

Liquid phase benzylation of *o*-xylene over pillared clays

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Iron, aluminium and mixed iron aluminium pillared clays have been prepared by partial hydrolysis method and doped with 10% Mo, V and Cr. The samples have been characterised by XRD, FTIR and surface area and pore volume measurements. The surface acid site distribution has been determined by temperature programmed desorption of ammonia. Vanadia incorporated systems show maximum acidity. Benzylation of *o*-xylene has been done as probe reaction to test catalytic activity. Benzyl chloride is a superior benzylating agent compared to benzyl alcohol in activity and selectivity. Cent percent selectivity towards monobenzylated product is obtained in all the cases. Fe pillared systems exhibit maximum activity. The catalytic activities of the systems can be correlated with the amount of strong acid sites. The effects of various reaction variables on the reaction have been studied. Presence of moisture has a diminishing effect on the reaction rate.

Naturally occurring montmorillonite clays are layered aluminosilicates held together by weak electrostatic forces. Intercalation of montmorillonite clays via exchange of cations located in their interlayer space with hydroxy metal cations, followed by a thermal treatment is an effective approach to modulate them to obtain catalysts, catalyst supports or adsorbents. The materials thus prepared are referred to as pillar interlayered clays (PILCs). The insertion of transition metal oxide pillars received much interest, as the pillar itself is catalytically active. Single as well as mixed metal oxides have been used as pillars. By varying the size, charge and shape of the entering ions, a homogenous network of micropores can be obtained with pore openings ranging in size from 16-30 Å. These pores are easily accessible for adsorption of gases and vapours¹⁻⁴.

Pillar interlayered clays are characterised by high surface area, pore dimensions larger than those encountered in most zeolites and substantial intrinsic acidity. These qualities have led to numerous attempts to apply pillared clays in catalysis, mainly of the acid type. Potential application of pillared clays in catalytic processes would require the pillar intercalated clay structure to accommodate transition metal ions, which are known to easily change their oxidation state⁵. Many interesting results have been obtained for processes of significant practical importance; hydroxylation of phenol by Cu-doped Al₂O₃-PILCs⁵, selective catalytic reduction of NO with NH₃ over V₂O₅ doped TiO₂ PILCs⁶, selective

catalytic reduction of NO by ethylene in presence of O₂ by Cu-doped TiO₂ PILCs⁷ etc.

Benzylation of *o*-xylene with benzyl chloride, which is a typical example of Friedel-Crafts alkylation, produces dimethyldiphenylmethanes (DMDPM's) used as synthetic intermediates for the production of dielectric fluid⁸. Traditionally, homogeneous acid catalysts like AlCl₃, BF₃ and H₂SO₄ are used for this type of reaction. However, use of Lewis acid catalysts is laden with several problems like difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity etc. These catalysts also catalyse other undesirable reactions like alkyl isomerisations and *trans*-alkylation reactions⁹. Moreover, these catalysts are moisture-sensitive and hence demand moisture-free solvent and reactants, anhydrous catalysts and dry atmosphere for their handling¹⁰. Hence world wide efforts have been made to prepare highly acidic solid acid catalysts like heteropoly acids¹¹, sulphated zirconia¹², Ga₂O₃ and In₂O₃ supported on mesoporous Si-MCM-41⁹, Al and Al/Ga pillared clays¹³ and Fe containing zeolites¹⁴.

In this paper, we report the benzylation of *o*-xylene with benzyl chloride and benzyl alcohol over Mo, V and Cr doped Al, Fe and Fe-Al mixed pillared clays. The results obtained for various catalysts and the effect of reaction variables on catalyst performance is also included. Catalytic activity in the presence of moisture and the heterogenous nature of the reaction have been investigated. The catalysts were

characterised by X-ray diffraction, FTIR spectroscopy, surface area and pore volume measurements. The surface acid site distribution was found out by NH_3 -TPD. Finally, the catalytic activities are correlated with the amount of strong acid sites as well as their availability for the reaction.

