Clays, Zeolites and Solid Acid Catalysts

by Arumugamangalam V. Ramaswamy

Recent developments on application of clays and zeolites as catalysts are reviewed. Examples cited here are limited to electrophilic substitution reactions, particularly the nitration and alkylation of aromatics, in which zeolites and clays form the heart of the process. A variety of zeolites have already found their way in several alkylation processes and further improvements in the design of solid acids are in the direction of improved selectivity, higher throughputs and better tolerance for impurities in the feedstock.

Solid acid-base catalysis is one of the most important areas of research and has assumed great relevance as an economic alternative to many homogeneously catalyzed, industrially important reactions. The solid acid catalysts have many advantages over liquid Brönsted and Lewis acid catalysts. They are non-corrosive, environmentally benign, and easily separable from the reaction mixture and pose few problems of disposal. The alkylation of aromatics through Friedel-Crafts reaction, for example, is of substantial industrial and pharmacological significance. Alkylation of aromatic nucleus has been traditionally carried out with well known Lewis acids or organometallic reagents using alkyl halides as the alkylating agents. In the course of more than hundred years of Friedel-Crafts chemistry, catalysts such as, $AlCl_3$, HF, H_3PO_4 and BF_3 have gained wide recognition. In spite of some unfavorable properties such as poor solubility in inorganic solvents, and sublimation at elevated temperatures, $AlCl_3$ is used widely in the synthesis of many fine chemicals and pharmaceutical intermediates. Although a significant number of other Lewis acids and pseudohalides are used in Friedel-Crafts reaction, none of them has achieved the wide applicability in solution chemistry as that of $AlCl_3$, BF_3 and HF as catalysts. In many cases, more than stoichiometric amounts of $AlCl_3$ are used for the reaction, giving poor product selectivity. Under the normal conditions, the reactants are very reactive and hence the absence of functional selectivity is related to the acid used, thus failing to discriminate among the different functional groups. Also, the presence of small amount of water lowers the yield drastically, because the catalyst rapidly decomposes or is deactivated by moisture. In addition to these, degradation, polymerization and isomerisation are also seen causing significant reduction of expected primary product yields. There are a number of other reactions, such as acylation, nitration, isomerisation, chlorination, condensation and so on, wherein replacement of homogeneous catalysts, such as H_2SO_4, $AlCl_3$ and others with heterogeneous catalysts is becoming more important in chemical and fine chemical industry in order to provide environmental benefits in addition to other advantages.

Table 1 - Acid strengths of some typical acids

Acid	*H_o (Hammett acidity scale)*
Sulfuric acid (100%)	-12
Hydrogen fluoride (anhydrous)	-10
Zeolites, RE-Y / H-ZSM-5 / Beta	-12 to -14
Kaolinite clay	+1.2 to -2
Acid-washed montmorillonite clay	-5 to -8
Amberlyst-15 resin	-2
Sulfated zirconia	-10 to -14

The solid acid catalysts can also be designed to give higher activity, selectivity, regenerability and longer catalyst life. In the last two decades, substantial progress has been made and several industrial processes that use solid acid-base catalysts have been introduced successfully. A comprehensive review of industrial applications of solid acid-base catalysts has appeared recently [1]. It is interesting to note that a majority of the important processes are acid-catalyzed reactions such as dehydration, condensation, isomerisation and alkylation and that more than 40% of the reported processes are catalyzed by zeolites. That brings us to the question of what makes a zeolite so acidic to catalyze a reaction that is normally done by a Brönsted or Lewis acid in the liquid phase. A comparative account of the acid strengths of some typical acids used in the industry may be given in terms of Hammett acidity function, H_o scale (Table 1). Some of the unique features of solid acids are:

Arumugamangalam V. Ramaswamy, National Chemical Laboratory - Pune 411008 - India.

Table 2 - **Designed porous materials**

Class of materials	*Examples*	*Pore structure*	*Pore size, nm*
Zeolites (Alumino-silicates)	Faujasites (X-Y type), Beta, ZSM-5	Small, medium & large pores 2 & 3 Dimensional	0.3-0.7
Silica molecular sieves	Silicalites, Metallo-silicates (Ti, V-, Sn-Cr-silicates)	Medium & large pores	0.5-0.8
Phosphate based Molecular sieves	Alumino-phosphate (AlPOs) & silica-alumino-phosphate (SAPOs)	Medium & large pores	0.5-1.0
Clays, pillared clays	Smectite, K-10 Intercalated with metal oxides, PILCs	2-Dimensional	>1.0
Mesoporous materials	Silica, silica-alumina MCM-41, MCM-48	Unidimensional	>2.0

a) their use as Brönsted and/or Lewis acids, depending on the conditions;
b) the differences in the acid strength and acid site distribution, which depend on the method of preparation;
c) catalytic activity at higher temperatures when they are less sensitive to water and alcohols (when methanol is used as an alkylating agent, for example);
d) shape selective characteristics in some solids;
e) diffusional resistance in some applications.

The use of a variety of solid acids and zeolitc materials in the production of aromatics and petrochemicals, such as xylene, ethylbenzene, cumene and linear alkylbenzenes are well known in the recent past [1]. There is a great scope for the introduction of solid catalysts in the synthesis of fine chemicals and pharmaceutical intermediates. These are hitherto essentially made by a multitude of steps, which generate by-products in each step, thereby contributing to loss of selectivity to the desired final product, and using catalysts that pose major disposal problems for the environmentally conscious industry today. This report makes an attempt to highlight some of the industrially important reactions catalyzed by clays and zeolites, based on the results of some of the recent reports. This is not purported to be exhaustive, rather only indicative of the potential of these solid acids.

