

CATALYTIC ACTIVITY OF IRON PILLARED MONTMORILLONITES FOR BENZYLATION OF BENZENE WITH BENZYL CHLORIDE

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Abstract : The development of cutting edge and cleaner processes is of topical interest to meet global competition and conform stringent environmental specifications. Friedel-Crafts alkylation is a very important tool for introducing alkyl substituents into the aromatic ring system. Conventionally, homogeneous acidic catalysts are used for the reaction. This presents several problems like tedious work up, use of corrosive chemicals, moisture sensitivity, decreased regioselectivity etc. The use of solid acids to replace waste generating soluble Lewis acids for the alkylation of arenes facilitates improved procedures. In this paper, we report the use of cleaner, shape selective iron pillared clay catalysts for Friedel-Crafts alkylations. Presence of surface acid sites as well as its nature influences the catalytic activity. A free radical mechanism has been suggested for the reaction.

Key Words: Iron pillared clays, catalysts, benzylation, surface acidity, free radicals

Introduction

Friedel-Crafts alkylation is an important means of attaching alkyl chains to aromatic rings and hence is a key reaction in organic chemistry. Diphenylmethane and substituted diphenylmethanes are industrially significant compounds used as heat transfer fluids, aromatic solvents, fragrances and monomers for polycarbonate resins. They are also precursors to benzophenones, synthesised by an air oxidation step in acetic acid medium in presence of manganese based catalysts. Traditionally, homogeneous acid catalysts like AlCl_3 , BF_3 and H_2SO_4 are used for Friedel-Crafts alkylations [1]. However, use of Lewis acid catalysts is laden with several problems like difficulty in separation and recovery of products, disposal of spent catalyst, corrosion, high toxicity etc. These catalysts also catalyse other undesirable reactions like alkyl isomerisations and *trans* alkylation reactions [2]. In order to reduce isomerisation and disproportionation in aromatic alkylation catalysed by AlCl_3 , the reactions are generally carried out at low temperature (below -10°C) and in solvents like carbon disulphide and nitromethane, which present hazards [3]. Moreover, these catalysts are moisture sensitive and hence demand

moisture free solvent and reactants, anhydrous catalysts and dry atmosphere for their handling [4]. Most of the catalysts have to be added in stoichiometric amounts, thereby adding to the cost of the desired product. Hence worldwide efforts have been made to replace the present environmentally malignant catalysts with solid acid catalysts. In this paper, we report the use of iron pillared montmorillonite and its transition metal exchanged analogues for the benzylation of benzene, a typical example of Friedel Crafts alkylations. The reaction has also been reported as a probe for the acidity of the catalysts since the ring is neither activated nor deactivated.

Experimental

Iron pillared clay was synthesised by the partial hydrolysis of 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution by drop wise addition of 0.3 M Na_2CO_3 solution under vigorous stirring. N_2 gas was bubbled through the solution to remove excess CO_2 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 80°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 air oven at 110°C overnight, followed by calcination for 6 hours at 450°C in muffle furnace. Exchange with transition metals was done at room temperature 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. The clay after exchange was washed 5-6 times with distilled water, filtered and dried in air oven at 110°C overnight and calcined at 500°C for 5 hours. The prepared systems are notated as X/Fe PM where X is the transition metal exchanged.

EDX analysis of the prepared samples was done in a JEOL JSM-840 A (Oxford make model I6211 with a resolution of 1.3 eV). The diffractometer traces of the catalyst samples were taken in RIGAKU D/MAX-C instrument using Cu K α radiation ($\lambda = 1.5405\text{\AA}$). The simultaneous determination of surface areas and pore volumes 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. Temperature programmed desorption of ammonia was done using a conventional flow type apparatus. Perylene adsorption experiments were carried out in a 50 mL stoppered U- tube by stirring 5 mL of freshly prepared perylene in benzene solutions of varying perylene concentrations (0.01- 0.02 mol L⁻¹ in benzene) and accurate amounts of catalyst for 4 hours. The contents were filtered after 24 hours and absorbance measured after dilution by ten times. In all cases, absorbance measurements were performed in the adsorbate concentration range where Beer Lambert law is valid. From Langmuir plots, limiting amount of perylene adsorbed on the catalyst surface, which is a measure of Lewis acidity is obtained. The absorbance measurements were done in a Shimadzu UV-160 A spectrophotometer at λ_{max} 439 nm using a 10 mm quartz cell.

The liquid phase benzylation 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. 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 Chemito 8610 Gas Chromatograph equipped with Flame Ionisation Detector and SE-30 coloumn. The percentage conversion (wt%) of benzyl chloride is the total percentage of benzyl chloride transformed into the products.