Materials and Methods

The starting montmorillonite was supplied by Aldrich Chemical Company, Inc (Milwaukee, USA). All pillared clays were prepared by partial hydrolysis method. The corresponding nitrate solution (0.1 M) was hydrolysed with the dropwise addition of 0.3 M Na_2CO_3 solution under vigorous stirring for 3 hours. N_2 gas was bubbled through the solution to remove excess CO_2 . The pillaring solution was aged for 24 hours, added to the clay, which was previously swollen for 24 h and stirred for 25 h [OH/M ratio of 2 and M/clay ratio of 20 mmol/g clay]. For Fe-Al mixed pillared systems, equimolar ratio of the metals was taken. For Al pillaring, temperature for exchange was 70°C and for others, 80°C. The clay after exchange was washed several times, dried in the air oven at 110°C and calcined for 6 h at 450°C. For doping with transition metal ions, calculated amounts (10% by wt) of the ammonium salt was added to the pillared clays and refluxed with magnetic stirring using acetone as the solvent. Acetone was dried off at room temperature and the clay was dried at 80°C and calcined at 300°C overnight. The prepared catalyst samples are notated as M/PM PILC where M is the incorporated transition metal and PM is the pillaring metal.

Surface area and pore volume measurements were done in a Micromeritics Gemini 2360 analyser. XRD profile of the samples was recorded with a Rigaku D Max C X-ray diffractometer using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) by powder XRD method. FTIR spectra of the samples were recorded in a Shimadzu spectrophotometer (DR 8001) using KBr pellet method. The total acidity of the samples was determined by temperature programmed desorption of ammonia (NH_3 -TPD). Sample (0.5g) was treated with N_2 at 300°C for 2 h, cooled to room temperature and ammonia was injected into the sample. This was kept as such for 15 minutes for the equilibrium adsorption of ammonia to all acidic sites. Excess ammonia was flushed off. The desorbed ammonia was collected at a temperature interval of 100°C into 0.02 N H_2SO_4 solution. This was quantified by direct titration with Na_2CO_3 solution using methyl orange indicator. The

amount of ammonia desorbed at 30-200, 201-400, 401-600°C were assigned as weak, medium and strong acid sites respectively.

The reactions were carried out in a closed 50 mL glass reactor fitted with a reflux condenser and a septum for withdrawing product samples. The temperature of the reaction vessel was maintained using an oil bath. The catalyst was activated for 2 h in a muffle furnace prior to reaction. In a typical run, appropriate amounts of *o*-xylene, benzylating agent and catalyst were allowed to react at specified temperatures (50°C for benzyl chloride and gentle reflux for benzyl alcohol) under magnetic stirring. Reaction mixture was withdrawn periodically and analysed using Chemito 8610 GC equipped with SE 30 column and FID. The percentage conversion (wt%) of benzyl chloride or benzyl alcohol is the total percentage of benzyl chloride or benzyl alcohol transformed.

Results and Discussion

Surface area and pore volume measurements

Table 1 shows the BET surface area and pore volume of the prepared samples. Pillaring increased the surface area of the parent clay significantly. Iron pillared samples exhibited maximum surface area. Incorporation of transition metals was found to have a diminishing effect on the surface area of the samples. This is indicative of the accumulation of the incorporated metals in the pores of the pillared clay structure. Pore volume measurements also support this observation.

X-ray diffraction

The *d* spacing of the (001) plane in the parent clay increased drastically as a result of treatment with the pillaring solution followed by subsequent calcination. Thus XRD profile was indicative of effective pillaring. The *d* spacing obtained for the different pillars are as follows: Fe PILC, 19.2 Å; Fe-Al PILC, 17.7 Å; and Al PILC, 17.9 Å. Fe pillaring was the most effective in propping apart the clay layers.