Porous materials and catalysts

When we talk of solid acids, the foremost among them are the zeolites, which are microporous, crystalline aluminosilicates, often classified into small, medium and large pore zeolites, the largest pore opening being 0.7 nm in faujasites (X-and Y-type). They possess both Brönsted and Lewis acid sites depending on the temperature in which they are used. The phenomenon of shape selectivity associated with the zeolites has its origin in the well-defined pore structure, which could be manipulated to some extent. Since diffusional restrictions are often encountered in zeolites with larger substrates, the quest for other materials that have well-defined, larger pore dimensions has been the subject of intense activity in the last two decades [2]. Table 2 summarizes the development of what we call designed porous materials, that go beyond the pore size of faujasitic zeolites (>0.7 nm openings) and include:

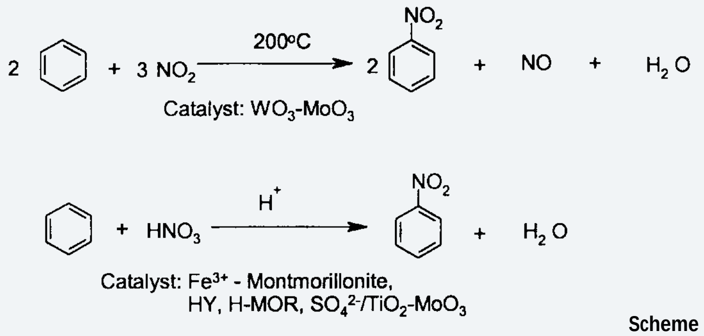
a) pillared layered structures, such as the alumina-pillared clays;
b) mesoporous molecular sieves of MCM-41 and MCM-48 type, prepared through the introduction large organic surfactants into the synthetic mixture.

Significant amount of work has been reported on the use of clays, which are layered silicates. These can be classified as two-layered and three-layered silicates, the former, such as kaolinite have idealized formula of $Al_2Si_2O_5(OH)_4$ and may be considered to have formed from the octahedral sheets of $Al(OH)_3$ and the tetrahedral sheets of $Si_2O_3(OH)_2$. In three-layered silicates, an octahedral layer is sandwiched between two tetrahedral layers. These are further divided into those having a dioctahedral structure which is electrically neutral having an idealized formula of $Al_2(Si_4O_{10})(OH)_2$ and those having a trihedral structure with a formula such as $Mg_3(Si_4O_{10})(OH)_2$ in which Mg^{2+} ions occupy all three sites in a unit cell. The diversity of clays had arisen from deviation with respect to the ideal formulas. Aluminum can be substituted for silicon in the tetrahedral layer. In the smectites a number of metallic cations such as Li^+, Mg^{2+} and Fe^{3+} can replace Al^{3+} in octadehral layers and Al^{3+} can replace Si^{4+} in tetrahedral layers. By the substitution, three-layered sheets can take on surplus negative charge. Kaolinite and smectites are the most extensively reported clay minerals that have been used as catalysts. The ensuing surface properties of the clays may be summarized as follows:

- negatively charged alumino-silicate sheets that can be separated by appropriate means;
- the delocalised negative charge makes the plane intro a polyelectrolyte, resulting in an electrical double layer, which is important for chemical reactions and liquid transport;
- surfaces are highly acidic, Brönsted acidity arising from terminal -OH groups or bridging oxygens (in the Hammett H_o scale, the acidity is between +1.5 and -3.0 for normal clays, which can increase to -6.0 to -8.0 for the acid treated clays);
- high acidity attributed to exchangeable cations that polarize coordinated water molecule and induce their dissociation (effect of humidity);
- the basal surfaces have a fixed charge, based on the clay structure and type, whereas the edges have a pH dependent charge;
- large specific surfaces, surface areas ranging from 15-20 m^2g^{-1} (for kaolinite) to >200 m^2g^{-1} (for montmorillonite).

Intercalated/pillared clays

The intercalation of smectites (trihedral structure) with polar organic molecules is well documented in the literature [3]. More than individual cation exchanges, positively charged organo metallics have been introduced at interlayer positions and used as catalysts in many interesting reactions. Subsequently, cross-linking of smectites unit layers with well defined oligomeric or polymeric species derived from metal hydroxides or chlorides has led to the development of pillared interlayered clays (PILC), which show better thermal stability than the parent clays, with added features of expanded interlayer spacings, well defined pore dimensions and higher surface areas. Starting from alumina as the pillared interlayer material, the literature is extensive with a variety of other pillaring materials such as zirconia, titania, silica, and many other individual and mixed oxides [3]. Catalysis by pillared clays provides a number of opportunities for the selection of alternative, efficient routes to synthesis of fine chemicals and other intermediates [4]. The accessibility of reactant molecules to the interlayer catalytic sites is facilitated. For the microporous zeolites, which are otherwise excellent solid acids, the pore dimension of 0.5 to 0.8 nm has restricted their application to bulkier substrates. The interlayer, interpillar distances are also known to exert a shape selective effect in pillared clays that can control the infusion rates of reactants, reaction intermediates and the products. Additional acidic character, both Brönsted and Lewis, could be introduced into the PILCs by proper selection of the pillaring materials and their composition. Deactivation by coking is still a major problem, which could be overcome by the introduction of small concentration of metals such as Pt or Pd in many catalyst formulations based on pillared clays. Recent trends and research have led to increased thermal and hydrothermal stability (>600 °C) for many PILCs [5]. It is also now possible to introduce redox centers on the pillars in a manner that we can get catalysts with dual functionality. We will now highlight some new developments of application of clays, zeolites and other solid acids in reactions that are of interest to chemical industry, mainly keeping in view of the selectivity advantages and environmental benefits of the new developments in the recent past and some that may soon become commercially viable.



