Selective benzylation of benzene over alumina pillared clays

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Aluminium pillared clays prepared by partial hydrolysis method has been subjected to room temperature exchange with transition metals of the first series. The resulting materials exhibit a fine porous network of exceptional stability as characterized by XRD, FTIR and NMR spectroscopy. EDX and surface area measurements indicate the presence of exchanged metals attached to the pillars. Acidity of the pillared clay benefits from the insertion of transition metals. Benzylation of benzene occurs efficiently over these catalysts with 100% monoalkylated product selectivity. An extensive study of the reaction variables points towards a carbonation mechanism for the reaction. The reaction depends to a large extent on the number and availability of the Lewis acid sites.

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Pillar interlayered clays constitute one of the widely studied groups among the new microporous materials developed by molecular engineering. These solids, also known as crosslinked clays are obtained by exchanging the interlayered cations of layered clays with bulky inorganic polyoxocations, followed by calcination. The intercalated polycations increase the basal spacing of clays and upon heating, are converted to metal oxide clusters by dehydroxylation and dehydroxylation. As a result, a two dimensional porous network is generated. Maintenance of a well-defined porous network up to relatively high temperatures along with the presence of acid sites immediately suggest potential catalytic applications for these solids.

Selective formation of the monoalkylated product occurs. The observed activities could be correlated with the strong/Lewis acidities of the catalyst. A thorough study on the structural stability of the catalysts as well as reaction variables has been carried out.

Materials and Methods

Aluminium pillared clay was synthesised by the partial hydrolysis of 0.1 M Al(NO₃)₃ solution by dropwise addition of 0.3 M Na₂CO₃ solution under vigorous stirring. N₂ gas was bubbled through the solution to remove excess CO₂ and aged for 24 hours at room temperature. Intercalation of pillaring species into the clay layers was done by treating the pillaring solution with a previously swollen clay suspension at 70°C (OH/metal ratio: 2 and metal/clay ratio: 20 mmol/g clay). The clay, after exchange, was washed several times with distilled water and filtered. This was dried in an air oven at 110°C overnight, followed by calcination for 6 hours at 450°C in a muffle furnace. Exchange with transition metals was done using 0.1 molar aqueous solutions of the
corresponding metal nitrate. For exchange with vanadium, requisite amount of ammonium metavanadate was dissolved in oxalic acid. Pillared clays were stirred mechanically with salt solutions for 24 hours at room temperature. The clay after exchange was washed 5-6 times with distilled water. This was filtered and dried in an air oven at 110°C overnight and calcined for 5 hours at 500°C. The pillared clays synthesised for the present study are noted as X/Al PM where X is the transition metal exchanged.

Cation Exchange Capacity measurements were done by ammonium acetate extract method. The evolved ammonia was quantified by microKjeldahl method. EDX analysis of the prepared samples was done in a Jeol JSM-840 A instrument with a resolution of 1.3 eV. Samples were prepared by dusting the clay powder onto double sided carbon tape, mounted on a metal stub. The diffractometer traces of the catalyst samples were taken in Rigaku D/MAX-C instrument using Cu-Kα radiation (λ = 1.5405Å). The simultaneous determination of surface areas and pore volumes of the catalyst samples was done on a Micromeritics Gemini analyser. Previously activated samples were degassed at 200°C under nitrogen atmosphere for 2 hours and then brought to nitrogen boiling point. FTIR spectra of the samples were recorded using a Perkin-Elmer RX-1 spectrometer by the KBr disc method in the range 400-4000 cm⁻¹. NMR spectra of samples were recorded on a 300 DSX Brucker spectrometer. Temperature programmed desorption of ammonia was done using a conventional flow type apparatus. Cumene cracking test reaction was done in vapour phase in a fixed bed, downflow vertical glass reactor. The catalyst (0.5 g) activated at 500°C was immobilised inside the reactor using glass wool, sandwiched between inert silica beads. Cumene was fed into the reactor with the help of a syringe pump at controlled flow rate. The products were collected downstream in a receiver connected through a water condenser and analysed using a Chemito 8610 gas chromatograph equipped with flame ionisation detector and FFAP column.

