, it was found that the 4,4′ selectivity of H-mordenite (Si/Al 20) can be greatly enhanced by poisoning the external surface sites with tributylphosphite (Fig. 23) [28]. This doped mordenite becomes the most convenient catalyst, since all the propene is selectively consumed in the aromatic alkylation and does not promote isomerization of 4,4′-diisopropylbiphenyl [28,233]. In contrast, propene undergoes undesirable side reactions in the presence of H-mordenite (Si/Al 40) which, in turn, isomerizes part of the initial 4,4? isomer [233]. Analysis of the products encapsulated in mordenite after the reaction has established 4-isopropyl and 4,4′-diisopropylbiphenyl as the principal biphenyl derivatives [186].

Analogously, deactivation of the external surface sites of highly dealuminated H-mordenite by impregnation with ceria (up 30 wt%) has been found to be a convenient method to improve the selectivity of the isopropylation of naphthalene toward the 2,6-diisopropyl isomer (Fig. 24) [234,235]. Studies by ^{129}Xe-NMR have shown that cerium is not in the pores and the effective pore diameter is not reduced by the impregnation [235]. Likewise, the selectivity for the alkylation of biphenyl with propene to form 4,4′-diisopropylbiphenyl over SAPO-11 has been improved by eliminating the contribution of the external acid sites [236]. This was achieved by preparing a hybrid catalyst having a SAPO-11 core covered with an $AlPO_4$ inert shell.

P- and Si-modified ZSM-5 were found to exhibit an enhanced selectivity to the *para*-xylene [159]. This fact has been ascribed to an inactivation of the external surface of the zeolite crystallites by deposition of the modifiers.

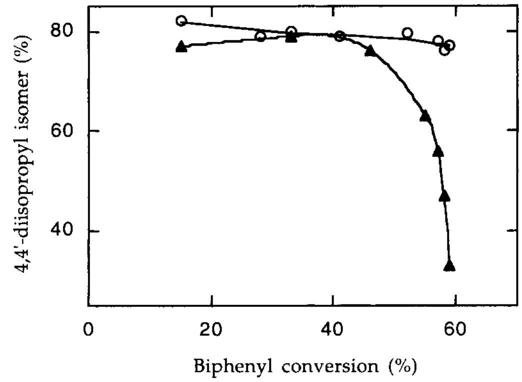


Fig. 23. Relationship between the level of biphenyl conversion and the selectivity for (▲) 4,4′-diisopropylbiphenyl on H-mordenite and (○) after poisoning the external sites with tributylphospite .

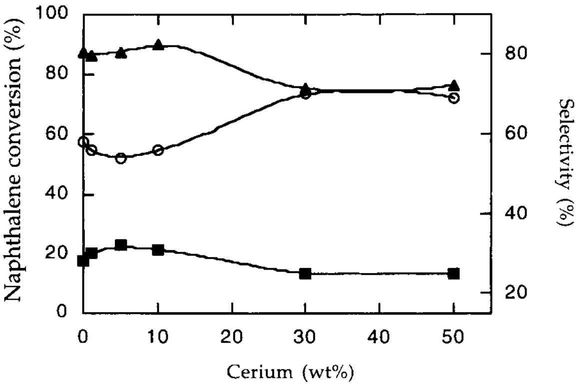


Fig. 24. Effect of modification of H-mordenite with increasing amounts of cerium on the isopropylation of naphthalene at 300°C after 4 h of reaction time: (▲) naphthaline conversion; selectivity towards the 2,6- (○) and 2,7- (■) diisopropylnaphthalenes.

Deactivation of the external acid sites of ZSM-5 and ZSM-12 has been found to enhance the yield of the *para*-acylphenol, improving the selectivity in the Fries rearrangement of phenyl acetate and benzoate [237].

Removal of the non-shape-selective acid sites from non-template synthesized ferrierite has been accomplished by framework dealumination of the surface by acid treatment [238]. These non-shape-selective sites were found to be located inside mesopores and on the external surface, and dealumination was claimed to affect non-uniformly in all the zeolite grains, but mainly in these outermost accessible sites.

Likewise, treatment of mordenites and MFI zeolites with ammonium hexafluorosilicate solutions leads to a preferential dealumination of the crystalline outer surface [239]. This treatment has been observed to cause a significant increase in the rates of ethylbenzene and *m*-xylene transformation which has been attributed to a decrease in the amount of coke formed on the outer surface of the crystallites [239].

The influence of the crystallite sizes of HZSM-5 catalysts on the isomerization of 2,7-dimethylnaphthalene toward the industrially more important 2,6 isomer has led to the conclusion that the most active HZSM-5 sample is that with the smallest and uniform particle size [240]. Both, activity and selectivity of catalysts with large crystallites were low. This was interpreted as the result of the large external surface of smaller crystallites which offers a higher number of pore entrances and enhances the reaction occurring inside the pore channels compared with catalysts having larger grains [240]. However, against this interpretation one may argue that the activity enhancement may be merely because the reaction takes place exclusively on the external surface, which increases as the particle size decreases.

2.5. *Leaching out of active extra-framework aluminum to the liquid phase*

One remarkable observation that deserves a special comment is the possibility that, in certain highly polar solvents, the major contribution to the zeolite activity corresponds to homogeneous rather than heterogeneous catalysis. In this regard, it has been noted that for the acylation of *meta*-xylene using benzoyl chloride, the chloride acylating agent interacts with non-framework Al, generating a catalytically active species (Table 9) [241]. This active non-zeolitic material can be soluble in certain solvents, like sulfolane, and the dissolved species leached out of the zeolite pores can become an active homogenous catalyst for the acylation [241]. This would imply that part of the activity attributed to acid zeolites could be due to species present in the homogenous phase. Careful controls should be carried out in order to rule out this possibility in other cases. Leaching of active extra-framework Al species can be related with reports on the remarkable influence in the acylation of *meta*-xylene with benzoyl chloride of sulfolane and nitrobenzene compared to non-polar solvents [242].

Table 9
Benzoylation of *m*-xylene with benzoyl chloride. Formation of homogeneous catalyst in sulfolane

	Conversion (mol%) over catalyst				
Solvent	none	γ-Al_2O_3	removed [a]	HY	removed [b]
None	0	0.5	—	36	—
Sulfolane	0	95	90	94	78

[a] Catalysts filtered off and fresh reaction mixture added to filtrate.
[b] 5 ml of filtrated product added to fresh reaction mixture.

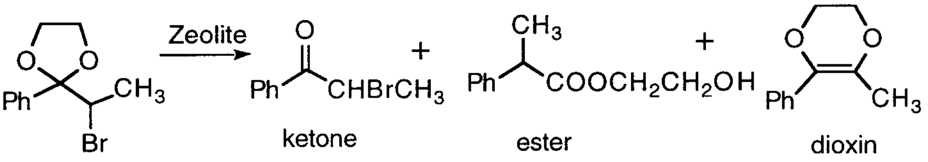
2.6. *Brönsted and Lewis nature of the sites*

Characterization of the Brönsted or Lewis nature of the acid sites present on zeolites and other solid acids, as well as their strength distribution, can be routinely accomplished by the pyridine adsorption–desorption method [1]. This well-established method basically consists in observing, by IR spectroscopy, the specific bands corresponding to pyridinium ions and coordinated pyridine adducts upon adsorption of pyridine vapors into dehydrated samples. The search for test reactions, specific either for Brönsted or for Lewis sites, therefore, appears to be of low importance. However, it is always highly recommended to disclose the nature of the sites responsible for the catalytic activity in order to develop a catalyst well-suited for a particular transformation.

In this regard, for the 1,2-phenyl shift of cyclic ethene acetals of α-bromopropiophenones leading to derivatives of 2-phenylpropanoic acid, it has been found that, while Brönsted acid centers specifically catalyze the undesired hydrolysis of the acetal moiety,

Table 10

Results of the reaction of cyclic ethene acetal of α-bromopropiophenone in chlorobenzene at 130°C in the presence of Brönsted and Lewis acid zeolites



Catalyst	Metal content	Conversion	Selectivity (%)				
	(mmol g^{-1})	(%)	ketone	ester	dioxin	ester/dioxin	k_{hydr} (h^{-1} g^{-1})
HY	0	100	91	0	0	—	1.4
ZnHY	0.78	98	66	8	2	4	1.1
ZnNaY	1.78	86	23	38	19	2	0.14
$ZnCl_2$	7.34	89	15	56	14	4	0.007
AgNaY	1.62	97	3	11	75	0.15	0.09
Hg_{NaY}	0.76	94	73	3	9	0.33	1.4
Hg_2Cl_2	4.23	6	—	72	28	2.5	—
ZnX	2.61	80	8.5	33	25	1.3	—
γ-Al_2O_3	—	4	19	21	53	0.4	0.12

Lewis sites are exclusively responsible for the skeletal rearrangement (Table 10) [243].

Likewise, toluene alkylation using benzyl alcohol or benzyl chloride has been investigated over a series of clays whose Brönsted/Lewis acidity had been characterized by the pyridine adsorption–desorption method [244]. A relationship between the rate of the alkylation and the Brönsted acidity was found when benzyl alcohol was the alkylating reactant, while for benzyl chloride the activity is controlled by the Fe^{3+} content of the clay, but not by the Brönsted site population. This pattern fits well with the general knowledge about catalysis of Friedel–Crafts reactions in organic chemistry, where Lewis acids are employed for alkyl halides, while protic acids are used when alcohols are the alkylating reagents [13].

For the vapor-phase chlorination of chlorobenzene over solid acids, in situ IR analysis has provided evidences that the active sites are Lewis centers having a Hammett acidity, $H_o > -3.0$ [245]. When *para*-bromochlorobenzene and *para*-dichlorobenzene react in the presence of HY, dehalogenation is the main process [246]. In contrast, the same reactants undergo isomerization over HZSM-5. An intermediate situation (dechlorination plus isomerization) occurs using H-mordenite. These results suggest that the acid sites effective for the dechlorination are different from those responsible for the isomerization [246].