FTIR measurements

In the FTIR spectrum of the parent, pillared and transition metal doped montmorillonites, the parent montmorillonite showed two bands on the OH stretching region; a band at 3740 cm^{-1} attributable to silanol groups of the external layer and a broader band at 3650 cm^{-1} due to Al_2OH group of the octahedral

Table 1—Surface area and pore volume measurements

Catalyst	BET surface area (m ² /g)	Pore volume (cc/g)
Fe PILC	179.6	0.1503
V/Fe PILC	53.7	0.0493
Mo/Fe PILC	46.8	0.0396
Cr/Fe PILC	41.2	0.0342
Al PILC	113.4	0.0912
V/Al PILC	39.6	0.0323
Mo/Al PILC	29.8	0.2490
Cr/Al PILC	27.2	0.0210
Fe-Al PILC	128.9	0.1113
V/Fe-Al PILC	43.3	0.0371
Mo/Fe-Al PILC	37.2	0.0312
Cr/Fe-Al PILC	34.8	0.0298

layer. In the pillared samples, the intensity of the band at 3740 cm⁻¹ increased with respect to the other. This can be interpreted as an effect of pillaring. The IR spectra in the fingerprint region were characterized by absorptions at 1200-1000 cm⁻¹ (asymmetric stretching vibrations of SiO₂ tetrahedra), a duplet around 800 cm⁻¹ (stretching vibrations of Al^{IV} tetrahedra) and absorptions at 526-471 cm⁻¹ (bending Si-O vibrations). 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.

Temperature programmed desorption of ammonia.

The NH₃-TPD method, widely employed to characterise the acidity of solid acids, lacks in selectivity, because ammonia can titrate acid sites of any strength and type. Moreover, ammonia molecule can be adsorbed by a hydrogen bond or a dipolar interaction. Figures 1, 2 and 3 show the acid site distribution of the various samples. In all the cases, weak and medium strength acid sites predominated the strong acid sites. Among the various pillars, Al pillars showed maximum acidity. Mixed oxide pillaring gave lower cumulative acidity, as compared to the parent pure oxide pillars. Transition metal incorporation considerably increased the cumulative as well as weak and medium strength acid sites in all cases. But the amount of strong acid sites did not vary much in almost all cases due to transition metal incorporation. Among the incorporated metal oxides, vanadia showed maximum acidity.

Catalytic activity of various systems

The catalytic activity of the transition metal doped pillared clays was checked by carrying out the

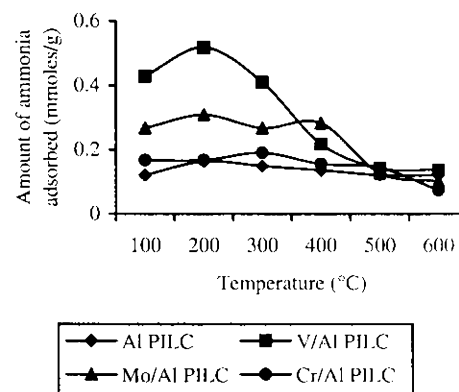


Fig. 1— Acid site distribution from temperature programmed desorption of ammonia for Al pillared systems.

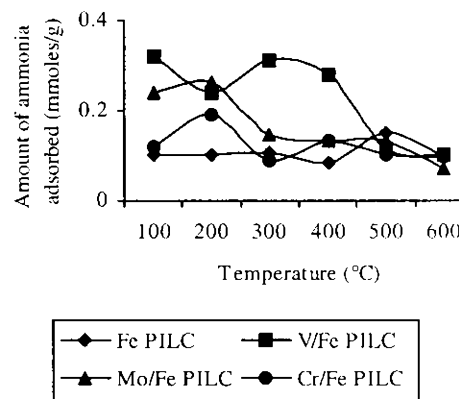


Fig. 2— Acid site distribution from temperature programmed desorption of ammonia for Fe pillared system.