Results and Discussion

Energy Dispersive X-ray Analysis

Energy dispersive X-ray analysis yields the chemical composition of the samples (Table 1). The parent clay has considerable amount of exchangeable cations, viz., Na, Mg, K and Ca. A drastic reduction in the amount of these elements occurs as a result of pillaring with iron and the amount of iron increases by 23.54%. Room temperature exchange with transition metals incorporates about 1-2.5% of the metals into the pillared system. Vanadium and zinc exchange best while copper and manganese exchange least. Si/Al ratio of parent montmorillonite is 3.18. After pillaring the clay with iron oligomeric species, Si/Al ratio remains 3.1.

Increase in iron content with corresponding decrease in the amount of exchangeable cations points to successive replacement of interlamellar cations with stable iron oxide pillars. Transition metal exchange again replaces the exchangeable cations from interlamellar spaces, in particular potassium with the respective metal. Si/Al ratio of a system before and after treatment, is an important parameter exhibiting structural stability. Differences in the ratio indicate dealumination from structural framework. This effect, highly important for zeolites is not usually observed in clays. Thus, conservation of Si/Al ratio indicates that pillaring does not affect structural framework of clay.

Table 1. Elemental composition of iron pillared systems

Catalyst	Element (%)							
	Na	Mg	Al	Si	K	Ca	Fe	TM*
V/Fe PM	0.29	1.38	14.09	46.96	1.11	0.41	33.43	2.33
Mn/Fe PM	0.31	1.52	14.71	46.85	1.07	0.44	35.1	1.19
Co/Fe PM	0.37	1.34	14.09	46.52	1.85	0.50	33.36	1.97
Ni/Fe PM	0.44	1.85	14.78	47.06	1.54	0.49	33.84	1.93
Cu/Fe PM	0.36	1.03	14.46	47.94	1.61	0.42	32.97	1.21
Zn/Fe PM	0.34	1.84	14.12	47.12	1.64	0.46	31.22	2.26
Fe PM	0.33	1.42	14.88	45.55	1.91	0.56	35.21	-
M	2.18	2.81	17.74	56.47	4.11	5.01	11.67	-

*- Exchanged transition metal

Surface area and Pore volume measurements

The surface areas of pillared clays are typically obtained by applying BET equation to the N₂ adsorption isotherm. 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 surface

areas and pore volumes of iron pillared systems are given in table 2. Montmorillonite has a BET surface area of 14.3 m²g⁻¹ and Langmuir surface area of 27.9 m²g⁻¹. As a result of pillaring, surface area and pore volume increases drastically. Pore volume also increases significantly on pillaring. Transition metal exchange decreases the surface area and pore volume, mainly in external surface area. Minimum surface area is exhibited by zinc exchanged system. Decrease in surface area can be roughly correlated to the amount of metal oxide incorporated as obtained from EDX measurements.

Table 2. Surface area and pore volume of iron pillared systems

Catalyst	Surface Area (m ² g ⁻¹)		Pore volume (ccg ⁻¹)
	BET	Langmuir	
V/Fe PM	160.7	234.2	0.1991
Mn/Fe PM	194.1	285.4	0.2086
Co/Fe PM	178.3	250.8	0.1957
Ni/Fe PM	164.8	226.5	0.1920
Cu/Fe PM	171.2	248.2	0.1992
Zn/Fe PM	147.7	234.8	0.1857
Fe PM	194.2	269.7	0.2157
M	14.3	27.9	0.0058

X-ray Diffraction

Figure 1 depicts XRD patterns of montmorillonite and Fe PM. 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 shows that long range face to face layer aggregation is present in the

pillared sample. Thus, it can be safely commented that the sample is not an edge to face delaminated clay. The characteristic d_{001} spacing of montmorillonite increased from 9.8 Å to 19.2 Å as a result of iron pillaring. Shifting of 2θ values clearly suggest expansion of clay layer during pillaring process. The relative intensity of the peaks, gives a measure of the extent of pillaring. In all cases, maximum intensity

(100%) was for the peak corresponding to increase in basal spacing. Hence the relative intensity was calculated comparative to the intensity of this peak. Insertion of iron oxide pillars increases the basal spacing up to 19.2 Å and the corresponding relative intensity is 42.39. Thus, XRD patterns underline the conclusions drawn from surface area and pore volume measurements.