2.7. *Synergic effects between Brönsted and Lewis acid sites*

Interaction between neighboring Brönsted and Lewis acid sites may result in an enhancement of the strength of the Brönsted sites. This type of synergic effect is widely accepted to explain the superacid behavior of Brönsted sites on sulfated zirconia and related oxides, and it is beginning to be recognized also for zeolites [1]. Comparison of the activity of hydrothermally dealuminated Y zeolites having extra-framework Al (EFAL) or after being freed from EFAL by treatment with aqueous dihydrogen ethylenediaminetetracetate solutions has revealed that toluene disproportionation is catalyzed by a limited fraction of strong acid sites [247]. These active sites are supposed to arise from the synergic interaction between framework hydroxy groups and non-framework aluminum species. In the same work it was observed the presence of a 'catalytically active coke' during on-stream operation of the catalyst, and this is responsible for a pronounced maximum in the activity of all the catalysts. The amount of active coke was

Table 11
2-Butene conversion, trimethylpentanes (TMPs) and dimethylhexanes (DMHs) obtained at 1 min on-stream on USY catalysts before and after $(NH_4)_2SiF_6$ treatment

	USY-1	USY-1 FM	USY-1 FV	USY-2	USY-2 F	USY-3	USY-3 F
Si/Al ratio							
Bulk	2.6	4.8	4.8	2.9	6.8	3.0	10.7
Framework	4.4	5.9	5.2	10.6	13.6	21.2	35.2
Al per unit cell							
FAL	36	28	31	16	13	9	5
EFAL	17	5	2	33	9	39	11
2-Butene conversion (%)	98.0	98.0	96.5	92.1	97.9	57.8	96.8
TMPs (wt%)	42.9	44.6	37.3	29.3	36.3	3.6	16.5
DMHs (wt%)	9.2	11.1	24.2	12.7	13.8	19.6	27.7

found to be related to the population of initial Brönsted sites [247].

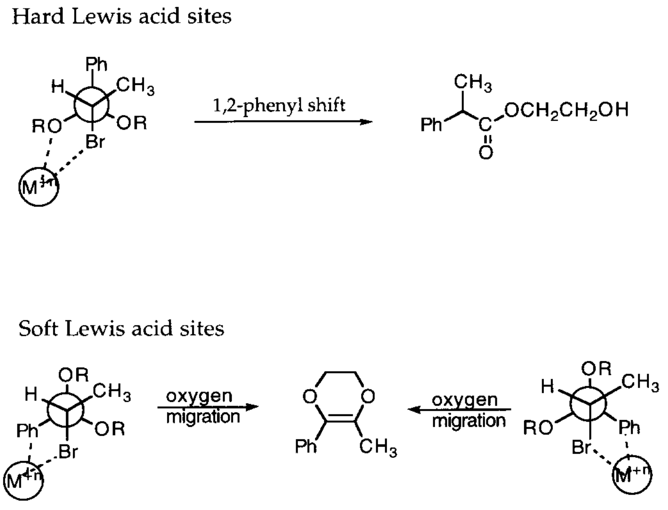
Likewise, comparison of the activity for ethylbenzene disproportionation of dealuminated Y zeolites, before and after removal of EFAL using dihydrogen ethylendiaminetetracetate, has led to suggest that there exists a synergic interaction between Brönsted sites and EFAL to yield sites of enhanced strength [247]. Similar results for toluene disproportionation and *o*-xylene isomerization have been obtained by alumination of dealuminated mordenites with $AlCl_3$ at different temperatures [248]. The enhancement of activity observed upon alumination has been correlated to the electron-withdrawing ability of EFAL species that intensifies the Brönsted strength of interacting bridging hydroxyl groups [248].

The influence of the framework and extra-framework composition of USY and beta zeolites on their activity, selectivity and deactivation behavior during the alkylation of isobutane with 2-butene has been studied by submitting the zeolites to different post-synthetic treatments (Table 11) [249,250]. Extra-framework Al-free samples were obtained by treating them with ammonium hexafluorosilicate. It was found that $(NH_4)_2SiF_6$ is more effective to remove cationic EFAL species, which are the predominant EFAL species in mildly steamed USY samples, than for extracting condensed-type EFAL present in highly dealuminated USY catalysts [250]. Elimination of EFAl decreases the alkylation activity of the catalyst, reinforcing again the assumption of a synergic effect of dispersed cationic EFAL species with framework hydroxyls to form Brönsted acid sites of enhanced acid strength. Synergism between Brönsted and Lewis acid sites for the isomerization of *n*-pentane has also been observed in dealuminated H-mordenites [22].

2.8. *Softness and hardness of Lewis sites*

While the pyridine adsorption–desorption method is a very convenient procedure for distinguishing between Brönsted and Lewis sites, this technique does not address possible differences in the hardness–softness of the Lewis centers on zeolites. Influence of the hardness–softness of the Lewis acids is well established for homogeneous catalysis. The fact that the hardness–softness balance of Lewis sites can also play a role in the catalysis over zeolites has recently been recognized [251].

In this context, the rearrangement of acetals of 2-bromopropiophenone has been proposed as a test reaction to characterize the softness and hardness of Lewis acid sites in zeolites (Scheme 16) [243,252]. Thus, for those samples having Brönsted or hard Lewis acid sites, hydrolysis of the acetal to the corresponding propiophenone is the predominant process. On the other hand, an excessive increase in the softness of the Lewis centers (Ag^+ or Hg^{2+} exchanged zeolites) tends to favor the competitive 1,2-alkoxy migration leading eventually to dihydro-1,4-dioxin or 2-alkoxypropiophenone, depending on the nature of the acetal moiety. A well-balanced Lewis site results in a higher selectivity toward the 1,2-phenyl shift, giving



Scheme 16.

rise to the corresponding ester of 2-phenylpropionic acid [243].

It is known that for orbital-controlled electrophilic aromatic substitutions, the *ortho/para* ratio may vary along with the softness and hardness of the attacking electrophilic species and, therefore, it varies with the nature of the Lewis catalyst. In this regard, changes in the *ortho/para* selectivity of the alkylation of toluene and *m*-xylene by methanol have been observed using a series of HY zeolites of different framework Si/Al ratio as well as H-beta containing Al, Al + Ga, Ga or B as trivalent framework elements [251,253]. These variations have been rationalized by quantum chemical calculations that show that by modifying the framework composition in a given zeolite, the energy of the frontier orbitals changes and, therefore, the softness and hardness of the acid sites (Fig. 25) [251]. Thus, the softness increases along the framework Si/Al ratio or when going from B to Ga to Al.

2.9. *Acid/base pairs playing a role in the catalysis*

Zeolites encompass simultaneously both acid and base sites located in different places of the solid. The former are associated either to bridging OH groups, to multivalent charge-balancing cations or to extra-framework Al species. Basic sites in the zeolites correspond to framework oxygens having high electron

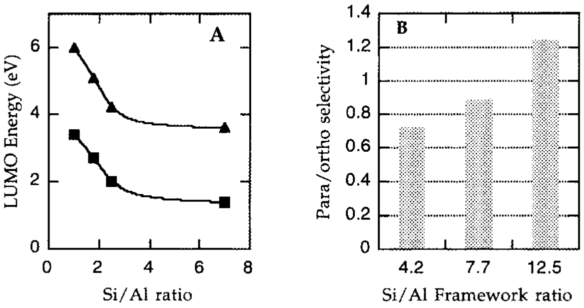
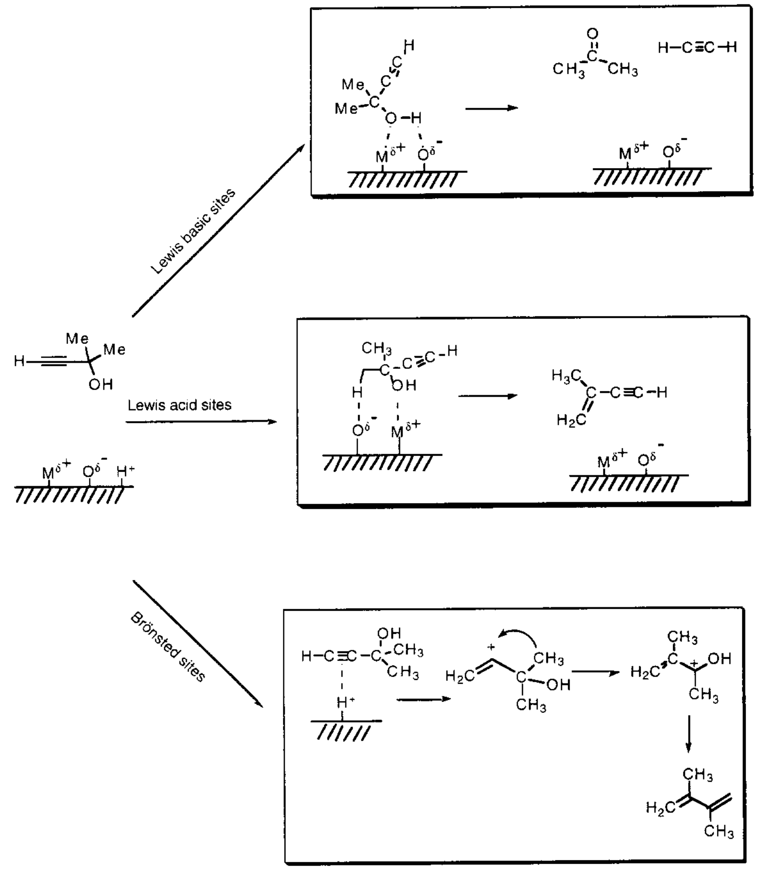


Fig. 25. (A) LUMO energy vs. Si/Al ratio: (▲) calculations made with the CEP-4G basis set; and (■) calculations made using the CEP-31G basis set; (B) Variations in the *para/ortho* ratio for toluene alkylation with methanol depending on the framework Si/Al ratio of Y zeolite at 498 K.

density. Zeolites provide an easy way to tune up the relative strengths of these acid and base sites by controlling the Si/Al ratio and the electropositivity of the counter cation. In this context, 2-methyl-3-butyn-2-ol has been proposed as a probe molecule to test the acid/base properties of ion exchanged zeolites (Scheme 17) [254]. Thus, Lewis base centers promote the cleavage of this methylbutynol to acetone and acetylene almost with 100% of selectivity, while on the other hand strong Lewis acid sites catalyze its dehydration to 3-methyl-3-buten-1-yne with high selectivity. In addition, strong Brönsted sites are responsible for skeletal isomerization of methylbuty-



Scheme 17.