The liquid phase benzylation of benzene was carried out in a closed 50 ml round bottomed glass flask equipped with a reflux condenser, magnetic stirrer and provision for withdrawing product samples. The temperature of the reaction vessel was maintained using a thermostated oil bath. In a typical run, appropriate amounts of benzene, benzyl chloride and catalyst were allowed to react at specified temperatures under magnetic stirring. Reaction mixture was withdrawn at specific intervals and analysed using gas chromatography using SE-30 column. The percentage conversion (wt %) of benzyl chloride is the total percentage of benzyl chloride transformed into the products.

**Results and Discussion**

**Residual cation exchange capacity measurements**

Cation exchange capacity of pillared clays is only partially compensated by the charge of oligomers. Even if the oligomer to clay ratio is very high, a part of exchangeable cations remains unchanged. The residual CEC provides an estimation of the fraction of layer charge, which is not compensated by cationic pillaring species. During exchange process, some monomeric forms of the pillaring species could as well be exchanged. The protons that are formed in final calcination step of pillaring process, when intercalated oligomeric cation is decomposed into metal oxide pillars, can also restore CEC of clay. Thus, residual CEC gives a measure of effectiveness of pillaring process. Montmorillonite shows a cation exchange capacity of 0.91 mmol g⁻¹ which reduces to 0.56 mmol g⁻¹ on pillaring with aluminium. 61.5% of the original CEC is retained on the clay. Aluminium polymeric solution contains Al monomeric and dimeric species and they also are considered to be exchangeable. Hence, residual CEC of Al PM is the CEC that has not been exchanged with Al₁₁₃ polymer or it is an indication of effectiveness of pillaring with Al₁₁₃ polymer.

**Energy dispersive X-ray analysis**

Energy dispersive X-ray analysis yields the chemical composition of the prepared samples. The elemental compositions of individual systems are presented in Table 1. It can be seen from the table that Si/Al ratio of parent clay decreases from 3.18 to 2.0. Decrease in Si/Al ratio is a direct consequence of the increase in aluminium content as a result of pillaring rather than structural instability of the clay layers. Aluminium content increases by 9.14% with corresponding decrease in amount of exchangeable cations. From the data, it can also be concluded that pillaring occurs at interlamellar sites in the place of exchange cations. This fact is supported by CEC measurements. Exchange with transition metals incorporates about 1-2% of the metal at the expense
of interlamellar cations. Vanadium exchanges best. Thus, exchange with the transition metals of the first series further replaces these cations.

In order to show the effects of exchange process on the original constituents of the clay, the elemental weights can be calculated to 100% after excluding the fixed transition metal oxide. This indicates that transition metal oxide was introduced without a significant deleterious effect on the clay structure and the pillars. Thus, on exchange with transition metal, metal oxides are incorporated into the pores or in between the pillars rather than exchanged in the location of pillars.

Surface area and pore volume measurements

The determination of surface area and pore volume in clays is a subject of controversy. The most convenient approach for textural characterisation of these materials is to obtain the adsorption isotherm at a temperature lower than or equal to critical adsorbate temperature. N₂ (at 77.2 K) is traditionally used as adsorbate. As gas pressure increases, adsorption proceeds by pore filling, starting from smaller pores. The potential energy fields from neighbouring surfaces overlap and the total interaction energy with adsorbate molecules becomes substantially enhanced giving rise to high gas volume adsorption at very low relative pressures. The surface areas of pillared clays are typically obtained by applying BET equation. The range of validity of BET equation for these materials is usually between $P/P_0 = 0.01$ and $0.1$. However, in microporous solids like pillared clays where the interlamellar distance is of the order of a few molecular diameters, monolayer formation on clay silicate layers occurs. Thus, surface areas approximated by Langmuir equation are reasonable representations of pillared clay surface areas. Hence in the present study, BET and Langmuir surface areas of various systems obtained directly are tabulated. The external and microporous surface areas were calculated from $t$-plot.