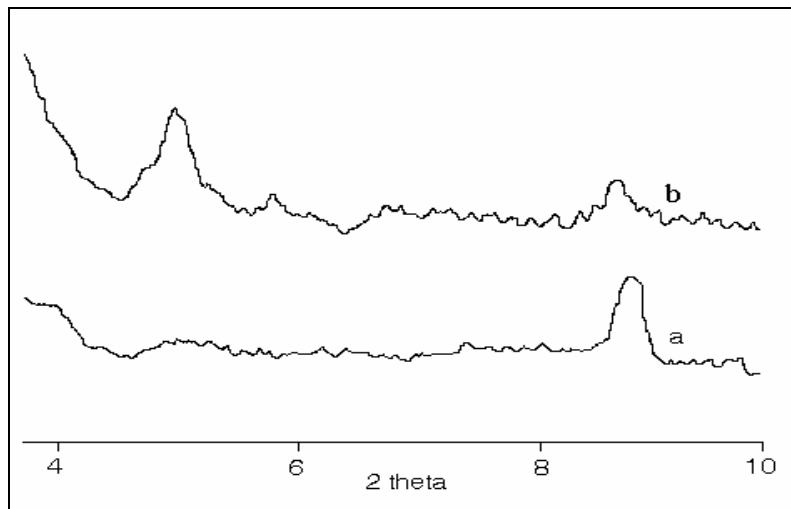


Figure 1. XRD profile
a) M b) Fe PM

The effect of exchange with transition metals on the XRD patterns of Fe PM was studied for representative samples. The XRD patterns were exactly identical to that of Fe PM. 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.

Temperature programmed desorption of ammonia

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. Ammonia adsorption on pillared clays can be physical ($\Delta H \approx 13 \text{ Kcalmol}^{-1}$) or chemical ($\Delta H \approx 33 \text{ Kcalmol}^{-1}$) 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 as well as BET surface area (tables 3 and 4). The former expression helps in quantifying acid sites per gram of clay while the latter helps in understanding the acidic structure of catalysts as a surface property which can be helpful in understanding reaction pathways for acid catalysed reactions.

Table 3. Acid site distribution/mass of iron pillared series

Catalyst	Weak (35-200°C)	Medium (201-400°C)	Strong (401-600°C)	Cumulative (mmolg ⁻¹)
V/Fe PM	0.722	0.159	0.088	1.068
Mn/Fe PM	0.715	0.311	0.182	1.208
Co/Fe PM	0.420	0.191	0.057	0.688
Ni/Fe PM	0.997	0.350	0.258	1.505
Cu/Fe PM	0.696	0.287	0.153	1.136
Zn/Fe PM	0.592	0.112	0.080	0.784
Fe PM	0.48	0.354	0.084	0.918

Table 4. Acid site distribution/surface area of iron pillared series

Catalyst	Weak (35-200°C)	Medium (201-400°C)	Strong (401-600°C)	Cumulative (x10 ⁻³ mmolm ⁻²)
V/Fe PM	1.80	0.398	0.22	2.418
Mn/Fe PM	1.51	0.66	0.386	2.556
Co/Fe PM	0.77	0.350	0.473	1.593
Ni/Fe PM	2.49	0.876	0.645	4.011
Cu/Fe PM	2.07	0.856	0.457	3.383
Zn/Fe PM	1.56	0.296	0.211	2.067
Fe PM	1.23	0.91	0.216	2.356

The tables reveal that Fe PM shows considerable acidity. Weak and medium strength acid sites predominate the strong sites. V, Mn, Ni and Cu exchange increases the amount of cumulative as well as strong acid sites. NH₃-TPD method lacks in discriminating the type of acid sites (Brönsted and Lewis). However it is generally accepted that evacuation of ammonia adsorbed at 400°C removes most of the Brönsted acid sites [5]. For pillared clays, it has been documented that ammonia adsorbs in Brönsted sites at temperatures around 250°C [6]. 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 where as Brönsted 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 Brönsted 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.

Perylene adsorption measurements

Perylene adsorption studies give information regarding Lewis acid sites in presence of Brönsted sites. The one electron donor transfers the electron to Lewis acid sites and gets adsorbed as perylene radical cation. The limiting value of perylene that is adsorbed on catalyst surface is a measure of Lewis acidity of the sample [7]. A clear picture of adsorption and limiting value can be obtained by plotting the amount of perylene adsorbed against equilibrium concentration. These graphs convince Langmuir type of adsorption over solid surfaces. However, perylene being large along with its sole ability for binding with electron acceptor centres has access only to exposed Lewis acid sites. The low values for perylene adsorption can also be due to the shape selective nature of the porous network hindering the access of bulky one electron donor to Lewis acid sites present inside the pillars.