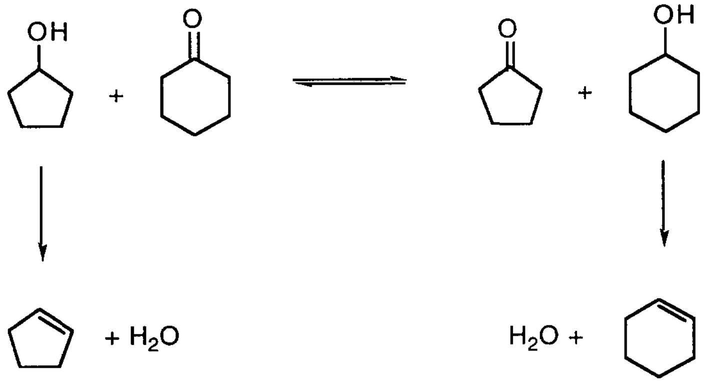
nol to 3-methyl-3-buten-2-one. It is, therefore, possible to characterize the acid/base nature of a solid simply by looking at the product distribution resulting after using methylbutynol as standard [254]. α-Alkynols in general may behave in a similar way over acid zeolites [255].

Although the situation still deserves a more detailed study, the product distribution in the transformation of allyl alcohol is slso highly dependent on the acid/base nature of the catalyst [256]. The products are almost exclusively one of the following possibilities: (i) hydrocarbons and coke (HNaY); (ii) acrolein (HCsY); (iii)propene (LiNaY); or (iv) diallyl ether (CsNaY) [256]. The mechanism of formation of these products has been proposed to involve the concerted action of Brönsted acid and basic sites depending on the nature of the catalyst. However, the intermediacy of allyl cation has been ruled out on the basis of the lack of influence of water addition in the course of the reaction [256] (Table 12)

Analogous assumption of a dual contribution of acid and basic sites has been claimed to explain the different results of the reaction of cyclopentanol in the presence of cyclohexanone at 350°C over zeolites (Table 13) [257]. It has been shown that alkenes and hydrogen transfer products are formed on the acid and on the basic sites of the catalyst, respectively [257]. Consequently, this type of analysis makes it possible to estimate the predominant nature of the solid.

Efficient and selective diazomethane methylation of alcohols and haloalcohols leading to the corresponding methyl ethers has been accomplished by using H^+-exchanged X zeolite as catalyst instead of H_2SO_4 [258]. The reactions with propene and isobutene glycols over zeolite provide regioselective methyla-

Table 12
Activities of different catalysts for the reaction of a cyclopentanol-cyclohexanone mixture



Product	Catalyst activity (10^{-3} mol h^{-1} g^{-1})					
	MgO	A	KA	NaCsX-1	NaCsX-2	NaCsX-3
Cyclohexanol	33	0	23	7	5	8
Cyclohexene	0	10	1	1	2	8
Cyclopentene	0	92	2	3	15	29

Table 13
Selectivities of ion-exchanged X zeolites for *N*-methylaniline formation (NMA) and Σ*N*-alkylation at various conversions at 673 K

Zeolites	Conversion (%)				
	5	10	27	40	60
NMA					
LiX	—	43.0	48.0	45.0	20.0
NaX	—	43.5	39.0	38.0	16.0
KX	82.5	68.5	39.0	38.0	—
RbX	83.5	72.5	57.0	—	—
CsX	72.5	65.0	75.0	81.0	86.0
ΣN-alkylation					
LiX	—	51.0	60.0	58.0	30.0
NaX	—	43.5	47.0	46.0	20.0
KX	100	85.4	70.0	76.0	—
RbX	100	88.0	85.0	—	—
CsX	80	73.5	77.5	86.0	92.0

tion of the primary OH, whereas secondary and tertiary OH also react using H_2SO_4 as catalyst. The reactions of 2-aminoethanol and 2-mercaptoethanol exhibited high chemoselective *N*-monomethylation and *S*-methylation, respectively [258]. The mechanism over zeolite is proposed to involve acid/base bifunctional catalysis in which the acidic site reacts with diazomethane to form its conjugated acid and the nucleophilicity of OH and SH groups is enhanced by interaction of the basic sites with the proton of the groups [258].

Alkali-exchanged beta and EMT zeolites catalyze the alkylation of aniline by methanol predominantly at the nitrogen atom [139]. By using a series of alkali exchanged X and Y faujasites on the methylation of aniline at 400°C, it has been shown that the activity and the selectivity depend on the acido/basicity of the catalyst (Table 13) [259]. The selectivity may be oriented toward alkylation on the nitrogen or on the aromatic ring. By comparing the selectivity at equal conversion levels, it has been established that the outcome of the reaction is governed by the balance between the basicity of the framework oxygen atoms and the Lewis acidity of the cation in the cages [259]. Thus, K-, Rb- and Cs-exchanged X and Y zeolites (X is more active but deactivates more rapidly) favor the formation of *N*-methylaniline, while Li- and Na-exchanged zeolites give rise to *para* and *ortho*-toluidine together with small amounts of 2,4- and 2,6-dimethylaniline and *N*,*N*-dimethyl-*para*-toluidine [259]. These conclusions have been further expanded by including in the series the Na^+-form of EMT, L and mordenite [260]. It was found that besides the acid/base properties of the solid, a geometric effect – characteristic of each structure – has to be taken into consideration when accounting for the ratio between *N* and *C*-methylation of aniline [260]. Similar influence of the acid/base site balance has also been found to be responsible for the results of aniline methylation over AlPOs, SAPOs and MAPSOs [261]. Other factors besides acid/base pairs and geometry of the micropores such as reaction temperature and contact time can also play a role on the selectivity masking the real influence of acid/base properties of the solid. Thus, it has been reported that the efficiency for the *N*-alkylation in the vapor phase reaction of aniline with isopropanol over Y and ZSM-5 zeolites decreases as the contact time or the reaction temperature increases [140]. The main *C*-alkylation product of this process is the *ortho* isomer.

Toluene methylation with methanol has been studied over a variety of solid acid catalysts including $AlPO_4$ and $AlPO_4$ supported on alumina [262]. It has been found that the selectivity toward xylenes or styrene depends critically upon the acid/base nature of the solid [263]. In Brönsted sites, methanol is preferentially adsorbed and attacks the aromatic ring of toluene. In contrast, toluene is more strongly bonded than methanol on strong basic zeolites [263]. An analogous situation also applies for ethylbenzene alkylation with methanol in the presence of X faujasites [264]. Thus, alkylation can occur either on the aromatic nucleus or on the lateral side-chain depending on the acidic or basic nature of the sites [264]. Magnesium aluminum hydrotalcites, considered moderately basic solids, have beeen found to be also active for the vapor phase alkylation of phenol with methanol [265]. The combined participation of acid and base sites to the success of the process has been invoked [265].

Aldolic condensations and related reactions can be catalyzed both in the presence of acids or bases [13]. By studying a series of alkali exchanged zeolites on the condensation of acetone, it has been concluded that the activity of the catalyst is better understood considering the solid as an acid–base pair rather than taking it as acidic or basic separately [266]. The partial negative charge on the framework oxygens would be an indication of the relative basicity of the sites, while the charge of the cation divided by the square of its atomic radius can be taken as an appropriate measure of its Lewis acidity. The same conclusions have been reported to apply to the methylbutynol rearrangements and to the reaction of monoethanolamine [266].

Cross aldolic condensation of acetaldehyde and formaldehyde into acrolein has been carried out over Y, mordenite and ZSM-5 [267]. It has been suggested that the activity of the solid catalyst depends on the balance between acidic and basic sites, rather than exclusively on its acid strength. In this regard, it has been found that oxides deposited over ZSM-5 and Y faujasite enhance the activity toward acrolein formation, 4 wt% MgO/ZSM-5 being the best performing catalyst of the series prepared. This results has been interpreted in terms of a cooperation between the basic MgO centers and the zeolite acid sites [268]. Analogously, condensation of isobutene and formaldehyde to isoprene can be effected using beta zeolite [269]. Vapor-phase condensation of aldehydes with ammonia to form pyridines has been reported over HZSM-5 as catalyst [270].

2.10. *Bifunctional acid catalysts*

Aromatic compounds result from the isomerization of dicyclopentadiene or its monomer over Pt-/H-ZSM-5 [271]. In this case, it has been established that the products having the structure of methylindane and tetralin are derived from the bridge-head C–C bond scission. The activity of the catalysts tested for this process was dependent both on the acidity and hydrogenation ability of the solid [271]. Although pentanes and cyclopentanes were found not to be intermediates in the dicyclopentadiene aromatization, reforming of alkylcyclopentanes can be carried out over Pt/H-Beta (Si/Al 260, 0.5 wt% Pt), its excellent performance being the result of the correct balance between Brönsted acidity and metal loading [272].

The presence of acid sites introduced by NH_4^+ or La^{3+} has been observed to play a negative effect on the dehydroisomerization of *n*-butane to isobutene over Pt/Cd4A catalysts [273].