Table 2 furnishes the surface area and pore volumes of various aluminium pillared systems. Surface area and pore volume of montmorillonite increases as a result of pillaring. Aluminium pillaring increase BET surface area to 132.9 m² g⁻¹ and Langmuir surface area to 192.3 m² g⁻¹. The pore volume increases to 0.1623 ccg⁻¹. About one third of the area can be attributed to external surface. As a result of transition metal exchange, surface area and pore volume decreases. Zinc and vanadium exchange brings about this effect to the maximum. Decrease in surface area and pore volume can be correlated well with the amount of metal oxide incorporated into the pillared system.
Increase in surface area and pore volume can be ascribed to the pillaring process. CEC measurements showed that 38.5% of original CEC was replaced by Al\textsubscript{13} polymer, while a lower surface area was obtained for the final pillared solid. This can be due to breaking of pillars on calcination. Similar observations were reported by Bakas et al\textsuperscript{10}. Breaking of pillars disrupts the porous network and hence decreases the percentage of microporous surface area compared to iron pillared systems. Transition metal exchange deposits the metal oxides near the pillars resulting in lower percentage of external surface.

X-ray diffraction

Apart from surface area and pore volume measurements, the easiest way to determine whether pillar intercalation is successful is to record the X-ray diffraction pattern of an oriented film of the product. Pillared clays are semi-crystalline in nature. The broad bands obtained in the XRD spectrum, instead of sharp peaks, can be attributed to the semi-crystalline nature of clays. Hence, indexing of the spectrum is not possible for this type of solid acids. The only data that can be obtained is the d spacing of (001) plane, which indicates the extent of propping apart of clay layers. X-ray diffraction peaks show that long range face-to-face layer aggregation is present in the pillared sample. Thus, it can be safely assumed that the sample is not an edge-to-face delaminated clay.

The characteristic d\textsubscript{001} spacing of montmorillonite is seen at 20 value of 9.8\AA. For Al PM, this value increased to 17.3 \AA. Shifting of 20 values clearly suggests expansion of clay layer during pillaring process. The major intercalated species giving rise to stable basal spacing in Al PM is the so called Al\textsubscript{13} polyhydroxy polymer or Keggin cation which has been characterised by small angle X-ray scattering\textsuperscript{14} and \textsuperscript{27}Al NMR\textsuperscript{12}. This polymer with structural formula, \([\text{AlO}_2\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}\) is a tri-decamer composed of one aluminium tetrahedron surrounded by 12 aluminium octahedra. It contains four layers of superimposed oxygen atoms needed for expanding clay basal spacings to 18 \AA. The expansion of (001) plane of clay layer near this value suggests that the intercalated species is the Al\textsubscript{13} polymer in Al PM.

The effect of exchange with transition metals on the XRD patterns of the pillared system was studied for representative samples. The XRD patterns were exactly identical to that of the parent pillared sample. Thus, it can be concluded that insertion of the second metal after the formation of stable pillars does not destabilise the porous network. Additional peaks corresponding to the exchanged metal oxides were not noticed. This may be due to the diminutive amounts (1-3\%) of the exchanged metal in these samples.

FTIR spectroscopy

The structural evolution of the aluminosilicate layer was characterised by FTIR spectroscopy. The parent montmorillonite shows a large band at 3620 cm\textsuperscript{-1}, typical of smectites with large amount of Al in the octahedra\textsuperscript{13}. Intensity of this peak decreases upon pillaring. Formation of a new band in the range of 3740-3770 cm\textsuperscript{-1} is an important observation. The identification of hydroxyl species on pillared clays is extremely difficult, because of the complexity of the system and the opaqueness of the sample in the corresponding IR region. It has been reported that isotopic exchange with mild deuterating agent C\textsubscript{6}D\textsubscript{6} has allowed identification of two acidic hydroxyls, with OH stretching modes at 3660 and 3740 cm\textsuperscript{-1}, the former referring to the unstructured band of the parent montmorillonite and the latter which seem to arise from the sealing of montmorillonite layer and the pillar\textsuperscript{14}. These can be represented as Si-O-Al-OH or Al-O-Si-OH. Thus, FTIR spectra of the three pillared samples also are indicative of effective pillaring.