Table 5. Perylene adsorption data

Catalyst	Perylene adsorbed ($\times 10^{-6}$ molg ⁻¹)
V/Fe PM	8.3
Mn/Fe PM	9.3
Co/Fe PM	8.8
Ni/Fe PM	9.5
Cu/Fe PM	9.2
Zn/Fe PM	4.1
Fe PM	5.1
M	-

The results of perylene adsorption studies for iron pillared systems are presented in table 6. Montmorillonite does not adsorb perylene. Substantial amount of perylene gets adsorbed on Fe PM. Introduction of transition metals, even in small amounts increases significantly the limiting value of the one electron donor adsorbed on catalyst surface. However, exchange with zinc reduces the one electron adsorption capacity of Fe PM. It has been reported that the Lewis acid sites in pillared clays originate from the pillars. The nonadsorption of perylene in pure montmorillonite supports this fact. Introduction of iron oxide pillars brings in Lewis acidity into the system and hence the substantial adsorption of perylene molecules. Exchange with transition metals increases the Lewis acidity of the material. It was observed from NH₃-TPD measurements

that ammonia adsorption in the strong acid region of the pillared clay, benefited from transition metal exchange.

Benzene benzylolation

Iron pillared systems show very high activity to benzyl chloride(BC) when benzene is the substrate (Table 6). With Fe PM, the reaction proceed to completion in one hour at a surprisingly low temperature (65°C). Exchange of the pillared clay with transition metals of the first series improves the activity further. Thus, Mn/Fe PM and Ni/Fe PM shows maximum activity with almost 100% conversion of benzyl chloride in 30 minutes. An initial induction period when there is no reaction is found in all cases. Cent percent selectivity to the monobenzylated product remains the same.

Table 6. Activity of various iron pillared systems for benzylation of benzene

Catalyst	Time (minutes)					
	10	20	30	40	50	60
V/Fe PM	0.0	0.0	0.0	1.2	18.9	100
Mn/Fe PM	0.0	29.3	89.8	100	100	100
Co/Fe PM	0.0	0.0	0.0	31.9	95.0	100
Ni/Fe PM	0.0	31.2	95.0	100	100	100
Cu/Fe PM	0.0	0.0	0.0	9.1	27.4	100
Zn/Fe PM	0.0	0.0	0.0	27.6	100	100
Fe PM	0.0	0.0	0.0	4.2	83.2	100

Temperature- 65°C, benzene/BC- 10, catalyst/BC- 0.1515

The high activity of the iron pillared clay catalysts can be attributed to the iron oxide pillars present in the interlamellar

space. The high surface area created by the pillars facilitate the easy diffusion of reactants in and products out of the catalyst

active site. The three dimensional porous network also presents steric hindrance for further attack of carbocations on the product, inhibiting the formation of polyalkylated products. The effect of pillaring have been conclusively evidenced by comparing the reaction rates over pillared and exchanged clays [8].

Friedel-Crafts alkylation is an aromatic electrophilic substitution reaction in which the carbocation is formed by the complexation of alkyl halide with catalyst. The carbocation attacks the aromatic species for alkylation and hence formation of carbocation is an important step in the reaction mechanism. Lewis acidic centres on the catalyst surface facilitate the carbocation formation [9]. Figure 2 compares the

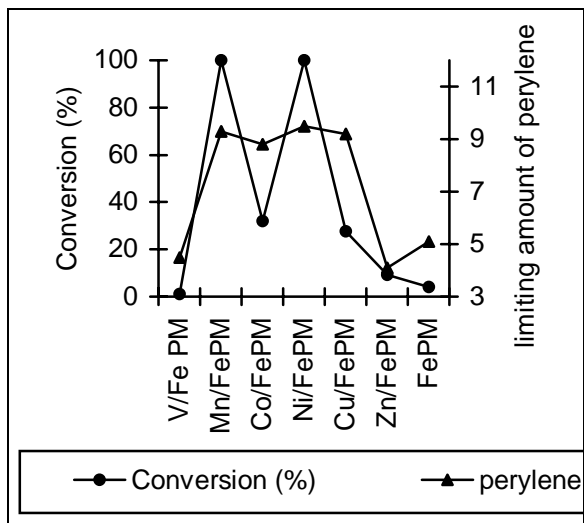


Figure 2. Correlation between activity and limiting value of perylene adsorbed

In order to get more insight on the mechanistic and kinetic properties of the reaction, the effects of various reaction variables were studied using V/Fe PM. The structural stability also was examined by the moisture sensitivity and metal leaching experiments. Leaching of metals from the catalyst surface can occur without much transformation in reaction profile, gradually changing the nature of reaction from truly heterogeneous to partly homogeneous [10].