The isomerization of small alkanes has been compared over Pt/H-mordenite and Pt/ZrO_2-SO_4, having similar concentrations of Pt and acid sites as well as similar strengths of Brönsted acid sites (Table 14) [274]. It was found that the apparent activation energy

Table 14
Reaction of *n*-pentane and *n*-butane over solid acid catalysts at 479 K

	PtHMor	Pt-ZrO_2/SO_4	
	n-pentane	*n*-pentane	*n*-butane
n-Alkane conversion (%)	16.9	24.8	3.45
Total conversion rate (10^{-7} mol g^{-1} s^{-1})	3.36	6.69	0.995
Isomerization rate (10^{-7} mol g^{-1} s^{-1})	3.26	6.13	0.944
Selectivity (%)			
$CH_4 + C_2H_6 + C_3H_8$	2.28	1.76	—
i-C_4H_{10}	—	—	94.8
i-C_5H_{10}	96.9	91.6	0.22

of *n*-pentane isomerization is significantly higher over the zeolite. This higher activation energy has not been rationalized, however, as reflecting differences in acid strength but, more likely, is due to the geometric constraints imposed by the one-dimensional micropore structure of mordenite [274]. Assuming isomerization as a bimolecular process via intermediate dimer formation, it would be more sterically inhibited inside the mordenite channel system. Comparison of Pt-loaded H-beta, H-mordenite and HZSM-5 for the isomerization of *n*-hexane has shown that Pt/H-beta exhibits the highest activity and selectivity, probably due to the three-dimensional topology of this zeolite as well as the medium strength of its sites (Table 15) [275]. By adjusting the balance between metallic and acid sites, a beta catalyst possessing the highest activity and selectivity was obtained [275].

Table 15
Isomerization of *n*-hexane on Pt-loaded zeolite catalysts

	Pt/H-Beta	Pt/H-mordenite	Pt/HZSM-5
Conversion (%)	72.4	14.2	46.0
Selectivity to isomerization (%)	95.6	81.3	89.4
$< C_6$	4.4	18.7	10.6
2,2-DMB [a]	8.7	6.0	0.1
2,3-DMB [a]	10.7	10.9	0.9
2-MP [b]	46.8	40.4	69.1
3-MP [b]	29.4	24.0	19.3

[a] Dimethylbutane.
[b] Methylpentane.

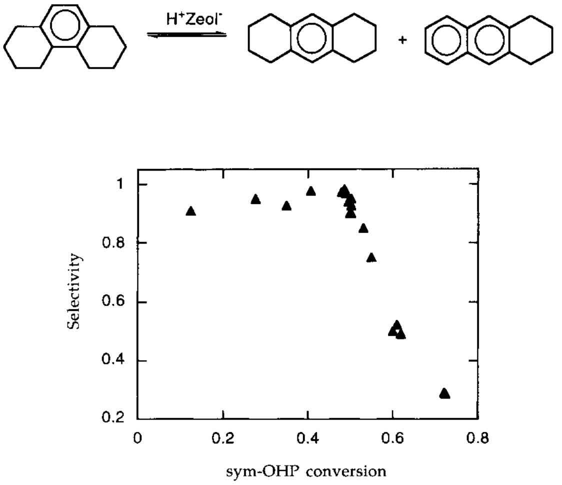


Fig. 26. Selectivity toward *sym*-octahydroanthracene plus 1,2,3,4-tetrahydroanthracene vs. conversion of *sym*-octahydrophenanthrene using a series of Y and mordenite zeolites as catalysts.

NiHY was found to be the least active but most selective catalyst among of a series of nine protonic and bifunctional Y and mordenite zeolites for the ring shift isomerization of *sym*-octahydrophenanthrene into *sym*-octahydroanthracene (Fig. 26) [276]. This effect has been ascribed to the lower total acidity and lower content of stronger acid sites of NiHY. On the other hand, Pt- or Pd- loaded H-mordenites display a high selectivity (nearly 100%) for the conformational isomerization of *cis*-decalin to the more stable *trans*-isomer (chemical yield $> 90\%$) [277]. Purely acidic zeolites like HY, LaHY and H-mordenite were found not to be as effective as the noble metal modified mordenites [277].

Alkali-earth exchanged NaY promoted with Ni has been found to be active for dimerization of butenes [278]. For these catalysts with similar activities, dimer selectivity increases with increase in the cationic size of the alkali-earth metal. This is attributed to the increased adsorption of olefins on the more acidic catalysts [278].

Catalytic conversion of acetylene to higher hydrocarbons has been accomplished by a bifunctional Ni modified HZSM-5, which combines the catalytic activity of the added Ni with the acidic/shape selectivity of ZSM-5 [279]. H_2O was found to be a necessary co-reactant for this process and it is believed that acetaldehyde arising from the hydration of acetylene is the primary intermediate which reacts further with acetylene to give propyne plus CO.

By using a bifunctional catalyst consisting of Pd supported on ZSM-5, it is possible to carry out the one-point transformation of acetone into methyl isobutyl ketone through hydrogenation of the mesityl oxide intermediate [280]. Shape selective hydrogenation of naphthalene to *cis*- or *trans*-decalin can be achieved using Pt- or Pd-loaded HY and H-mordenites [281]. Pt/HY shows a high selectivity (80%) toward *cis*-decalin, while selectivity for *trans*-decalin increases with the fraction of weak acid sites on the zeolite [281].

Acidic Cu-exchanged mordenite has been found to promote the nucleophilic aromatic substitution of chlorobenzene with H_2O to give phenol [282].

2.11. Acid sites as single-electron acceptors

Spontaneous generation of radical cations of electron-rich organic compounds by adsorption into acid zeolites is a well-documented process that might have implications on the mechanisms of catalytic reactions. Thus, mere adsorption of thianthrene into Brönsted acid zeolites affords the corresponding thianthrenium radical cation, [283] a probe species that has been thoroughly studied in solution. This thianthrenium radical cation has been characterized inside the zeolite matrix by diffuse reflectance spectroscopy (Fig. 27), IR and EPR spectroscopies. Thianthrenium radical cation embedded within HZSM-5 was found to be stable for periods longer than several months [283]. Radical cation of fluorene was also observed on H-mordenite [284]. By preparing a consistent series of samples having exclusively Brönsted or Lewis acid sites, it was shown that the single electron acceptor ability of the zeolite is related to Brönsted acid sites [283,284].

In fact, by means of variable temperature EPR techniques it has been shown that radical cations of olefins generated by pulse radiolysis undergo rapid isomerization reactions inside the zeolite micropores, even at 4 K [285]. That this type of intermediates may be more general in catalysis over zeolites than it is currently recognized can be exemplified by the fact that adsorption of 4-*n*-propylanisole onto ZSM-5 allows to detect the corresponding radical cation of the anethol (Scheme 18) [286]. Probably, this type of electron acceptor sites capable to generate radical cations are also related to the superacidic behavior of sulfated zirconia [287,288].

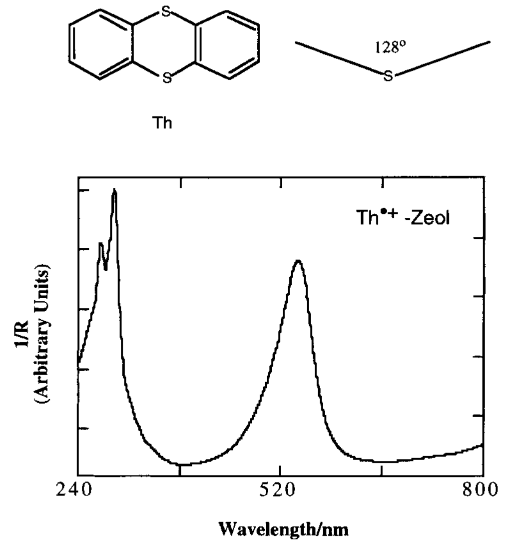
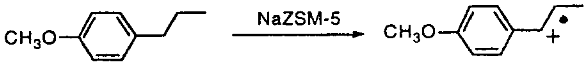


Fig. 27. Diffuse reflectance spectrum of thianthrenium radical cation ($Th^{\bullet +}$) generated by simple adsorption of neutral thianthrene (Th) onto acid-5. The characteristic dihedral angle defined by the benzo groups of Th is also shown.



Scheme 18.

Mononitration of aromatics with dinitrogen tetraoxide has been investigated over silica–alumina and large-pore beta zeolite [199,289]. It was found that the activity correlates better with the ionization potential of the aromatic than with the Hammett parameter. This finding conflicts with the classical electrophilic aromatic substitution, but agrees with the formation of an aromatic radical cation intermediate and its coupling with a nitrogen dioxide radical [199]. It has been suggested that the electron acceptor sites on the catalyst surface are generated by the nitrogen dioxide radicals.

2.12. Acidity scale by in situ NMR studies

NMR spectroscopy has proved that liquid superacids can generate at low temperatures five-coordinated carbonium ions and primary carbenium ions with a persistence and concentration high enough to allow their detection and a study of their properties. Generation and stabilization of carbenium ions has been, therefore, considered as the most genuine characteristic of superacids.

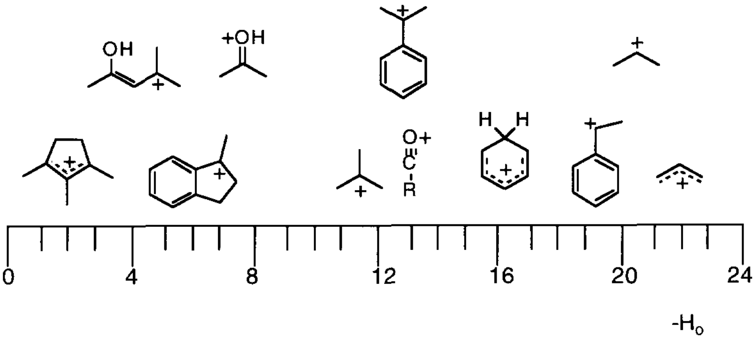
Many of these positively charged species are generally believed to be reaction intermediates in zeolite catalysis. The question arises whether the lifetime of these carbenium ions and their concentration on zeolite surfaces is sufficiently high to be characterized by in situ NMR techniques. The results of a systematic study of more than 80 ^{13}C-labeled probe molecules adsorbed on dehydrated zeolites at different temperatures has led to the conclusion that only relatively stable free carbenium ions are formed in high concentrations upon incorporation of convenient precursors, while other more unstable carbenium ions like ethyl, isopropyl, allyl, phenethyl carbenium ions cannot be detected as free ions or are not formed at all [290].