The IR spectra in the fingerprint region are characterised by absorptions at 1200-1000 cm\textsuperscript{-1} due to asymmetric stretching vibrations of apical oxygens of Si\textsubscript{2}O tetrahedra and the large band due to combined stretching and bending vibrations of the Si-O bonds related to basal oxygens\textsuperscript{15}. The band around 900 cm\textsuperscript{-1} often provides information on the composition of the octahedral sheets. In montmorillonite, it reflects partial substitution of octahedral Al by Mg. Absorptions at 526-471 cm\textsuperscript{-1} echo bending Si-O vibrations. Thus, the framework vibrations contain information about the structural characteristics of the material and their preservation after thermal treatments may be considered as a proof of the structural stability on pillaring. Absence of additional peaks suggests that no bond formation occurs between the montmorillonite and the pillars unlike other clays like saponite\textsuperscript{16}.

\textsuperscript{27}Al NMR spectroscopy

Clay minerals and pillared clays have been the subject of several solid state NMR investigations\textsuperscript{17,18}. \textsuperscript{27}Al NMR can detect the co-ordination of Al atoms in clays containing as little as 0.26\% of Al\textsubscript{2}O\textsubscript{3}. Therefore, this technique is of particular use in
studying octahedral and tetrahedral sites in the extra framework Al species contained in aluminium pillared samples. Montmorillonite shows two resonances: one at +1.38 ppm that can be ascribed to octahedral Al atoms and the other at +66.0 ppm attributable to tetrahedrally coordinated Al atoms. For aluminium pillared samples, δ ppm values for octahedral Al atoms shifts to +1.98 ppm. This is due to overlapping of signals of Al atoms of intercalating polymer with that of original signal. Two resonances can be distinguished at tetrahedral region: resonance at +66.4 ppm belonging to clay tetrahedral sites and resonance at +60.3 ppm corresponding to tetrahedral sites in the pillar. An important conclusion is that the intercalated species is not transformed into a spinel-like structure. When aluminium hydroxides like gibbsite and boehmite are the pillars, corresponding resonances are between +8 and +9 ppm and above +68 ppm, signifying spinel-like structure. Further, no resonance is observed at around +30 ppm demonstrating the absence of pentacoordinated Al atoms. Thus, it can be unambiguously concluded that pillared species is the Keggin Al12 polymer for Al pillared systems. The Keggin cation contains a central Al tetrahedron linked to 12 Al octahedra and has the formula [AlO2Al12(OH)24(H2O)12]+.

The effect of transition metal exchange on structural stability of pillared clays was examined by taking 27Al NMR spectra of copper and cobalt doped aluminium pillared systems as representative systems. As a result of exchange with transition metals, peak width as well as peak positions do not vary. This shows that incorporation of transition metals does not affect the structural stability of layers and pillars. Hence 27Al NMR data supports the inference drawn from surface area and pore volume measurements, that metal oxides are incorporated into porous network rather than attached to pillars.

29Si NMR spectroscopy

For Si nucleus (spin I = 1/2), chemical shift is affected mainly by the electron density on oxygen atoms of Si tetrahedron. Therefore, nature of neighbouring atoms coordinated to these oxygen atoms can influence the shift. The spread of these shifts is not only a function of the structural disorder but depends also on nature of the second neighbours. The connectivity of Si nuclei in silicate species is described by the usual Qn notation. Q represents a silicon nucleus connected to four oxygen forming a tetrahedron. The superscript n is the number of other Q units attached to the central SiO4 tetrahedron. Thus Q° denotes monomeric orthosilicate anion SiO4-, Q1 denotes end groups of chains, Q2 denotes middle groups in chains or cycle, Q3 denotes chain branching sites and Q4, three dimensionally cross linked groups. Montmorillonite shows a single resonance centred at -93 ppm. The peak shows a main peak at -93.98 ppm and two shoulder peaks; a large one at -104.5 ppm and a diminutive one at -90.3 ppm. The peak at -93.98 ppm can be attributed to Q1 (Si1Al) units representing Si(IV) atoms linked through oxygen atoms to three other Si(IV) and to one Al(III) (or Mg) in the clay octahedral layer. The shoulder peak at -104.5 ppm can be ascribed to Q3 (Si3Al) where Si is linked to Si only through oxygens, while the small peak at -90.3 ppm is due to Q2 (Si2Al). Thus, majority of the silicon tetrahedra is linked to 3 Si atoms and one Al atom. A very small portion is linked to 2 Al atoms and 2 Si atoms, while a part of the Si tetrahedra is linked to Si atoms alone. This distribution of silicon tetrahedra into various environments is not affected by pillaring. A slight shift in ppm values was noticed for pillared samples. Data show that Lowenstein rule, which states that two tetrahedral Al cannot be next neighbours, is obeyed.