Scheme 1

Nitration of aromatics

Nitration of aromatics is an electrophilic substitution reaction and is strongly exothermic. Industrial scale nitration is usually carried out with a mixture of nitric and sulfuric acids, normally in the ratio of 20% nitric acid, 60% sulfuric acid and 20% water (15:30:55 mole ratio, respectively). It is probably the most potentially hazardous process. Nitration is done occasionally with aqueous nitric acid, nitric acid in acetic acid or nitric acid in acetic anhydride. The nitronium ion, NO_2^+, formed by the protonation of nitric acid by sulfuric acid, is considered to be the active species. During large-scale production, nitration is controlled more by mass transfer than by kinetics, which is extremely complex [6]. In the batch or continuous process the operation generates large amounts of spent sulfuric acid waste, which requires to be neutralized before disposal or concentrated for recycle. The major drawback of the use of sulfuric acid could be overcome by the use of solid acid catalysts. Even though the use of sulfuric acid is both practical and economical, the efforts to develop acid catalysts are more in tune with the concern for environmental safety and increasing regulatory measures for protection of soil. Zeolites and other solid acid catalysts including clays have been reported to be extremely useful in the nitration of benzene, toluene and other aromatic substrates [7]. These include zeolites (HY, H-mordenite, H-beta, H-ZSM-5), cation exchanged zeolites, partially dealuminated zeolites, ion-exchanged resins (polystyrene sulfonic acid), clays (K-10, clay supported metal nitrates), modified silica, silica-alumina and supported heteropoly acids, sulfated silica, zirconia and other mixed oxides. Nitric acid, NO_2, N_2O_4, acyl nitrates and alkyl nitrates have been used as nitrating agents, either in the liquid phase or in vapor phase reactions, with or without solvents. In couple of examples shown below, even metal nitrates supported on K10 clay, for example, are effective in nitration of aromatics.

Table 3 - Vapor phase nitration of benzene [10]

Catalyst	Si/Al (bulk)	Nitrobenzene (yield), % 1 h	Nitrobenzene (yield), % 20 h	HNO_3 selectivity, % 1 h	HNO_3 selectivity, % 20 h
HM 21	5.8	69	67.5	84	85
HM 22	5.8	64.5	36.5	96	99
HM 23	9.6	74.5	71	85	93
HM 31	20	68	67	71	78
HM 35	59	76	76	96	96
HM 37	69	80	78	89	91

Conditions: fixed bed, down-flow micro reactor; atmospheric pressure; temperature: 170 °C; HNO_3 to benzene: 0.5 (mol); catalyst: 1.5 g; WHSV (benzene): 1.0 h^{-1}; N_2 carrier gas

Nitration of benzene

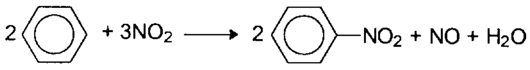
One of the earliest references in the vapor phase nitration of benzene using a solid acid catalyst is a patent [8], which claims the use of medium pore zeolites of the type ZSM-5 and ZSM-48, with a SiO_2/Al_2O_3 ratio of at least 12 and a constraint index of 1 to 12. These zeolites are shown to have a high activity and produce no by-products such as dinitrobenzenes (Scheme 1). Bertea *et al.* have reported efficient catalysts for the nitration of benzene by dilute nitric acid based on modified Y zeolite [9] and a modified mordenite catalyst [10]. They report the advantages of modifying the acidic and textural properties of a synthetic Y-zeolite or mordenite by a combination of thermal and acid treatments. While dealuminating mordenite, the formation of extra framework alumina species is shown to induce a severe catalyst deactivation through pore blocking. Through extensive characterization of mordenites with different degrees of dealumination, a sample with a Si/Al ratio of about 59, devoid of extra framework alumina was found to be a stable

Table 4 - Nitration of benzene with dilute HNO_3 (70%): comparison of long term activity of clay, heteropoly acid and mixed oxide catalysts [14]

TOS	*Al^{3+}-Montmorillonite clay*	*$H_{1.5}Cs_{1.5}(PMo_{12}O_{40})$/ 0.5 H_3PO_4*	*$SO_4^{2-}/TiO_2(4)$-$MoO_3(1)$*
4	95.0	89.6	91.3
24	87.3	84.0	91.0
48	83.5	78.2	89.6
120	76.8	73.1	87.5
216	72.0	70.0	87.3
288	-	-	87.0
360	-	-	87.3
480	-	-	87.5
528	-	-	87.1