Based on the acid strength of the carbenium ions that can or cannot be detected, as well as on the scale to measure the acid strength in liquid superacids consisting in the use of relative shifts in the ^{13}C signals of mesityl oxide [291], it has been concluded that the acid strength of zeolites compares to a 70% aqueous solution of sulfuric acid. Therefore, the claim that acid zeolites are superacid solids appears to be incorrect (Scheme 19).

Aldolic condensation of aldehydes and ketones can be carried out over basic [292] and acid solids [293]. The course of this reaction on acid zeolites has been investigated by solid state ^{13}C-NMR of ^{13}C-labeled acetone and cycloalkanones [293]. The primary aldolic condensation is followed by secondary reactions such as double-bond migration, hydrogen transfer and cracking. The strength of the initial complex between the starting ketone and the Brönsted acid sites of the zeolite can be determined quantitatively by the significant changes in the isotropic chemical shift of the carbonyl group carbon [293]. The extent of proton transfer may vary from almost complete proton transfer for mesityl oxide and crotonaldehyde to almost complete absence of proton transfer for chloroacetones [294]. For acetone, the hydrogen-bonded adsorption complex is stable at room temperature and coverages below one molecule per Brönsted site [294]. It was found that the strength of the sites follows the order HZSM-5 > HY > HX. As the most salient conclusion, zeolites do not exhibit a superacidic behavior at 25°C, since hydroxycarbenium ions or free carbenium ions do not form as long-lived, detectable species under these conditions [267,293]. After solid–liquid extraction of the reaction products, their chemical structure and distribution do not differ with those obtained in solution, although minor shape-selectivity was observed in the formation of trindane from cyclopentanone on large pore zeolites but not on medium pore zeolites [293].

3. Ordered mesoporous molecular sieves as acid catalysts

In many cases the reactant is too large to diffuse into the channels and cavities of the zeolites and, then, most of the reaction occurs on the external surface of



Scheme 19.

the zeolite crystallites. Certainly, one may decrease the crystal size of the zeolite and, therefore, increase the external surface area, but there is no doubt that it will be more adequate to use acid catalysts with larger pore diameters.

Recently, researchers from Mobil have discovered a new family (M41S) of long-range ordered mesoporous materials, whose pores are arranged in a hexagonal (MCM-41) or cubic (MCM-48) structure [295]. The wall of these materials can be formed by tetrahedrally coordinated silicon and aluminum, and then the resulting products have Brönsted acid sites similar to those of amorphous silica–alumina [296]. The resulting acidity is milder than that of USY zeolites but, nevertheless, should be able to catalyze reactions requiring sites with low and medium acid strengths.

The benefit in the combination of large pores and mild acidity has been shown during the Friedel–Crafts alkylation of 2,4-di-*tert*-butylphenol with cinnamyl alcohol [297]. While a large-pore HY zeolite has the adequate acidity to carry out this reaction, only very minor amounts of the desired Friedel–Crafts product di-*tert*-butylbenzopyran were observed, being dealkylation with loss of the acid labile *tert*-butyl group the major process over acid faujasite. There is little doubt that the diffusional restrictions of bulky di-*tert*-butylphenol through the windows of faujasite are responsible for the difference in the observed product distribution. However, when using an aluminum-containing MCM-41 with pore size of 30 Å, dihydrobenzopyran is formed via the intramolecular ring closure of the primary cinnamylphenol. Analogous pore-size effects were observed during the *tert*-butylation of anthracene, naphthalene and thianthrene [298].

The mild acidity combined with the large pores of MCM-41 has been especially useful for carrying out reactions such as acetalyzation, [299] Beckmann rearrangement, [300] glycosidation [301] and aldol condensations [302]. In this way, the acetalation of differently sized aldehydes with orthoformate, [299] such as *n*-heptanal, 2-phenylpropanal and diphenylacetaldehyde, clearly shows that when the reactants can diffuse through the pores of zeolites (zeolite Beta), the activity of the micro is larger than that of the mesoporous catalyst. However, when a bulkier reactant has to be used, the activity of the mesoporous MCM-41 can be much larger.

In the case of organic reactions occurring in the liquid phase, one has to be aware that not only the initial activity of the catalyst is important, but it is also very important for the success of the process to avoid, or at least to slow down, the deactivation of the catalyst during the reaction. The acetalation of the bulky diphenylacetaldehyde is a very nice example of the importance of the rapid diffusion of the products to minimize catalyst deactivation. This is clearly revealed by the reaction rate of acetalation on HY, which is initially higher than that for MCM-41, but it decreases rapidly as the zeolite becomes poisoned due to by-products which are not able to diffuse outside the *a*-cavities, thus resulting in a conversion smaller than 60%. In contrast for MCM-41, even though the initial rate is somewhat smaller, the catalyst decay is slower than for HY and, consequently, 100% conversion is achieved within sufficiently long reaction time.

MCM-41 is also active in catalyzing the acylation of activated aromatic rings such as 2-methoxynaphthalene with acetic anhydride. At 132°C and using chlorobenzene as solvent, turnover numbers of 20, 17 and 11 were obtained when using acetic, benzoic and isobutyric anhydride, respectively, as acylating agent. However, most of the acylated product corresponds to the 1-acylated 2-methoxynaphthalene, being the very little yield of the most desired six position isomer.

It is highly surprising how little work has been reported on the applications of MCM-41 and MCM-48 to the field of fine chemicals. There is no doubt that, when these materials will be more readily available to organic chemists, the impact of these materials as catalysts for organic reactions will be strongly felt.

4. Heteropolyacids as catalysts for organic chemistry

Heteropolycompounds are formed by the condensation of two or more different type of oxoanions, as for instance:

$$12\,WO_4^{2-} + HPO_4^{2-} + 23\,H^+ \longrightarrow PW_{12}O_{40}^{3-} + 12\,H_2O$$

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 it can also be others, such as U, Nb, Ta, single or in combination. Most of the catalytic work has been done on the Keggin structure ($XM_{12}O_{40}$), and more specifically with the 12-tungstophosphoric acid (HPW).

In the case of heteropolyacids, and owing to 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. However, from the point of view of catalysis, more important than total acidity is the number of acid sites which are accessible to reactants. Thus, in the case of HPAs with surface areas $< 10\,m^2\,g^{-1}$, it may occur that one may use only a part of the potential acidity of the material. Fortunately, this is not the case when dealing with polar reactants. Indeed, HPAs can take up polar molecules in amounts that correspond to more than 100 surface layers and, in this case, their catalytic behavior has been called 'bulk-type catalysis' [303]. When this occurs, the reaction takes place not only on the surface but also in the bulk solid, being the practical effect as if one would have a highly concentrated solution in which all acid sites are accessible to reactants. Thus, HPAs are very active catalysts for carrying out the dehydration of alcohols, being the rate of the reaction proportional to the catalyst weight regardless of its specific surface area [304]. There is no doubt that if a catalyst is highly active for a given reaction (dehydration of alcohols), it should also be very active for the opposite reaction (hydration of olefins to alcohols), provided that the reaction conditions are adequate. In the case of HPAs, they are commercially applied for performing the hydration of propene to isopropanol with a conversion $> 70\%$, and a selectivity of 99% [305–308].

Isobutene is selectively hydrated in the presence of *n*-butene, and this fact can be used to separate both gases in the C_4 streams from steam and catalytic cracking. When the process is carried out in a multi-stage reactor, isobutene is 100% converted, while $< 1\%$ of *n*-butene is hydrated. In this case, the heteropolyacid not only acts as a strong acid catalyst but is also able to increase the solubility of butene, while stabilizing the reaction intermediates by coordination to the polyanion [309].

Heteropolyacids have also shown very interesting possibilities as esterification catalysts for the production of phthalic acid diesters in the acid catalyzed esterification of phthalic anhydride by the corresponding alcohol [310].

Other acids such as *para*-nitrobenzoic and dipicolinic acid (DA) have also been esterified with ethanol and butanol on HPAs and its salts to produce ethyl *para*-nitrobenzoate (intermediate for the preparation of anesthetics), and DA diester (intermediate for pharmaceutical) [311].

When non-polar reactants have to be used, then one is forced to increase the surface area of the heteropolyacid. This can be done in two 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 ($> 70\,m^2\,g^{-1}$) due to the packing of the small particles (< 150 Å) in which they are synthesized [312]. The final surface area is strongly dependent on the level of proton substitution by the large monovalent cation as well as on the nature of the cation [303]. A compromise should be found in this case between the increase of surface area upon alkaline ion exchange, and the acidity lost by proton substitution. An optimum appears to occur for cation contents between 2 and 2.5 (out of a maximum of three) [312–314].

The second procedure for increasing the surface area of the HPAs consists in supporting them on a high surface-area carrier. Suitable carriers should not have basic properties and Si, C, ZrO2 and MCM-41 are suitable ones [303,315–318].

The salts and the supported HPAs have been used for alkylation of phenol with olefins with better results than more conventional acid catalysts such as resins and H_2SO_4 [319–324].

Condensation reactions such as the condensation of acetone to mesityl oxide and alkylbenzenes, the condensation of ketones and phenols to produce bisphenols, and the condensation of isophytol with 2,3,5-trimethylhydroquinone for the synthesis of vitamin E[325–327] have been successfully carried out on heteropolyacids.

More demanding reactions, such as the acylation of aromatics and aliphatic hydrocarbons with acyl chlorides as well as with anhydrides and even acids, can also be carried out on supported HPW and HSiW, as well as on Cs^+ salts of HPA [312,328–331].

We see from the foregoing that many opportunities are still open for the use of heteropolyacids in the field of organic chemistry, substituting environmentally unfriendly Brönsted and Lewis acids such as H_2SO_4, $AlCl_3$, $ZnCl_2$, etc.

5. Sulfated zirconia as solid acid catalyst

In contrast to zeolites, it is widely accepted that sulfated zirconia and related promoted oxides can behave as superacid solids. This assumption is mainly based on the acid demands of the reaction types that can be catalyzed by sulfated zirconia under moderate conditions. The influence of the various parameters during the preparation of sulfated zirconia on the resulting acidity and performance of the material has been the subject of intensive studies [332–337]. An example is presented in Fig. 28.