activity of systems with limiting amount of perylene adsorbed on the catalyst surface. Perylene, being large in size may not be accessible to all the Lewis acid sites present inside the three dimensional network and hence the slight deterioration from perfect correlation. A perfect correlation is obtained between catalytic activity and amount of strong acid sites (ammonia desorbed in the temperature region of 401-600°C). Thus strong acid sites may be considered to be involved in the benzylation of benzene with benzyl chloride. Though the pillared clay surface provides both Lewis and Brønsted acid sites, the above observations clearly indicate the dominating impact of Lewis/strong acid sites for the benzylation of benzene with benzyl chloride.

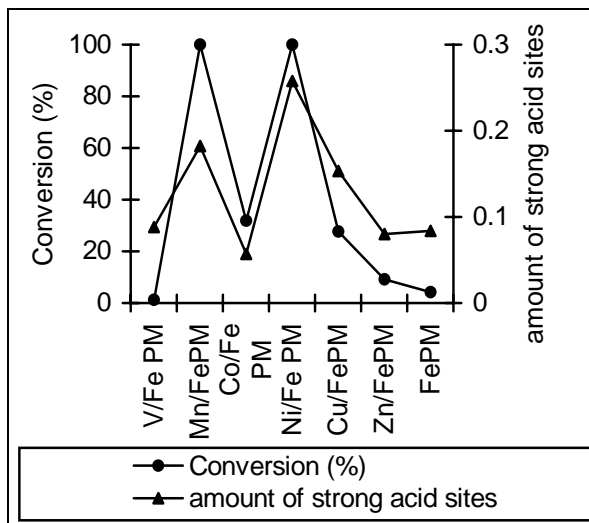


Figure 3. Dependence of activity on amount of strong acid sites from NH_3 -TPD

Fe in the clay can be reduced and this has every chance of combining with Cl^- ions from benzyl chloride, forming FeCl_3 . This fact questions the heterogeneous nature of the reaction. Hence, the effect of leaching of iron was studied at 35 minutes, by continuing the reaction for further 25 minutes, after filtering off the catalyst. The results are given in table 7. The presence of Fe^{3+} was further examined qualitatively by addition of thiocyanate ions to the filtrate

Table 7. Metal leaching studies

Time (minutes)	Conversion %
	69.6
35	75.2
25*	

(* after filtering off the catalyst)

Temperature- 70°C, benzene/BC- 10, catalyst/BC- 0.1515

For iron containing system, percentage conversion at the time of filtration of catalyst is 69.6, which increase to 75.2 on continuing the reaction for 25 minutes after the removal of the catalyst. On addition of thiocyanate ions, reaction mixture give blood red colour, confirming the presence of leached out iron ions. The increase in product yield, though diminutive is significant. The result itself is suggestive of a partly homogeneous reaction. Fe from the pillaring species has been leached out into the reaction mixture, which then combines with chloride ions to give FeCl_3 . The presence of blood red colour on addition of thiocyanate ions confirms the presence of Fe^{3+} ions in the reaction mixture. This is responsible for the reaction even after the removal of the active catalyst.

Similar results have been reported by Arata *et.al* for benzylation reactions using benzoyl chloride over sulphate and tungstate modified Fe_2O_3 [11].

The Lewis acid catalysts usually used for Friedel-Crafts alkylations are moisture sensitive. Hence, conventional catalysts demand moisture free solvent and reactants, anhydrous catalyst and dry atmosphere for their handling. In order to test the effect of moisture on catalyst performance, the catalyst and substrate were saturated with water vapour, by keeping them over deionised water in a dessicator for 72 hours at room temperature. The reaction was carried out as usual. The results are given in figure 4.