Conditions: temperature: 140 °C; W/F = 14.8 (g cat. h/mmol); SV = 1,500 (ml/g h); $Bz/HNO_3/H_2O/N_2$=1/0.5/0.75/2.75 (molar ratios). Nitrobenzene yield based on HNO_3

catalyst, giving a high benzene (99.7%) and nitric acid (80-100%) selectivity at a fairly high space time yield (STY) (0.6 kg of nitrobenzene/kg cat. h) for more than 120 h on stream (Table 3). Sato and Hirose have investigated other solid acids such as SiO_2-Al_2O_3, ZnO-TiO_2 and WO_3-MoO_3 for the nitration of benzene with NO_2 as the nitrating agent (Scheme 1) in the mole ratio of NO_2 to benzene of 2.3 at 200 °C at a high space velocity [11]. In the overall reaction, the complete utilization of by-product NO by *in situ* oxidation with molecular oxygen,



$$NO + 0.5O_2 \rightarrow NO_2$$

needs to be addressed satisfactorily. The mixed metal oxide comprising WO_3 and MoO_3 in the ratio of 75% and 25% is claimed to have a fairly high and stable activity. Sumitomo have further developed two types of catalysts [12]. These are, a) montmorillonite based clays, ion-exchanged with multivalent metal cations such as Al^{3+}, Fe^{3+}, Cr^{3+} or Zr^{4+}, and b) mixed metal oxides containing Ti or Zr as essential catalysts for the vapor phase nitration of benzene using dilute nitric acid, which allows complete utilization of nitric acid without any by-product (STY of 0.64 nitrobenzene/kg cat h) with >97 selectivity to nitrobenzene [13]. Efforts to improve the space time yield further lead to modification of the catalysts used and a TiO_2-MoO_3 (4:1) mixed oxide treated with sulfuric acid at 500 °C showed higher activity and for more than 525 hours on stream gave 87% yield of nitrobenzene with improved STY of 0.72 kg/kg cat. h [14]. The report also included partially neutralized heteropoly acid as a catalyst for the nitration. A comparison of activity stability of the three catalysts is given in Table 4 adopted from [14].

Nitration of toluene and nitro-toluenes

Nitration of toluene is energetically more favorable, but the reaction invariably continues with the formation of dinitro- and other higher nitrotoluenes with selectivity to mono-nitrotoluenes (2- and 4-nitrotoluene) being impaired. Among the mono-nitrotoluenes, the selectivity to either *ortho*- (2NT) or *para*-isomer (4NT) is another consideration that could depend on the type of catalyst used.

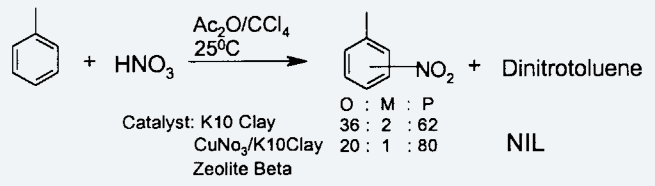
Cornelis *et al.* [15] reported the nitration of toluene over K10 clay with a mixture of nitric acid and acetic anhydride in CCl_4 to give *ortho-*, *meta-* and *para*-nitrotoluenes in the ratio of 36:2:62 (Scheme 2). A $CH_3COO^-NO_x^+$ intermediate has been proposed for this reaction with a turnover of >850. In the nitration of toluene, polynitration cannot be normally avoided. They further report the use of $Cu(NO_3)_2$ impregnated K10 clay as an improved catalyst for the nitration of toluene at room temperature with acetic anhydride and CCl_4. Acetic anhydride could also trap the water formed during the reaction. 'Claycop' which is the designated catalyst for this reaction produces no higher nitrotoluenes. Almost 100% mono nitrotoluene in the ratio of 20:1:79 of the three isomers is obtained in about 120 h. The regio-selectivity to *para* isomer is rather characteristic of many solid acid catalysts, particularly the zeolites and the layered clay materials.

The use of zeolite-beta, for example, can be more beneficial because of the shape selectivity that allows the product composition more in favor of *p*-nitrotoluene. The *para* isomer has the greatest commercial value and hence is more desirable. Vassena *et al.* [16] have studied the vapor phase nitration of toluene at 158 °C in a flow reactor at atmospheric pressure using 65% nitric acid (nitric acid to toluene mole ratio of 1) and H-beta, H-ZSM-5, polysiloxane bearing alkylsulfonic acid as catalysts. Compared to the latter two catalysts, zeolite beta (Si/Al=11.4) exhibited en-

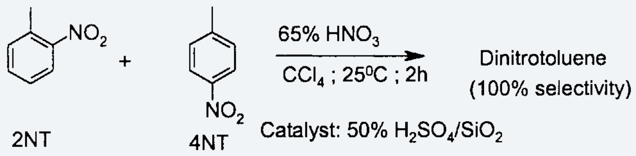
Table 5 - Nitration of a mixture of 2-nitro and 4-nitro toluenes with 65 wt.% HNO_3 over solid acids [19]

Catalyst	*Catalyst: H^+/HNO_3*	*Conversion (%)*	*DNT yield (%)*	*Others (%)*	*2.4 DNT/2.6 DNT ratio*
$NaHSO_4$ (17 wt.%)/SiO_2	-	0.4	0.4	-	-
WO_x/ZrO_2	-	1.4	1.4	-	-
SO_4^{2-}/ZrO_2	-	0.2	0.0	0.2	-
H-MOR (Si/Al=63.5)	-	1.8	0.5	1.3	-
Heteropoly acid (20 wt.%)/ SiO_2	-	2.1	1.1	-	-
50% H_2SO_4/SiO_2	1.2	59.0	58.9	-	4.5
Fresh	3.2	89.8	89.8	-	4.9
Fresh	6.3	95.0	94.3	-	4.8
Reused	6.3	83.5	83.5	-	4.6