A series of sulfated zirconia samples varying the preparation procedure and the presence or absence of metal dopants have been tested for the regioselective dehydration of 4-methyl-2-pentanol to afford 4-methyl-1-pentene [338]. Other by-products include the more substituted 4-methyl-2-pentene, and isomeric C_6 olefins as well as the 4-methyl-2-pentanone. The acid–base properties of the catalyst appear to play a role governing the product distribution. A well-balanced number of both acid and base sites seems to be necessary in order to achieve a good selectivity to the desired terminal alkene. Isopropanol conversion over sulfated zirconia has also been studied [339]. Other alcohol dehydrations that have been effected over sulfated zirconia include cyclohexanol [340].

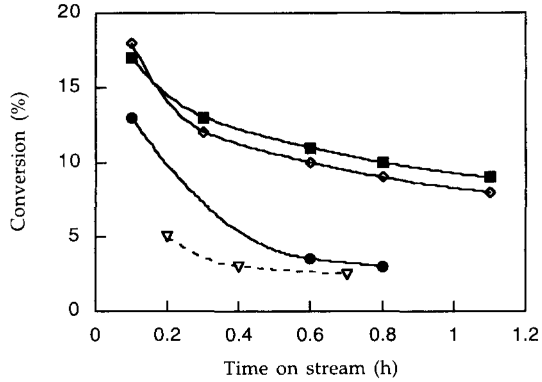


Fig. 28. Variation of *n*-butane conversion with time on-stream during the isomerization of *n*-butane on a sulfated zirconia (SZ) series working at 150°C and W/F 40 g_{cat} h $(mol_{c4})^{-1}$. (■) SZ, sulfur content 2.6 wt%, S_{BET} 125 $m^2\ g^{-1}$, peak on DTA 851 K; (◇) SZ, sulfur content 2.4 wt%, S_{BET} 127 $m^2\ g^{-1}$, peak on DTA 836 K; (●) SZ, sulfur content 1.3 wt%, S_{BET} 71 $m^2\ g^{-1}$, peak on DTA 835 K; and (▼) SZ, sulfur content 1.3 wt%, S_{BET} 71 $m^2\ g^{-1}$, peak on DTA 724 K.

Oligomerization of ethene and cyclopropane and H–D exchange can be effected over sulfated zirconia [341]. Dimerization of butene in the presence of doped sulfate and tungstate zirconia has been studied. Beneficial influence of dispersed NiO toward the selectivity of linear octenes has been interpreted as resulting from tempering of the surface acid strength [342].

A distinctive behavior of sulfated zirconia compared to titania and zinc oxide has been observed by FTIR after adsorption of allylbenzene onto these solid acids [343]. While the former gives rise to extensive polymerization, adsorption on ZnO and TiO_2 allowed to characterize an intermediate identified as the π-allylbenzyl which can undergo subsequent benzylic C–C bond breaking leading to oxidized degradation products. The preferred attack on the C=C double bond or on the allylic/benzylic positions seems to be related with the nature of the sites.

Zirconium phosphates (P-to-Zr ratio lower than two) have been used for the vapor and liquid phase alkylation of anisole with alcohols. It was found that, for the methylation in the vapor phase, the product distribution including phenol and methylated anisoles is similar to that exhibited by Nafion-H resins, but zirconium phosphate activity was found to be higher than that of superacid Nafion-H resins [344]. Efficiency of sulfated zirconia as catalyst for the transalkylation of diisopropylbenzene with benzene and substituted benzene has been found similar to those of zeolites and acid-treated clays [345].

Protium-deuterium exchange occurs between isobutane and D_2O-exchanged sulfated zirconia [112]. It has been observed that the induction period characteristic when the reaction is carried out below 100°C is suppressed adding small amounts of isobutene, indicating that H–D exchange may occur through the alkene as reaction intermediate [112].

Isomerization of linear alkanes, including propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-hexadecane and methylcyclopentane at low temperatures (typically ranging from room temperature to 60°C) using sulfated zirconia has attracted considerable attention in recent times. A review covering the various aspects of the preparation procedures of sulfated zirconia superacids for their use as catalysts in the reaction of butanes and pentanes has been recently published [346]. It was found that the pH of precipitation of the precursor $Zr(OH)_4$ has a profound effect on the crystalline ZrO_2 and on its subsequent catalytic properties [334]. Sulfated tetragonal phase rather than sulfated monoclinic ZrO_2 seems to be the active crystalline phase of this material [347,348]. The optimum calcination temperature has been found to be ca. 600°C [348–350] and the isomerization efficiency is strongly dependent on the presence of H_2O, both in the catalysts and in the feed [351]. Using *n*-hexadecane as test molecule and carrying out the reaction in a batch reactor, it has been found that the activity of the sulfated zirconia is independent on the source and method of sulfur addition, including $(NH_4)_2SO_4$, H_2S, SO_2 and H_2SO_4 [352].

A relationship between the number of superacidic sites and the activity for *n*-butane isomerization has been observed (Fig. 29) [334]. It has been found that the isomerization of *n*-pentane over Pt-doped sulfated zirconia is seven times higher than that of *n*-butane [353]. Comparison of the performance of sulfated zirconia with zeolite beta for the *n*-butane isomerization and isobutane alkylation of 2-butene has revealed a higher activity and selectivity of sulfated zirconia (Fig. 30) [332]. This catalyst is active at much lower reaction temperatures than the zeolite [288]. This higher efficiency of sulfated zirconia has been related to the presence of superacidic sites. A different conclusion based on the confinement of the acid sites in a restricted space has been proposed to explain the difference in activity of Pt-doped sulfated zirconia and Pt/H-mordenite [274]. Under conditions where *n*-butane isomerization is rapid over Pt/ZrO_2-SO_4, it is undetectable over doped mordenite. It has been discussed that the rate of a bimolecular pathway such as isomerization of *n*-butane or hydride-ion transfer would be sterically inhibited in the one-dimensional micropores of mordenite [274]. Observation that the addition of CO reversibly suppresses the activity of sulfated zirconia toward *n*-butane isomerization at 150°C, together with IR analysis of the CO adsorbed onto ZrO_2/SO_4, has led to the conclusion that Lewis acid sites play a dominant role in the catalysis [354]. In other reports, based on IR spectroscopy of adsorbed pyridine, it has been proposed that for *n*-butane isomerization at 150°C there is a simultaneous contribution of both Brönsted and Lewis acid sites. Raman, diffuse-reflectance and ESR spectroscopic analysis of deactivated sulfated zirconia have revealed that allylic and polyenylic cations as well as polycyclic aromatic compounds are responsible for the deactivation of this superacid solid during *n*-butane isomerization at tem-

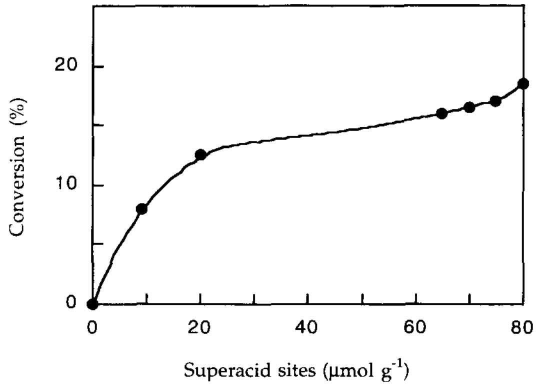


Fig. 29. *n*-Butane conversion on sulfated zirconia catalysts as a function of the population of superacidic sites measured by ammonia TPD.

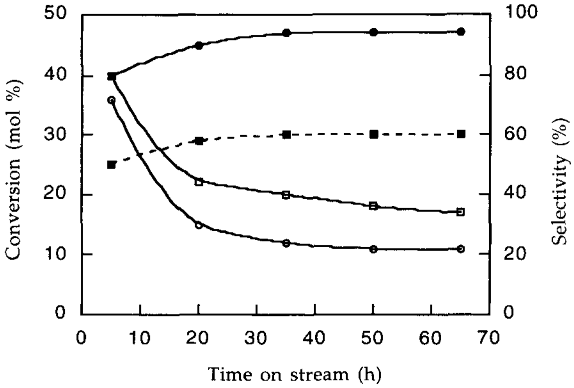


Fig. 30. *n*-Butane conversion (○,□) and selectivity to isobutane (●,■) as a function of the time on-stream, obtained on sulfated zirconia catalyst at 250°C (○,●) and H-Beta zeolite at 300°C (□,■) reaction temperaturre.

peratures between 120° and 200°C. The formation of these poisons is largely prevented by the presence of H_2 as co-feed [355].

Zirconia–silica aerogels exhibit higher activity in 1-butene isomerization than mechanically mixed samples or each single component of the aerogel separately [356,357]. Even at levels as low as 1–5 mol%, silica retards surface-area loss, zirconia-phase transformations while enhancing the catalytic activity [356]. Activity of sulfated zirconia for skeletal isomerization and hydrogen transfer processes of cyclohexene reaction was found to be higher than that of the non-sulfated oxide [358].