Inversion of silicon tetrahedra can occur with intercalation of polymeric species in clays like beidellite and saponite where the layer charge is localised in tetrahedral layer19. Such an inversion is not anticipated in montmorillonites since layer charge is not localised. 29Si NMR spectra confirm this point since the shift in δ ppm values is less than 1-2 ppm in all pillared samples. The contributions of different Si environments also remain the same. This confirms the nonexistence of chemical bonds between exchanged polymeric species and clay layers. Thus, as anticipated, pillaring which is only a cation exchange process does not affect the short range order within clay layers. If any bond that forms Al-O-Si linkage between the pillars and silicate layers been formed, the spectra would have contained Q3 (Si3Al) resonance.

The effect of exchange with transition metals on the structural stability of clay as well as pillaring process was exposed by taking the 29Si NMR spectra of two of the exchanged systems of the aluminium pillared series, viz., Co/Al PM and Zn/Al PM. It can be inferred that δ ppm values do not alter much as a result of exchange with transition metals. Thus incorporation of transition metals on the pillared
systems does not alter the local environment of Si atoms. Hence, it can be inferred that metal oxides are not in the immediate environment of Si layer. They may be present in the porous network of the pillared system. This has been evidenced by surface area data and $^{27}$Al NMR spectra.

**Temperature programmed desorption of ammonia**

It is generally recognised that ammonia is an excellent probe molecule for testing acidic properties of solid catalysts as its strong basicity and small molecular size allow detection of acidic sites located in very narrow pores also. Although, there is widespread use of TPD in the studies of surface acidity, NH$_3$-TPD spectra are often poorly resolved. However, the procedure is a standardisation method since ammonia allows the determination of both protonic and cationic acidities by titrating acid strengths of any strength.

Ammonia adsorption on pillared clays can be physical ($\Delta H \approx 13$ Kcalmol$^{-1}$) or chemical ($\Delta H \approx 33$ Kcalmol$^{-1}$) type. Acid site distribution profiles show the presence of weak (ammonia desorbed between 35-200°C), medium (201-400°C) and strong (401-600°C) acid sites. The acid site distribution at various temperatures has been calculated as functions of mass of the sample.

The acidic structure of aluminium pillared catalysts as obtained from NH$_3$-TPD is presented in Table 3. Exchange with transition metals does not improve the acidity and weak and medium acid sites predominate the strong sites. Thus, a good distribution of weak and strong acid sites is present. Acidity in the medium strength region decreases as a result of incorporation of metals. Acidity expressed as a function of surface, has values comparable to Al PM. It can be concluded that an effective distribution of acid sites of varying strength is present in the prepared systems. Consequently, they can be used as suitable catalysts in acid catalysed reactions. Exchange of transition metals blocks the hydroxyl groups in the structural framework, reducing the Brønsted acidity.

NH$_3$-TPD method does not discriminate the type of acid sites (Brønsted and Lewis). However, it is generally accepted that evacuation of ammonia adsorbed at 400°C removes most of the Brønsted acid sites$^{20}$. For pillared clays, it has been documented that ammonia adsorbs in Brønsted sites at temperatures around 250°C (ref.11). Again, it is implied that coordinatively bound ammonia on strong Lewis site can be desorbed only at high temperatures and hence acidity in strong region can be correlated to the amount of Lewis sites. In pillared clays, Lewis acidity is considered to originate from pillars whereas Brønsted acidity arises from structural framework of aluminosilicates. Pore volume values indicate presence of exchanged cations inside the porous network. Hence, increase in number of strong sites can be attributed to contribution of these cations in pillars. This is substantiated by the fact that amount of medium acid sites (correlated to Brønsted acidity), arising from structural framework decreases as a result of transition metal exchange. This may be due to shielding of these sites by the deposition of metals in the pores, near the structural framework.