Conditions: bath reactor; HNO_3/Nitrotoluene=1(mol); temperature 25 °C; solvent: CCl_4 (5 ml); catalyst: 1-5 g; time: 24 h



Scheme 2



Scheme 3

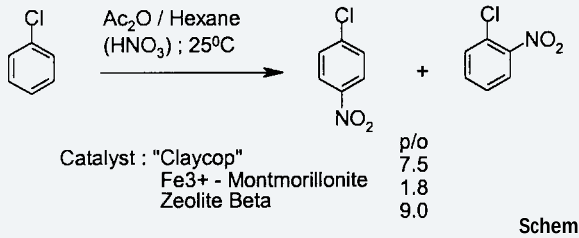
hanced *para* selectivity which decreased with time on stream. Since the dealuminated H-beta did not show any further enhancement in *para* selectivity, the activity is essentially due to the concentration of acid sites. The catalyst is deactivated in about 26 hours of operation due to the deposition of the side-chain oxidation products in the micropores of the zeolite, which are identified as coke precursors. However, these zeolites did not undergo either chemical or structural damage during the nitration of toluene. The XRD pattern of the used catalyst did not show any loss of crystallinity, nor is there any leaching of aluminum (^{27}Al-MAS-NMR data) under the reaction conditions.

Smith *et al.* [17] have studied the deactivation of ZSM-5, mordenite, H-beta, L-zeolite and mesoporous MCM-41 during nitration of toluene both in vapor phase (with NO$_2$ as nitrating agent) and in liquid phase (with *n*-propylnitrate). High selectivities to *para*-nitrotoluene have been obtained with all the zeolite catalysts, but deactivation remains an issue. At low temperatures (65-100 °C), the dominant form of deactivation is the plugging of the pores by the aromatic molecules, as the desorption of the product molecules is not facilitated, while at higher temperatures (150-200 °C) the pore plugging decreases, but the catalysts deactivate by coke formation.

The nitration of toluene using 65% or 100% HNO$_3$ occurs without a catalyst due to the self-protonation equilibrium of nitric acid, which is the basis of the single acid DNT process developed by Olin corporation [18]. There is very little catalytic effect in the liquid phase nitration of toluene or nitrotoluenes under these conditions. Indeed, silica-supported NaHSO$_4$, silica-supported heteropoly acid, WO$_x$/ZrO$_2$, sulfated ZrO$_2$ or dealuminated mordenite did not show much catalytic effect in the nitration of toluene or in the nitration of a mixture of 2- and 4NT at 25 °C, using 65% HNO$_3$ [19].

However, sulfuric acid supported on silica has been found to be extremely active (Table 5). At 25 °C in a batch reactor, in completely non-aqueous conditions, 60 to 95% conversion of nitrotoluene is reported [19], depending on the proton concentration of H$_2$SO$_4$ on silica (catalyst concentration in the mixture) with almost 100% selectivity to dinitrotoluene (Scheme 3). Moisture plays a crucial role in the reaction and the catalyst handling is hence very important. It is interesting to note that although 65% HNO$_3$ is used in the reaction, no loss of sulfuric acid from silica during the nitration has been observed.

In situ activation of the catalyst is reported to be very effective leading to almost 100% conversion of nitrotoluene in repeated cycles, within 2 hours of the reaction time. In the nitration of toluene, near 100% selectivity to mono-nitrotoluene could be achieved at low acid concentration (50% sulfuric acid on silica), for a given mole ratio of HNO$_3$ to toluene of 2 at 25 °C using CCl$_4$ as solvent. Higher loading of sulfuric acid on to silica (70%) was not effective in the nitration. Impregnation of silica with sulfuric acid essentially results in the interaction of sulfate ions with the surface of SiO$_2$. The SO$_4^{2-}$ ions occupy the pores of silica in a manner that there is a 50% reduction of the surface area with a corresponding reduction in the pore volume, while the pore dimensions (8 and 13 nm pore diameter for two types of silica used) are almost similar to the parent and acid treated silicas [19].