Transition metal doping including Zn, Ni, Co, Fe, Mn, W, Ir, Pt, Rh, Ru, Os has been found to greatly promote *n*-alkane rearrangement [359–365]. A systematic study of the doping with first-row transition metals led to the conclusion that the activity of the promoted sulfated zirconia for the *n*-butane isomerization increases from right to left in the Periodic Table (Fig. 31) [366]. It has been reported that a sulfated oxide of zirconium, iron and manganese can isomerize *n*-butane at 35°C with rates two-to-three orders of magnitude higher than sulfated zirconia [366–368]. A study of the effect of the Pt concentration on the activity and selectivity of sulfated zirconia for the hydrocracking and hydroisomerization of *n*-hexadecane has shown that the maximum increase in conversion occurs at the 0.6–1.0 wt% Pt concentration [369]. Further increase of Pt up to 5 wt% does not vary the activity. At constant conversion, the selectivity for isomerization and cracking is independent on the Pt content [369]. Sulfated zirconia doped with two different transition metals have been tested for the *n*-butane isomerization [370]. Combination of two metals can result in an enhancement or diminution of the catalytic activity of the sulfated zirconia [370]. Addition of 0.4 wt% of Pt to Fe and Mn-doped sulfated zirconia increases 2.5 times the activity for *n*-butane isomerization at 35°C compared to Pt-free doped sulfated zirconia [371]. Apparently, the metal limits its role to favoring hydrogenation/dehydrogenation mechanisms, inhibiting the formation of carbonaceous deactivating poisons. Thus, metal promoters would allow the operation of a bifunctional mechanism enhancing the surface concentration of olefins rather than increasing the acid strength of the sites [372]. As a result, a remarkable increase in the lifetime of the catalyst is observed [373] According to this scheme. it has been found that Ir- and Pt-doping gives the most active sulfated zirconia [337,373]. Besides hydrogen, small quantities of adamantane have been used as suitable hydrogen transfer agents to increase isomerization rate while inhibiting accompanying cracking reactions [374].

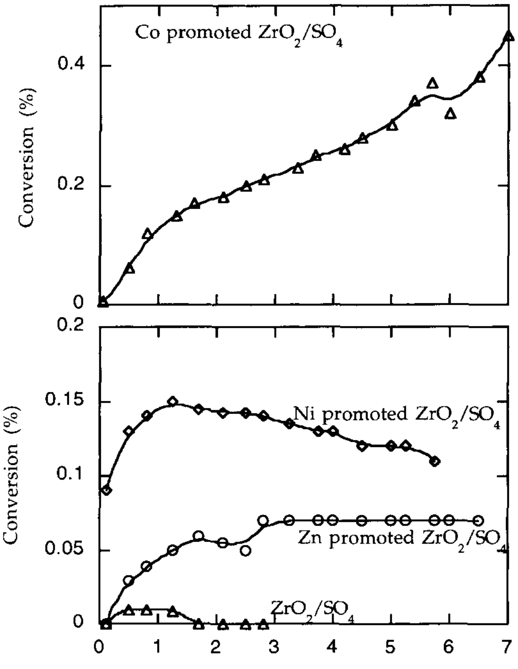


Fig. 31. *n*-Butane conversion in a flow reactor in the presence of cobalt promoted sulfated zirconia (A) as well as nickel- (B,◇), zinc (B,O) promoted, and unpromoted sulfated zirconia (B,△).

Concerning the mechanism of this skeletal isomerization, analysis of double ^{13}C-labeled *n*-butane shows that at low temperatures rearrangement is a intermolecular process that involves the intermediacy of a C_8 surface-bound intermediate which rearranges before undergoing ß-scission. The iso-C_4 fragments are desorbed as *i*-butane [375]. However, similar studies conducted at 250°C using single ^{13}C-labeled *n*-butane lead to the opposite conclusion that isomerization is a unimolecular process [372]. According to a kinetic study, the isomerization rate for *n*-butane is conveniently described by a reversible, bimolecular surface reaction between two adsorbed *n*-C_4 species, probably through a C_8 intermediate, to form one *i*-C_4 species

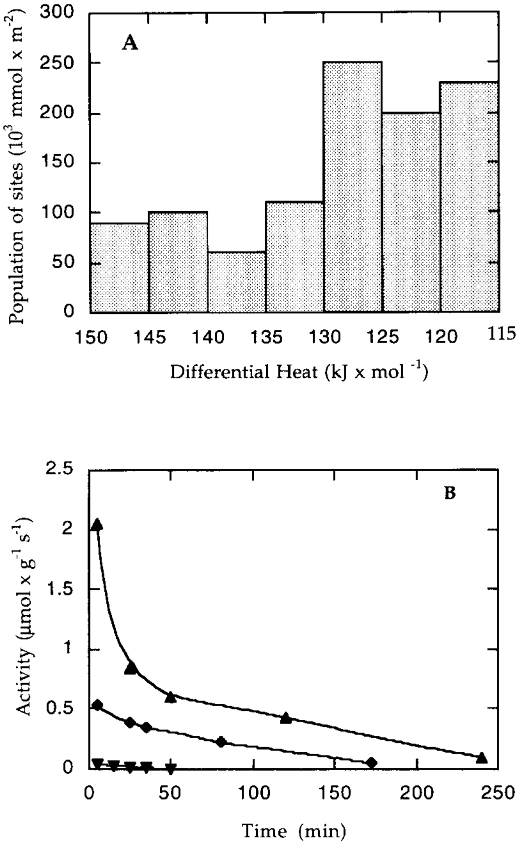


Fig. 32. (A) Histograms of acid strength distribution for a sulfated zirconia catalyst (sulfur content 1.8 wt%, S_{BET} 98 m^2 g^{-1}, calcined at 848 K) determined from plots of differential heats of NH_3 adsorption versus adsorbate coverage. (B) Rate of *n*-butane isomerisation at 150°C vs. time for the same fresh sulfated zirconia catalyst (▲) as in panel A, (◆) after poisoning with 30 mmol g^{-1} and (▼) 69 mmol g^{-1} of ammonia.

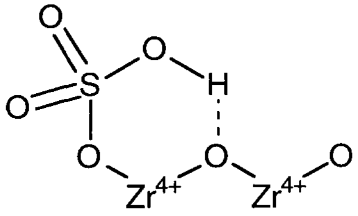
[376]. While the major operating mechanism for C_4 isomerization is intermolecular, *n*-pentane isomerization was found to be intramolecular [274]. Analogously, neopentane cracking at 450°C catalyzed on sulfated zirconia appears to be a monomolecular process giving rise to methane and *tert*-butyl cations as the primary species. No influence of iron or manganese doping was observed for this high-temperature process in contradiction of related reports on low-temperature *n*-butane isomerization [377]. On the other hand, selective poisoning of sulfated zirconia acid sites by controlled amounts of ammonia has shown that Brönsted acid sites of intermediate strength having ammonia adsorption heats between 125 and 140 kJ × mol^{-1} are more efficient and do not deactivate as fast as the strongest sites reaching 165 kJ × mol^{-1} (Fig. 32) [378,379].

The mechanism of the *n*-butane isomerization at 50°C has also been investigated over unpromoted as well as Fe, Mn-promoted sulfated zirconia using ^{13}C-labeled butane [380]. For both types of solids, the mechanism was found to be consistent with an intermolecular pathway involving a C_8-intermediate and probably olefins [380]. The acidity of the catalyst appears to be unaffected by the presence of metal promoters. Therefore, it was suggested that the role of transition-metal promoters in sulfated zirconia is to increase the surface concentration of butenes that, subsequently, intervene in the formation of the C_8 intermediates leading to isobutane [380]. The presence of small amounts of butene in the *n*-butane feed increases the rate of isomerization over Pt-doped sulfated zirconia [381]. Butene intervenes while generating the initial carbenium ions but it is immediately regenerated, thus, facilitating the chain pathways of the isomerization.

As a matter of fact, the superacidic strength of sulfated zirconia has been subjected to much controversy and revision. It has been suggested that Hammett indicators are not adequate to determine the strength of acid sites on solids. Instead, the possibility to use the protolytic cleavage of diphenylmethane at room temperature (a reaction specific to Brönsted acid sites) as a way to assess the protonic acid strength has been proposed [382]. Thus, ZrO_2/SO_4 was found more active for diphenylmethane degradation than SnO_2/SO_4, TiO_2/SO_4 or ZrO_2/WO_3, while Fe_2O_3/SO_4 and 100% sulfuric acid were totally inactive [382]. The lack of activity of pure sulfuric acid to effect the protolytic cleavage of diphenylmethane would indicate that this reaction is specific of superacidic catalysts.

In contrast to the above-mentioned claim of ZrO_2/SO_4 as superacid solid, ^1H-NMR and FTIR spectroscopic analysis using acetonitrile as probe molecule has shown that the Brönsted and Lewis sites possess a similar strength and that the lower OH frequency of doped and undoped sulfated zirconia is similar to that of acid protons in HY, but weaker than those of HZSM-5 (Table 16) [383]. These measurements suggest that the remarkable activity of

Table 16
Shifts of the OH stretching modes of some solid acids upon adsorption of CD_3CN



Samples	ν_{OH} (cm^{-1}) before adsorption	Subband A after adsorption	Subband B after adsorption	Center of the broad band
HZSM-5	3610	2770	2400	2500
HY	HF 3630	2950	2450	2750
	LF 3550			
HNaY	HF 3647	2980	2430	2800
	LF			
CsHY	HF	—	—	3200
	LF 3554			
Sulfated zirconia	3630	—	—	3200
Metal-doped sulfated zirconia	3630	—	—	3200

promoted sulfated zirconia solids (Fig. 33) may not be due to exceptionally strong acid sites, but to other reasons like stabilization of the transition state complex at the surface [383]. Likewise, 1H-NMR studies of the interaction of known amounts of H_2O molecules with sulfated zirconia at 4 K, using the broad line technique, or MAS at 300 K has established that the acidity of the solid acid is comparable to that of H_2SO_4, which means that, not being more acidic than H_2SO_4, it cannot really be described as a superacid [384].