**Cumene cracking**

Cumene is a conventional model compound for testing catalytic activity since it undergoes diverse reactions over different types of acid sites. Major reactions taking place during cracking of cumene are dealkylation or cracking to benzene and propene and dehydrogenation to α-methyl styrene. Small amounts of ethylbenzene and toluene can be formed by cracking of side chain, which on dehydrogenation gives styrene. Cracking of cumene is generally attributed to Brønsted acid sites by a carbonium ion mechanism whereas α-methyl styrene is formed on Lewis acid sites$^{21,22}$.

### Table 3 — Acid site distribution/mass of aluminium pillared series

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weak (35-200°C)</th>
<th>Medium (201-400°C)</th>
<th>Strong (401-600°C)</th>
<th>Cumulative (mmolg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V/Al PM</td>
<td>0.521</td>
<td>0.133</td>
<td>0.223</td>
<td>0.894</td>
</tr>
<tr>
<td>Mn/Al PM</td>
<td>0.530</td>
<td>0.248</td>
<td>0.100</td>
<td>0.868</td>
</tr>
<tr>
<td>Cu/Al PM</td>
<td>0.655</td>
<td>0.394</td>
<td>0.079</td>
<td>1.128</td>
</tr>
<tr>
<td>Ni/Al PM</td>
<td>0.669</td>
<td>0.334</td>
<td>0.192</td>
<td>1.195</td>
</tr>
<tr>
<td>Cu/Al PM</td>
<td>0.514</td>
<td>0.253</td>
<td>0.058</td>
<td>0.825</td>
</tr>
<tr>
<td>Zn/Al PM</td>
<td>0.53</td>
<td>0.427</td>
<td>0.169</td>
<td>1.126</td>
</tr>
<tr>
<td>Al PM</td>
<td>0.652</td>
<td>0.441</td>
<td>0.105</td>
<td>1.198</td>
</tr>
</tbody>
</table>
The catalytic performance of Al PM and the effect of transition metal exchange on pillared clays are given in Table 4. All systems show considerable activity towards cumene cracking under the specified conditions. Appreciable selectivity towards the dehydrogenated product is obtained for all catalysts. Ethylbenzene and styrene were formed in small quantities and in some cases toluene also was detected. All the dealkylated products are grouped together and Lewis to Brønsted ratio gives the ratio between the dehydrogenated and cracked products. aluminium pillared clay exhibits high activity towards the reaction with Lewis/Brønsted acid ratio of 1.42. Exchange with transition metals results in reduction in acidity except for nickel and cobalt exchanged systems as indicated by conversion of cumene. A critical scrutiny of Table 4 shows that the decline in acid sites is mainly due to decrease in the number of Lewis acid sites.

**Benzylation of benzene with benzyl chloride**

Benzylation of benzene is an important probe reaction to check the acidity of the catalysts since the ring itself is not activated or deactivated by substitution. Moreover, the reaction gives diphenylmethane, an important synthetic intermediate as the product. The reaction always gave monoalkylated product regardless of temperature, time and reactant molar ratio. The catalytic performance of the prepared systems towards benzene benzylation is given in Table 5. Al PM shows a conversion of 12% in 1 hour under refluxing conditions. However, catalytic activity increases as a result of transition metal exchange. V/Al PM exhibits 100% conversion of benzyl chloride in 1 hour. A 100% selectivity to monoalkylated product is not changed with any catalyst. The three dimensional porous network of pillared clay systems brings about the reaction between the aromatic species and benzyl chloride in a shape selective manner, leading to cent percent diphenylmethane selectivity. Presence of exchanged cations increases the catalytic efficiency.