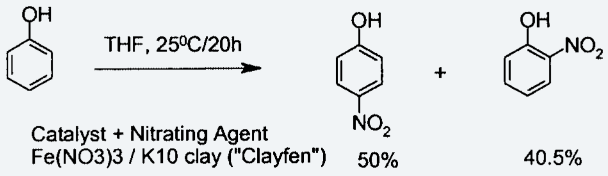


Scheme 4

Selective nitration of aromatics employing Fe^{3+} montmorillonite in the presence of acetic anhydride and nitric acid has been reported by Choudary *et al.* [20]. The use of acetic anhydride or alkyl nitrates becomes expensive for further exploitation of the results from these studies. Invariably, the vapor phase nitration of benzene or toluene employing clays and zeolites results in low space time yields. Choudary *et al.* recently reported [21] a simple methodology that dispenses with the use of acetic anhydride. The rate of addition of nitric acid (60-90%) to the (batch) reactor containing powder catalysts such as beta zeolite or Fe^{3+}-montmorillonite and substrate is matched with the rate of removal of water present in nitric acid and the reaction products through extractive distillation with a Dean-Stark apparatus. Zeolite beta with a Si/Al ratio of 44 and Fe^{3+} montmorillonite clay are claimed to give high space time yields of 10-26 (kg product/kg cat. h) with excellent *para* substitution for toluene, chlorobenzene and other aromatic substrates, under reflux conditions [22]. In the case of clay based catalysts (both Fe^{3+}-montmorillonite and K10), the *ortho* to *para* ratio of the products from toluene is 1.2 to 0.86, whereas with beta zeolite the ratio is around 0.5. Even with the deactivated halobenzenes, a STY of 12-20 is reported with still higher *para* selectivity for the nitro-halobenzenes (*o*/*p*=0.4 to 0.1). Interestingly, it is claimed that even under the reflux conditions, zeolite beta did not undergo any leaching of Al and could be reused a number of times [21].

Nitration of halobenzenes

Nitration of chlorobenzene is an industrially important reaction that gives chloro-nitro derivatives, which are intermediates for a variety of fine chemicals (Scheme 4). The halo-



Scheme 5

gen substituent deactivates the aromatic ring to some extent and hence the rates are slower for nitration. Laszlo and Pennetraeu [23] reported the use of $Cu(NO_3)_2$ loaded K10 clay (Claycop) as an effective catalyst for the nitration of chlorobenzene at room temperature. They have obtained an *o:p* ratio of 1:7.5 with 73% yield.

The *para*-selectivity of the nitro-chlorobenzene is quite remarkable. Fe^{3+}-montmorillonite clay is also active with 90% HNO_3 at room temperature and a STY of 26 (kg of product/kg of cat. h) are claimed when the water from the system is continuously removed, while nitric acid is continuously added [21]. A *para*-selectivity of 90% has been reported. Zeolite-beta is pretty active in the nitration of other halobenzenes with a STY in the range of 12.0 to 20 (kg product/kg cat. h) under similar conditions.

Selective synthesis of *para*-nitro derivative from chlorobenzene using nitric acid is the subject of another report from Yadav and Nair [24]. They report the use of sulfated ZrO_2 (average pore size of 4 nm) which is further modified with a polymer coating and carbonization to get a novel shape-selective catalyst (pore size of 1.7 nm) that improves the *para*-selectivity from 91.3% to 93% for the new catalyst, without much change in the conversion (HNO_3 conversion, 45-47% for the reaction at 30 °C in 1.5 h).

Nitration of phenols

The nitration of phenol using “Clayfen”, which is a $Fe(NO_3)^{3-}$ loaded K10 clay as catalyst and tetrahydrofuran as solvent at room temperature is reported (Scheme 5). We do not see very high *para*- selectivity, the ratio of *p*- to *o*-nitrotoluene is about 1.3, with some *m*-nitrotoluene in the product. Cornelis *et al.* [15] have earlier reported the nitration of estrone using the same catalyst in toluene at room temperature (Scheme 6). The nitro-product is pharmacologically active, estrogenic derivative, useful for further transformation.

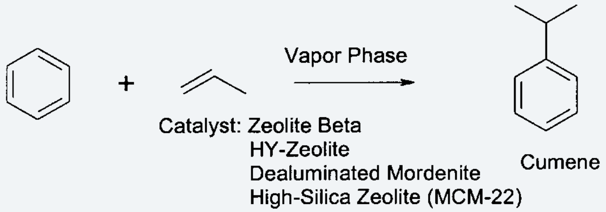
Table 6 - Catalyst performance in the alkylation of benzene by propylene [27]

Parameters	*Catalyst MCM-22*	*Catalyst MCM-56*
Temperature, °C	112	113
Propylene, WHSV, h^{-1}	1.3	10.0
Propylene conversion, %	98.0	95.4
Selectivity, %		
- Cumene	84.35	84.98
- Diisopropyl benzene	11.30	13.20
- Triisopropyl benzene	2.06	1.28
- C_3 Oligomers	1.8	0.52
- *n*-Propyl benzene, ppm	70	90

Scheme 6

Alkylation of aromatics

Great in-roads have been made to manufacture alkylaromatics using zeolites and several processes have been commercialized in the last two decades. These are the large volume petrochemicals, such as ethylbenzene, cumene, and linear alkylbenzene, which are well documented in the literature [1, 25]. Significant advantages in improvement of selectivity to the desired product, longer catalyst life and environmental benefits have been the hallmarks of these developments. HZSM-5, H-beta, MCM-22, MCM-56 and silico-aluminophosphates have been introduced in several new processes. We will cite a few examples wherein additional advantages due to the use of improved catalysts have been claimed.



Scheme 7

Production of cumene

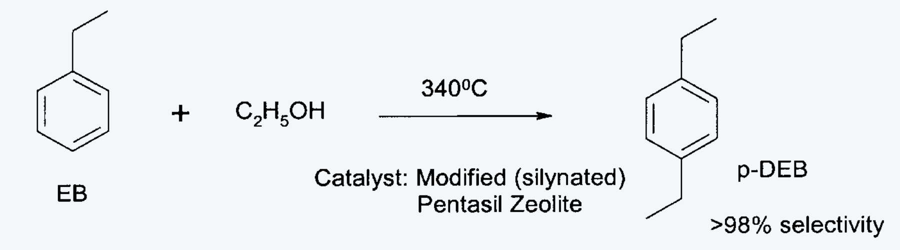
The solid phosphoric acid based process for the alkylation of benzene with propylene is being modified in many units with zeolite-based catalysts (Scheme 7). Revamp of existing units with zeolitic catalysts has proved to be advantageous. Further improvements are being introduced to reduce heavier alkylates and products of side reactions, such as oligomerization of propylene.