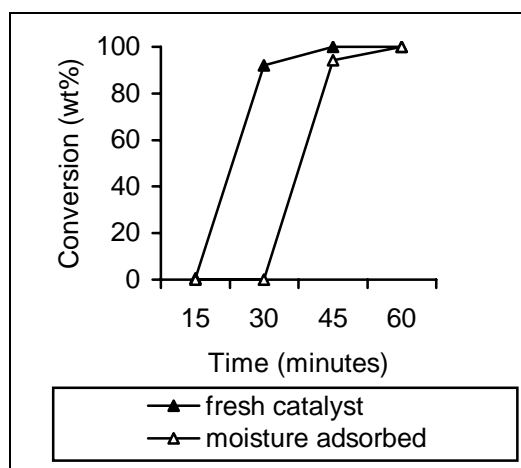


Figure 4. Moisture adsorption studies
Temperature- 70°C, benzene/BC- 10, catalyst/BC-0.1515

The induction period for the reaction increase in presence of moisture, after which, the reaction proceeds as in

moisture free conditions. However, the increase in induction period is quite low (15 minutes). The increase in induction period is

suggestive of water molecules occupying the active sites prior to reaction, from where Cl^- ions displace them. Thus induction period is the time required for replacing the adsorbed moisture by the reactants to start the reaction⁶. Once the sites are freed from water molecules, reaction goes on as in moisture free conditions. this leads us to the conclusion that the catalyst systems are active even in presence of moisture. The

increase in reaction induction period was reported by Choudary *et.al* also [12].

Time plays an imperative part in the reaction (figure 5). The figure shows the reaction rate is nominal for a particular period of time, after which, it continually increases. Further it is worth mentioning that no polyalkylated products are formed even after complete conversion of benzyl chloride unlike other reports [13].

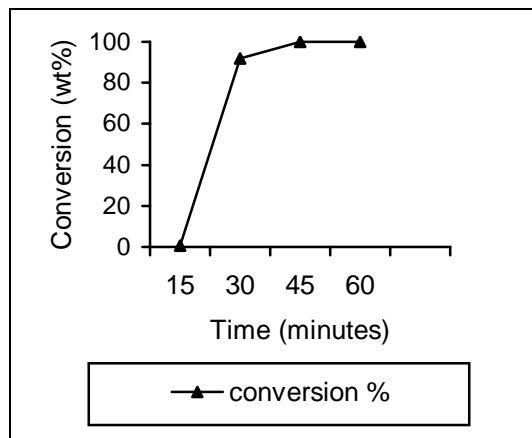


Figure 5. Dependence of time on conversion %
Temperature- 70°C, benzene/BC- 10, catalyst/BC- 0.1515

The continual increase in percentage conversion with time is indicative of the heterogeneous nature of the reaction. Selective formation of monoalkylated product can be attributed to the porous two dimensional structure of pillared clays restricting the attack of benzyl cation on the bulky product species. The side products are supposed to be dibenzyl benzene and higher products, which are formed through secondary reactions and these were not observed. The presence of induction period is suggestive of a different type of mechanism for the reaction.

The effect of temperature on benzylation of benzene using transition metal doped pillared clays was studied. The results are presented in figure 6. It can be seen that temperature plays a prominent promotional role in the reaction. Alkylation of benzene with benzyl chloride proceed to

completion at a low temperature (60°C) in 2 hours. Even a slight increment in temperature has an extremely beneficial effect in the time required for complete conversion. The conversion at a given time as well as time required for complete conversion is most advantageous at the reflux temperature of benzene. At the reflux temperature of benzene, the reaction proceed to completion in 30 minutes. Thus, alkylation with benzyl chloride need much lower activation energy over iron pillared systems. Another interesting feature of the reaction is the initial induction period, when there is no reaction. This period, which is 90 minutes at 60°C reduce to 45 minutes as the temperature is enhanced by 5°C. Increase in temperature does not have any detrimental effect in the cent percentage selectivity to diphenylmethane.

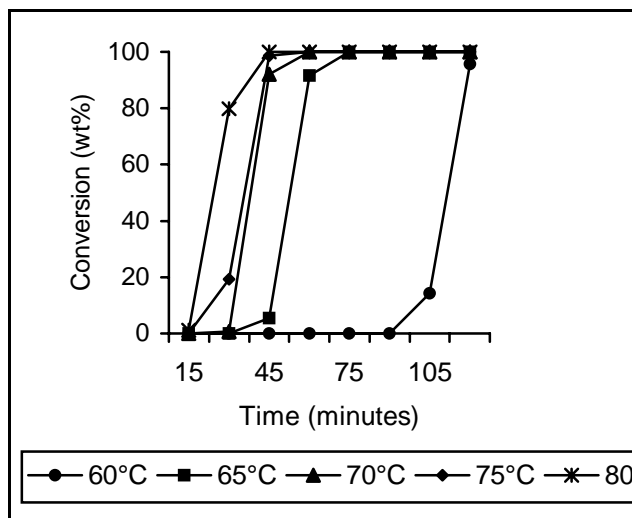
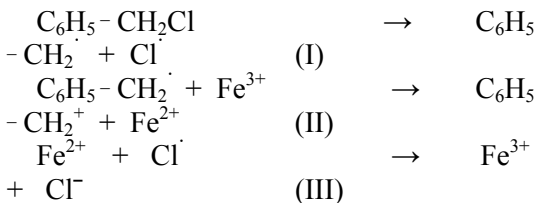