Perhaps one of the most remarkable findings concerning the activity of sulfated zirconia is its ability to generate radical cations from benzene and alkylbenzenes [288,385]. The number of electron acceptor sites of the solid depends on the sulfur concentration while the presence of molecular oxygen from the air promotes their strength. Benzene reacts over sulfated zirconia giving a phenyl ester (sulfite or sulfate) which forms phenol by hydrolysis as well as a complex mixture of alkylbenzenes and polycyclic aromatics (Table 17) [287]. The initial step appears to be a single-electron transfer from benzene to sulfated zirconia (Scheme 20). It has been proposed that a similar scheme would apply for alkane isomerization. A fraction of substrate would form alkyl esters which then ionize to carbocations [287]. This interpretation

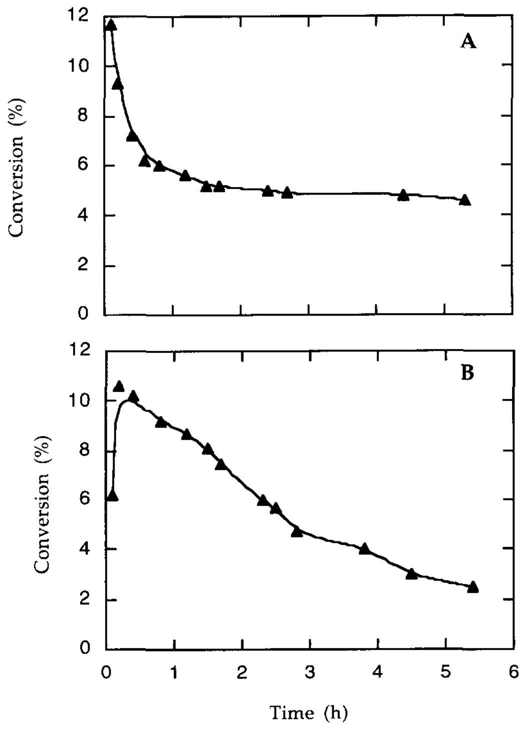


Fig. 33. *n*-Butane isomerisation into isobutane (A) in the presence of unpromoted sulfated zirconia (1.1 wt% of S) at 180°C and (B) transition metal promoted sulfated zirconia (S, 0.9 wt%; Fe, 1.5 wt%; Mn 0.5 wt%) at 60°C.

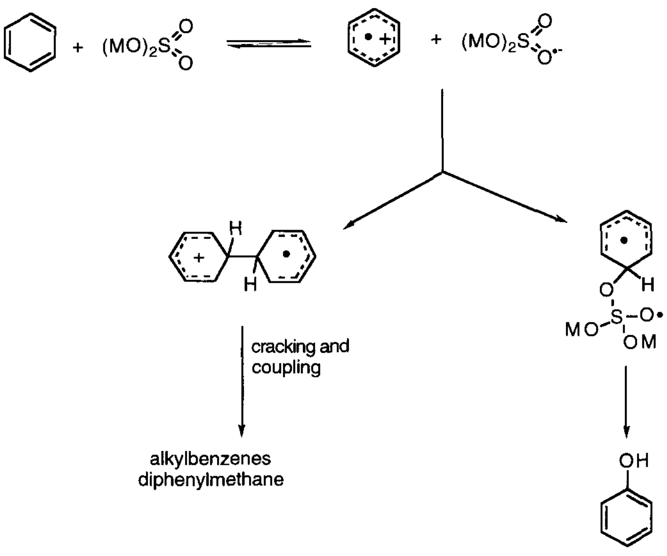
Table 17
Relative amounts normalized to diphenylmethane of reaction products after adsorbing benzene on sulfated zirconia at 100°C for different times

Product	Time	
	0.5 h	24 h
Alkylbenzenes	—	1.70
PhC_6H_{11}	—	0.18
Ph–Ph	—	0.37
Diphenylmethane	1	1
$PhCH_2CH_2Ph$		0.05
PhOH	2.98	0.28
Total conversion	6.80	17.3

is also in agreement with the results obtained in the reaction of adamantane over sulfated zirconia at temperatures from 65° to 135°C (Table 18) [386]. Small amounts of 1-adamantanol and adamantanone were observed, indicating that the reaction is really an oxidation process followed by hydride transfer. Diadamantanes were also detected, proving that the oxidation to carbocations goes through the free radical stage. At 150°C, formation of 1- and 2-adamantanethiols indicates that sulfate reduction to sulfide has truly occurred [386]. Therefore, it was concluded that the increase of activity of sulfated zirconia over the parent oxide for carbenium ion generation can be ascribed to initiation through a single electron transfer oxidation of the hydrocarbon by sulfate species [386]. In this regard, it has been observed that sulfated zirconia samples exposed to dry air at 450°C are more active for *n*-butane isomerization than those samples calcined in helium, thus, suggesting the implication of a metal 'oxy' species [387]. This oxy species may be responsible for the oxidizing abilities of active sulfated zirconia and would contribute together with acid sites to alkane isomerization [387].

IR spectroscopic studies of calcined (600°C) sulfated zirconia (2% S) have allowed to characterize SO_3 groups that were very sensitive to water, disappearing at a H_2O/S ratio close to 1.388 Upon increasing water adsorption, changes in the IR spectra are observed that have been assigned to the successive formation of adsorbed H_2SO_4, HSO_4^- and SO_4^{2-}. Based on knowledge gained about the nature of the surface groups, quantum-chemical calculations at ab initio level suggest that the acid strength of sulfated zirconia equals that of pure sulfuric acid [388]. This would imply that sulfated zirconia is not really a solid superacid but a strong acid.

Although the list of general organic transformations that has been successfully achieved using sulfated zirconia is still limited, acetalation and tetrahydropyr-



Scheme 20.

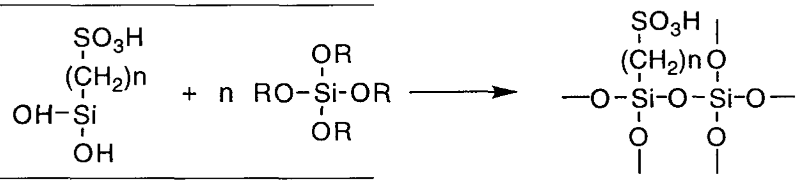
Table 18
Relative amounts of selected products in the reaction of adamantane over sulfated zirconia (SZ)

Catalyst [a,b]	Calculated T (°C)	Reaction condition	S/AdH molar ratio	Products				
				Ad–Me	AdOH	Ad=O	Ad–Ad	S comp
SZH-0.95-1	600	90°C,432 h	1.51	1	2.3	5.4	traces	—
SZH-0.95-2	600	120°C,48 h	1.40	1	0.6	4.4	6.8	—
SZH-0.95-3	600	65°C,432 h	0.93	1	18	23	6.7	—
SZH-0.95-4	600	135°C,48 h	0.98	1	0.1	0.1	traces	—
SZH-0.95-5	600	150°C,72 h	1.59	1	—	—	traces	—
SZH-0.95-3	600	150°C,48 h	1.00	1	1	9.9	—	7.3
SZO-0.95	550	150°C,168 h	1.38	1	—	12.61	0.15	4.8
SZO-2.00	550	150°C,72 h	3.15	1	0.25	0.70	—	1.1

[a] SZH and SZO have been prepared, starting either from $Zr(OH)_4$ or ZrO_2, respectively.

[b] The number 0.95 or 2.00 after the three letter code corresponds to milliliters of 0.5 M H_2SO_4 per gram of zirconia employed to prepare the sulfated catalyst.

anylation, [389] formation of acylals of aldehydes and ketones, [390] esterification of phenetyl and cyclohexyl alcohols with acetic acid has been reported. [391] C–C Bond formation between the trimethylsilyl ether of cyclohexanone and aldehydes can also be catalyzed by sulfated zirconia [392]. Co-precipitation of SiO_2 and ZrO_2 brings about a mixed oxide that exhibits superacidic behavior ($-11.4 < H_0 < -13.8$) in contrast to the separate single oxides SiO_2 or ZrO_2 which only possess weak acid sites [340]. Sulfated zirconia has proved to be an efficient catalyst for the methoxymethylation of alcohols [393]. Formation of butylated hydroxytoluene, an important commercial antioxidant, has been accomplished by reaction of *p*-cresol and isobutene over sulfated zirconia [394].



6. Organic–inorganic composites as solid acid catalysts

A series of materials involving organic and inorganic moieties have been prepared containing Brönsted acid sites. Among them, layered compounds containing layers of Zr diphosphonate groups, and pillared with organics containing sulfonic acids having high surface areas (200—350 $m^2 g^{-1}$) with a bimodal pore distribution (6, 48 Å) and strong acidity [395]. The acidity of the sulfonic group is able to carry out hydrolysis of esters and Friedel–Crafts alkylations [396,397]. However, the interlayer space can present strong diffusion limitations for bulky reactants, and because of this it can be perhaps more adequate in those cases to use polysiloxane materials. There are alkylsulfonic groups bonded to a silica matrix forming an organic–inorganic polymer with acidic properties that have been prepared via a sol–gel process [398]:

The organic–inorganic composite has high resistance to chemical attack and oxidative degradation and contrary to organic resins, it does not swell in organic media. Up to now, the number of reactions studied on these materials is limited (condensation of phenol and acetone to give bisphenol A) but they show great opportunities for alkylation, condensations, esterifications and acylations, among other.

It was known since long time ago that Nafion has very strong acid sites able to catalyze a great number of reactions occurring through carbocations [399]. However, Nafion has the handicap of a low surface area which renders it unrealistic for practical use. This limitation has been overcome recently by DuPont's research, who has produced a high surface-area Nafion resin–silica, nanocomposite with strong acid properties [400]. In the composite, the dispersed small Nafion particles offer an external surface area of 5–150 $m^2 g^{-1}$, which is much higher than the surface area of the normal polymer beads. This material is highly active for alcohol dehydration, Friedel–Crafts aromatic alkylation, α-methylstyrene dimerization and acylation of *m*-xylene with benzoyl chloride.

We are expecting the number of reactions carried out on Nafion–silica composites to enormously increase in the coming years, and to substitute other less environment-friendly acids such as HF or H_2SO_4.

7. Conclusions

It is possible to say that researchers working in material chemistry and catalysis have developed a large number of solid acids in which the acidity can go from mild to the superacid level. More than that, the acidity can be tuned and adapted to the particular reaction avoiding, to a large extent, other undesirable reactions to occur. When on top of tuning of acidity it is possible to control the pore size of the solid, and we have an additional tool to improve the selectivity in organic reactions. In reactions involving bulky reactants and products, we are not limited any more by the relatively narrow pore of microporous zeolites, since the new mesoporous materials open new opportunities for reactions requiring mild acidities.

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