The Mobil-Badger cumene process probably uses a novel zeolite catalyst (believed to be MCM-22) whose acidity is controlled in such a manner that both coke formation and propylene oligomerisation are kept to a minimum [26].

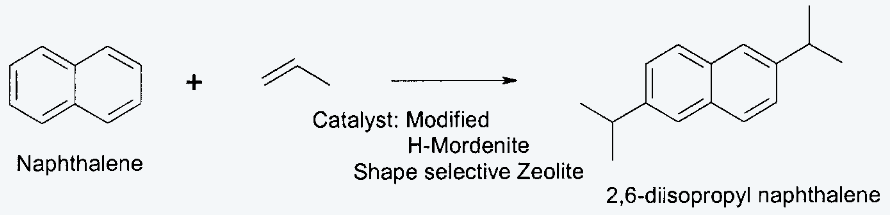
All unwanted by-products (ethylbenzene, *n*-propyl benzene and butyl benzenes) are claimed to be less than 250 ppm. MCM-22 has an unusual pore structure, consisting of two independent two dimensional pore system that is claimed to be responsible for the observed benefits for high activity and selectivity to cumene. A recent Mobil patent claims another catalyst, labeled as MCM-56 to be superior to MCM-22 in cumene production [27]. The data given in Table 6 show a high propylene conversion even at higher space velocities (almost one order of magnitude higher) on MCM-56, compared to MCM-22. At these conditions, C_3 oligomers and tri-isopropyl benzene are lower, while cumene selectivity remains similar.

Selectivity improvement

Selectivation is a new direction to avoid producing unwanted and lower value by-products in some of these processes.
Although zeolites and clays as such are shape selective due to ordered porosity, further pore or pore mouth modification enhances the shape selectivity to a desired *para*-isomer. Examples of selective coking of the catalyst, such as the medium pore HZSM-5 in the new MSTDP process (Mobil, 1991) or the one seen in the nitration of chlorobenzene could be cited. We show here few examples of shape selective alkylation over zeolites. The first is the production of *p*-diethyl benzene from ethylbenzene using a HZSM-5 catalyst, which is silynated *in situ* to a level that the *para*-selectivity improves beyond what normal medium pore zeolites could give (Scheme 8). The pore modification or pore-size engineering either by selective coking or silynation leads to enhanced product shape selectivity. In the case of *p*-diethylbenzene, a selectivity of >99% could be achieved at a per pass conversion of ethylbenzene of 15% at 340 °C at ethylbenzene to ethanol (mole) ratio of 4 to 10 [28].



Scheme 8

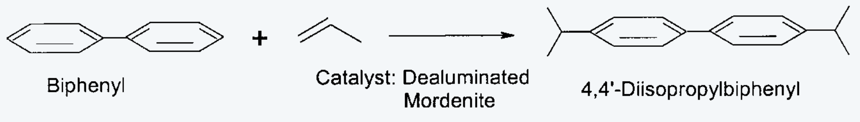


Scheme 9

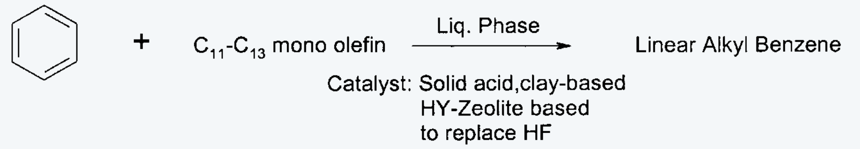
The silynated zeolite is expected to have a normal cycle length of 6 months between regenerations. Polycyclic aromatic compounds such as naphthalene or biphenyl are alkylated with an alkylating agent such as propylene to produce selectively 2,6-dialkylnaphthalene or 4,4'-dialkyl biphenyl, respectively.
The di-substituted isomers of polycyclic aromatic compounds are useful as monomers in the preparation of thermotropic, liquid crystal polymers. The selective alkylation is carried out in the presence of an acidic zeolite such as mordenite, under conditions sufficient to produce a mixture of substituted polycyclic aromatic compounds, enriched in the *para* alkylated isomers. The catalyst is normally tuned to be selective to such isomers, and characterized by a definite silica to alumina ratio, porosity, NMR characteristics and a symmetry index. The isopropylation of naphthalene to give selectively 2,6-diisopropyl naphthalene (Scheme 9) has been successfully realized using a suitably modified mordenite catalyst. Several patents describe the fine-tuning of the catalyst for the selectivity improvement using other catalysts [29-33]. The selective formation of 4,4'-dialkyl biphenyl, which is again an important intermediate for resins, is another interesting example of shape selective alkylation (Scheme 10).
The alkylation of biphenyl with propylene to give selectively 4,4'-diisopropyl biphenyl has been commercialized by Dow Chemical Co. and the process is reportedly based on a modified H-mordenite catalyst [34].

Linear alkylbenzene (LAB)

The development of a solid acid catalyst for the alkylation of benzene with linear olefins for the production of LAB is another landmark in the history of heterogeneous catalysis (Scheme 11). This development allows for the elimination of potentially hazardous HF acid in the present process, with obvious advantages of operational safety and environmental protection. The use of alumina-pillared montmorillonite and zeolites as catalysts for the alkylation of benzene with 1-octene and 1-dodecene has earlier been reported [35].