Figure 6. Dependence of activity on temperature.
benzene/BC- 10, catalyst/BC- 0.1515

It is evident from figure 6 that the reaction temperature has a vital role in the benzylation of benzene. Increase in reaction rate with subsequent increase in temperature is probably due to speedy desorption of product at higher temperatures, thus exposing the catalyst active sites for further adsorption of reactants, resulting in enhanced reaction rates. The increase in alkylation activity can also be recognised with increase in intrinsic activity of acid sites on the bare catalyst surface. The initial induction period is suggestive of a particular mechanism, once benzyl chloride is the benzylating agent. Fe in the clay can be reduced at room temperature producing free radicals. Radicals are powerful reductants, oxidised in presence of reducible metallic ions like Fe^{3+} , Sn^{4+} etc. The high activity thence observed could be ascribed to different initiation of the reaction, for instance, homolytic rupture of C - Cl bond followed by oxidation of radical [8,14].



In this mechanism, homolytic rupture of the C - Cl bond should be the rate determining step. It can be deduced that the

energy of rupture will prevent it from taking place at lower temperatures. The benzyl carbocation attached to the catalyst surface facilitates the attack of the arene molecule.

Benzene to benzylating agent molar ratio was studied by taking appropriate amounts of benzene, keeping the amount of catalyst and benzyl chloride fixed. The results are given in table 8. An inverse relationship is observed between benzene to benzyl chloride molar ratio and conversion % at any given time. Thus, higher amounts of benzene in the reaction mixture prolong the time required for complete conversion. It is worth mentioning that self condensation of the reagent or 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. This can be explained as, lower the reactant molar ratio, higher the amount of benzylating agent and hence increase in reaction rate. Thus, the catalyst is very efficient for the creation of the benzyl carbocations even at high concentrations of the reagent. Higher reactant molar ratios result in insufficient interaction with catalyst surface for the formation of free radicals, consequently prolonging the induction period. Thus, this

result also is indicative of free radical type initiation reaction.

Table 8. Dependence of activity on benzene to benzyl chloride ratio

Benzene/BC	Time (minutes)					
	15	30	45	60	75	90
5.0	3.2	90.8	100	100	100	100
7.5	4.7	58.9	100	100	100	100
10.0	0	5.5	91.5	100	100	100
12.5	0	0	0	0	2.3	84.6

Temperature- 70°C, catalyst/BC- 0.1515

The effect of catalyst concentration on benzylation of benzene was scanned by varying the amount of catalyst, keeping the amount of reactants constant. The percentage conversions obtained at a time interval of 15 minutes are summarised in table 9. The amount of catalyst is expressed as wt% of benzyl chloride. The table shows that presence of catalyst even in trace amounts has marked influence in product yield. Increase in catalyst concentration, enhance the percentage conversion and at a stage, the reaction rate levels off. Thus, only a small amount of catalyst is needed for easy

completion of reaction. Cent percentage selectivity to monoalkylated product even at high catalyst concentrations is commendable. Higher amounts of catalyst result in an enhanced amount of active sites and hence increase in reaction rate. Since the systems under study are very efficient Friedel-Crafts catalysts, only a small amount of catalyst is needed for the reaction. Speedy adsorption and desorption of the reactants and products from the catalyst surface coupled with higher amount of strong acid sites may be responsible for the high performance.

Table 9. Dependence of catalyst concentration on conversion (%)

Catalyst/BC	Time (minutes)			
	15	30	45	60
-	0	0	0.9	2.8
0.0758	0	0	85.2	99.8
0.1515	0	0.6	92.0	100
0.227	0	3.6	96.5	100
0.303	0	14.5	95.8	100

Temperature- 70°C, benzene/BC- 10/1.

The effect of substrate on percentage conversion was studied with different substrates, both activated and deactivated (Table 10). Temperature for the reaction of fluorobenzene and chlorobenzene was respective refluxing temperatures. The observed order of reactivity of substrates is *o*-xylene > toluene > benzene > chlorobenzene > fluorobenzene. Also, the induction period for hydrocarbons is very low compared to halobenzenes. From the

results it can be inferred that the activating and deactivating effect of substituting groups in the benzene ring has a profound influence on the rate of the reaction. The observed order of reactivity is exactly the same as the order of electron releasing effect of the substituting group in the benzene ring. The inductive effect of methyl group makes the reaction more facile with toluene and still higher for xylene due to the cumulative effect of two methyl groups. Similar results

have been reported by Jun *et.al* [15]. The electron withdrawing effect of halo group

decreases the reaction rate for halobenzenes.