**Table 4** — Catalytic activity of various systems towards cumene cracking. [Temp: 400°C; WHSV: 7 h⁻¹; time on stream: 2h]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>α-Methyl styrene</th>
<th>Dealkylation products</th>
<th>Lewis/Brønsted</th>
</tr>
</thead>
<tbody>
<tr>
<td>V/Al PM</td>
<td>28.8</td>
<td>58.8</td>
<td>41.2</td>
<td>1.42</td>
</tr>
<tr>
<td>Mn/Al PM</td>
<td>26.0</td>
<td>55.4</td>
<td>44.6</td>
<td>1.24</td>
</tr>
<tr>
<td>Co/Al PM</td>
<td>31.4</td>
<td>50.8</td>
<td>41.7</td>
<td>1.22</td>
</tr>
<tr>
<td>Ni/Al PM</td>
<td>33.6</td>
<td>56.8</td>
<td>43.2</td>
<td>1.22</td>
</tr>
<tr>
<td>Cu/Al PM</td>
<td>19.2</td>
<td>44.9</td>
<td>55.1</td>
<td>0.81</td>
</tr>
<tr>
<td>Zn/Al PM</td>
<td>26.5</td>
<td>59.1</td>
<td>41.1</td>
<td>1.44</td>
</tr>
<tr>
<td>Al PM</td>
<td>28.5</td>
<td>58.6</td>
<td>41.4</td>
<td>1.42</td>
</tr>
</tbody>
</table>

**Table 5** — Activity of aluminium pillared systems for benzylchlorination of benzene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V/Al PM</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Mn/Al PM</td>
<td>72.3</td>
<td>100</td>
</tr>
<tr>
<td>Ni/Al PM</td>
<td>48.5</td>
<td>100</td>
</tr>
<tr>
<td>Co/Al PM</td>
<td>69.8</td>
<td>100</td>
</tr>
<tr>
<td>Cu/Al PM</td>
<td>24.8</td>
<td>100</td>
</tr>
<tr>
<td>Zn/Al PM</td>
<td>44.5</td>
<td>100</td>
</tr>
<tr>
<td>Al PM</td>
<td>12.0</td>
<td>100</td>
</tr>
</tbody>
</table>

![Fig. 1 — Correlation of conversion (%) with α-methyl styrene selectivity.](image)

In the present study, an attempt has been made to correlate catalytic activity with the amount of Lewis acidity obtained by the two independent acidity estimation techniques elaborated earlier. Lewis acidity as indicated by α-methyl styrene selectivity in cumene cracking reaction is in line with catalytic performance of aluminium pillared systems (Fig. 1).

Figure 2 shows that catalytic activity along the series follows the order of the amount of strong acid sites (ammonia desorbed in the temperature range of
Dependence or activity on experiments. The probability of aluminium leaching is remote and structural stability of the catalysts occur without much transformation in the reaction conditions. Hence, stability of the catalysts was checked by metal leaching and moisture absorption experiments.

Leaching of metals from the catalyst surface can occur without much transformation in the reaction profile, gradually changing the nature of reaction from truly heterogeneous to partly homogeneous. The probability of aluminium leaching is remote and has not been reported so far. In the present study, metal leaching was studied at 35 min by continuing the reaction for further 25 min, after filtering off the catalyst. No noticeable change was observed even after 25 min of reaction, in the absence of catalyst. Hence a truly heterogeneous reaction can be envisaged with aluminium pillared systems.

In order to test the effect of moisture on catalyst performance, the catalyst and the substrate were saturated with water vapour, by keeping them over deionised water in a desiccator for 72 hours at room temperature. The induction period for the reaction increased in presence of moisture. After this short span of time (1 hour), the reaction proceeded as in moisture-free conditions. Presence of induction period is suggestive of water molecules occupying the active sites prior to reaction, from where Cl ions displaced them. The high induction period can be attributed to the high activation energy over these catalysts.

**Effect of reaction variables**

Influence of various reaction variables like time, benzene to benzyl chloride ratio and substrate and catalyst concentration on the extent of reaction was studied extensively using Mn/Al PM as reference in order to arrive at a plausible mechanistic pathway for the reaction. Study shows the reaction rate to be nominal for a particular period of time and then continually increasing with time. Absence of polyalkylated products is a significant result. The continual increase in percentage conversion with time is indicative of heterogeneous nature of the reaction. Selective formation of the monoalkylated product can be attributed to the porous two dimensional structure of the pillared clays restricting the attack of the benzyl cation on the bulky product species.