Scheme 10



Scheme 11

The reaction was carried out in a continuously stirred batch reactor, at atmospheric pressure and at 80 °C.
A comparison of the alkylation activity of the solid catalysts given in Table 7 makes an interesting reading.
The conversion of 1-dodecene is correlated with the amount of Brönsted acid sites in the Al-PILC, which depends on

Table 7 - Activity comparison of Al-pillared montmorillonite with other solid zeolites in benzene alkylation reaction with 1-octene and 1-dodecene [35]

Catalysts	*Percent conversion of*	
	1-octene	*1-dodecene*
Al-pillared montmorillonite	56.3	99.2
HY zeolite	100.0	99.3
H-mordenite	52.8	20.0
H-beta	28.1	38.0
H-ZSM-5	0.0	0.0

the pretreatment temperature [35]. It is interesting to note the difference in the conversion of the two olefins used on the one hand on Al-pillared montmorrillonite catalyst, and different orders of activity between the Al-PILC and the microporous zeolites on the other. With a channel dimension of 0.75 nm and a super cage of 1.3 nm, HY zeolite is very active compared to other zeolites. Al-PILC with a basal spacing of 1.8 to 1.9 nm is non-restrictive for the large molecules and demonstrates the effect of shape selectivity. It is in line with such studies that the recent UOP process for the production of LAB (Detal process) uses a solid acid catalyst. The process now commercialized both in Canada and India is the outcome of collaborative research efforts since 1980s by UOP and Petresa.

The Detal process in addition yields a superior product compared with that from the HF technology [36]. The Detal catalyst is a proprietary UOP solid acid, believed to be based on a clay material. A typical comparison of the products from the two (UOP) processes is given in Table 8.

It is seen that the product from the Detal process is higher and the total tetralins are lower. LAB from Detal contains more 2-phenyl alkanes and so the resulting linear alkyl sulfonate is more soluble in liquid formulations. Simultaneously, a zeolite-based catalyst was developed for the production of LAB [37]. The catalyst consists of a rare earth exchanged Y-zeolite with ion-exchanged transition metals in the zeolite structure and is found to be superior to a variety of solid acids studied. A delicate balance between the metal function and the acidity of the zeolite provides for selective hydrogenation of diolefins in the feed to monoolefins with very little loss of mono-olefins to paraffins. This reduces the formation of diphenyl alkanes and any polymeric material that is responsible for the deactivation of the catalysts. The objective was to lower the deactivation rates so as to achieve a normal cycle length between successive regenerations. The process is carried out at a temperature of about 100 °C, a pressure in the range of 1 to 10 bar and LHSV of 1 to 10 h^{-1}. Under these conditions, all the linear olefins in the feedstock are substantially converted to LAB. The process is undergoing trails in a pilot plant of 2 MT/day of LAB capacity since 1995.

Conclusions

A brief review of some newly emerging applications of clays, zeolites and other solid acids in the nitration of aromatics without the use of sulfuric acid is presented. The options are either liquid phase nitration at room temperature or the vapor phase reaction at temperatures in the range of 100-200 °C using solid acids. High Brönsted acidity of the solid catalysts and its retention through several cycles or long hours of steady state activity are demanded. Modified montmorillonite or supported acids appear to be suitable for liquid phase nitration, while zeolite beta or improved mixed oxide formulations may be useful in vapor phase. The notable feature in all the recent reports is the continuous improvement in the stability of the catalyst and higher space-time yields, which will encourage pilot plant trails in the near future. The other examples are on the alkylation of aromatics. The production of ethylbenzene and cumene using zeolites has been commercial since 1980s.

The zeolite catalysts have replaced the Lewis acids such as $AlCl_3$, BF_3 or solid phosphoric acid with tremendous advantages to the industry. Selectivity improvements through fine tuning of the pore structure of the zeolites are seen in the production of *p*-diethylbenzene, 2,6-diisopropyl naphthalene and 4,4'-diisopropyl biphenyl which are important intermediates. The production of linear alkyl benzene using a solid acid catalyst (either clay-based or zeolitic) to replace presently used HF, highlights the concern as well as success of the efforts of catalysis research in recent times. ◆

Table 8 - Comparison of products and quality from Detal and HF LAB processes of UOP [36]

	Detal Process	*HF process*
n-Alkyl benzene, wt.%	95	93
2-Phenyl alkanes, wt.%	>25	15-18
Tetralins, wt.%	<0.5	<1.0
Klett colour of 5% active LAB solution	10 to 30	20 to 40

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Argille, zeoliti e catalizzatori solidi acidi

Nell’articolo vengono illustrati recenti sviluppi sull’applicazione di argille e zeoliti come catalizzatori. Gli esempi citati si limitano alle reazioni di sostituzione elettrofila, in particolare nitrazione e alchilazione di molecole aromatiche, in cui argille e zeoliti giocano un ruolo chiave. Numerose zeoliti sono state impiegate in diversi processi di alchilazione e ulteriori miglioramenti nella progettazione di catalizzatori solidi acidi sono rivolti a un miglioramento della selettività, maggiori capacità di smaltimento e migliore tolleranza delle impurità presenti nel materiale di carica dell’impianto.