Table 10 Dependence of substrate on conversion (%)

Substrate	Time (minutes)								
	15	30	45	60	75	90	105	120	135
<i>o</i> -xylene	74.3	100	100	100	100	100	100	100	100
toluene	61.2	100	100	100	100	100	100	100	100
benzene	0.0	4.6	92.0	100	100	100	100	100	100
chlorobenzene	0.0	0.0	30.9	63.5	96.1	100	100	100	100
fluorobenzene	0.0	0.0	0.0	0.0	0.0	0.0	5.73	39.9	100

Temperature- 70°C, benzene/BC- 10, catalyst/BC- 0.1515

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 [16]. Hence a redox mechanism was suggested for the reaction.

Based on the observations of present study, a plausible reaction mechanism is suggested for the reaction (Figure 7). The mechanism is similar to the mechanism of alkylation reaction catalysed by an M^+-H species present on synthetic transition metal oxide $SiO_2-Al_2O_3$ systems [17]. The alkylating agent, benzyl chloride interacts with the active species and forms the alkylating moiety $M^+-CH_2-C_6H_5$ that in turn attacks the benzene molecule forming a pi-complex. This is possible due to the partially filled d- orbitals of Fe(III) present in the pillars. The framework Fe does not contribute to the formation of pi 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 [18]. Thus the intermediate of the alkylating 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 [19].

Conclusions

Transition metal exchange of iron pillared montmorillonite resulted in materials with good acidic and textural properties. Studies on elemental composition and surface area indicate the presence of exchanged metal inside the porous network. XRD evidences the effective expansion of the clay sheets on pillaring. An important property of the pillared clays, *viz.*, acidity benefited much on transition metal exchange in particular the strong/Lewis acid sites. Benzylation of benzene occurs efficiently over these catalysts. Cent percent monoalkylated product selectivity is obtained with these catalysts. Studies on reaction variables are suggestive of free radical type initiation for the reaction over iron pillared montmorillonites.

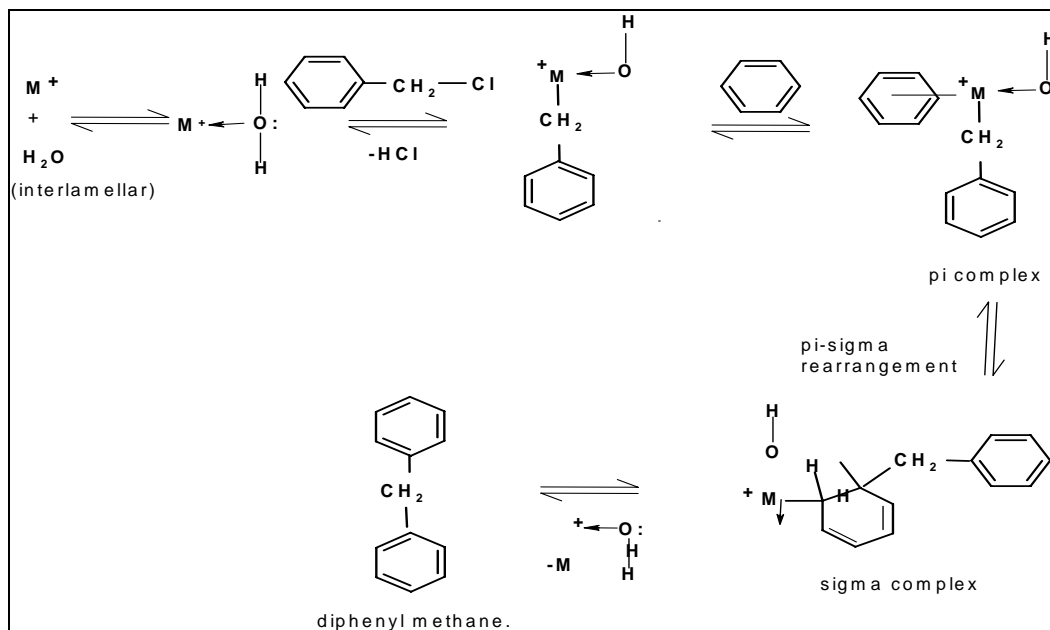


Figure 7. A plausible mechanism for benzylation of benzene with benzyl chloride over pillared clays. M^+ is Fe^{3+} .

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