Benzene to benzylating agent molar ratio was studied by taking appropriate amounts of benzene, keeping the amount of catalyst and benzyl chloride fixed. An inverse relationship was observed between benzene to benzyl chloride molar ratio and conversion % at any given time. Higher amounts of benzene in the reaction mixture prolonged the time required for complete conversion. It is worth mentioning that polyalkylation does not occur even at high concentrations of benzyl chloride. Since benzene is taken in excess, the reaction is supposed to follow pseudo unimolecular mechanism. Therefore, the reaction should have an equivalent relation with the amount of benzyl chloride. Thus, the catalyst is very efficient for the creation of benzyl carbocations even at high concentrations of the reagent.

The effect of catalyst concentration on the reaction was studied by varying the amount of catalyst added.
keeping the amount of reactants constant. Results show that the presence of catalyst even in trace amounts has a marked difference in the product yield. Increase in catalyst concentration, enhanced the percentage conversion and at a stage, rate of the reaction levelled off. After this, increase in catalyst concentration had no pronounced effect on the reaction rate. Thus, only a small amount of catalyst is needed for easy completion of the reaction. Cent percentage selectivity to monoalkylated product even at high concentrations of the catalyst is commendable. Increase in reaction rate with catalyst concentration is suggestive of heterogeneous mechanism for the reaction. Higher amounts of catalyst result in higher amounts of active sites and hence the increase in reaction rate. Since the systems under study are very efficient Friedel-Crafts catalysts, only a small amount of catalyst is needed.

The effect of substrate on percentage conversion was studied with different substrates. The observed order of reactivity of substrates is o-xylene > toluene > benzene. As expected, the reaction rate for hydrocarbons was lowered over aluminium pillared systems and halobenzenes did not react at all over these catalysts under the specified conditions. From the results it can be inferred that the activating and deactivating effect of the substituting groups in the benzene ring has profound influence on reaction rate. The observed order of reactivity is exactly the same as that of electron releasing effect of the substituting group in the benzene ring. The inductive effect of methyl group makes the reaction more facile in the case of toluene and still higher for xylene due to the cumulative effect of two methyl groups. Similar results have been reported by Jun et al.\textsuperscript{24}. The higher activation energy due to electron withdrawing effect of the halo group is responsible for the non occurrence of the reaction over these catalysts.

**Mechanism of the reaction**

Several mechanisms have been put forward by various authors for benzylation with benzyl chloride. Predominant among them are the classical carbocation mechanism and the redox mechanism involving free radicals. Yadav et al. investigated the alkylation of toluene by benzyl chloride on sulphated zirconia, a very strong Lewis acid and reported a surprisingly low activity\textsuperscript{25}. Hence, a redox mechanism was suggested for the reaction.

![Scheme 1](image-url)
Based on the observations of present study, a plausible reaction mechanism is suggested for the reaction (Scheme 1). The mechanism is similar to the mechanism of alkylation reaction catalysed by an M\(^{2+}\)-H species present on synthetic transition metal oxide SiO\(_2\)-Al\(_2\)O\(_3\) systems\(^{26,27}\). The alkylation agent, benzyl chloride interacts with the active species and forms the alkylation moiety M\(^{2+}\)-CH\(_2\)C\(_6\)H\(_5\), which in turn attacks the benzene molecule forming a \(\pi\) complex. This is possible due to the partially filled \(p\)-orbitals of Al(III) and \(d\)-orbitals of Fe(III) present in the pillars. The framework Al and Fe does not contribute to the formation of complex or pure montmorillonite would have shown much better activity. The \(\pi\)-complex rearranges to give the alkylated product diphenylmethane. The platelets of clay intercalated with transition metal oxide pillars are capable of stabilising highly polar transition states converting it into products whereas it is formed in lesser amounts or even not obtained in homogeneous conditions\(^{28}\). Thus, the intermediate of the alkylation moiety, the \(\pi\) complex and the sigma complex could be stabilised which in turn enhances the conversion to diphenylmethane. When the reactants are constrained to diffuse in a porous solid, which have layered structure like clays, their encounter frequencies increase. Also, organic molecules congregate in the compartment like structures of the clay matrix. Thus, pores locally increase the interaction between reactants\(^{29}\).

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References