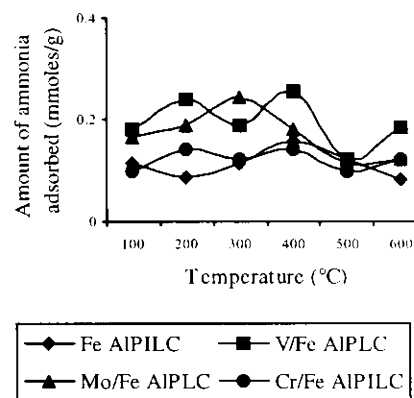


Fig. 3— Acid site distribution from temperature programmed desorption of ammonia for Fe-Al pillared systems.

benzylation reaction of *o*-xylene giving dimethyldiphenylmethanes. The reaction was studied using two benzylating reagents viz. benzyl chloride and benzyl alcohol. Benzylation with benzyl chloride was found to give exclusively the *p*-product, while benzylation with benzyl alcohol gave *o*-product in preference to *p*-product (Table 2). It is noteworthy that no di- or polyalkylated products were formed in both the cases. This can be attributed to the porous two dimensional structure of pillared clays, restricting further alkylation of the bulky product. The data in Table 2 also show that the reaction was much faster, when the catalyst contained Fe. Since the redox potential of Fe^{2+}/Fe^{3+} is low, the conversions, which are a measure of activities, were higher for iron containing catalysts¹⁵. Among the incorporated metals, V showed the maximum activity, irrespective of the benzylating agent. The catalytic activities can be well correlated to the amount of strong acid sites obtained from NH_3 -TPD. The influence of certain reaction variables in the catalytic behaviour was

studied using Fe-Al PILC as the reference.

Effect of temperature

Temperature plays a vital role in the reaction (Table 3). Alkylation with benzyl chloride proceeded to completion at a lower temperature (70°C) in 15 min while with benzyl alcohol, gentle refluxing of the reaction mixture for 75 min was needed to complete the reaction. Again, with benzyl chloride, 10° increase in temperature increased the conversion by 20% while with benzyl alcohol, a 10° rise in temperature produced a threefold enhancement of the reaction rate. Thus, alkylation with benzyl chloride needed much lower activation energy when compared to benzyl alcohol. This result is suggestive of a particular mechanism, once benzyl chloride is the benzylating agent. Fe in the clay can be reduced at room temperature and can produce free radicals. Radicals are powerful reductants, which should be oxidised in presence of reducible metallic ions like Fe^{3+} , Sn^{4+} , etc. The high activity observed with these

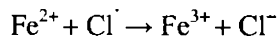
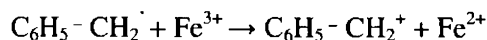
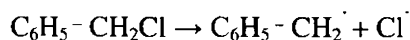
Table 2—Catalytic activity of various systems towards benzyl chloride. (temp-50°C, time-10 min, *o*-xylene: benzyl chloride-10:1, catalyst/benzyl chloride-0.152) and benzyl alcohol (temp-gentle reflux, time-60 min, *o*-xylene: benzyl alcohol-10:1, catalyst/benzyl alcohol-0.0859)

Catalyst	Benzyl chloride		Benzyl alcohol	
	Conversion (%)	Conversion (%)	Selectivity (%)	
			<i>o</i> -product	<i>p</i> -product
FePILC	100	91.3	96.3	3.7
V/FePILC	99.2	100	100	-
Mo/FePILC	99.2	99.2	100	-
Cr/FePILC	99.3	93.7	100	-
AlPILC	14.2	6.3	65.7	34.3
V/AlPILC	27.5	11.7	53.0	47.0
Mo/AlPILC	13.2	7.3	56.4	43.6
Cr/AlPILC	12.7	3.5	76.8	23.2
Fe-AlPILC	60.5	93.0	84.0	16.0
V/Fe-AlPILC	100	50.9	71.8	28.2
Mo/Fe-AlPILC	46.5	32.1	50.5	49.5
Cr/Fe-AlPILC	32.9	18.3	79.3	20.7

Table 3—Effect of temperature *o*-xylene: benzyl chloride-10:1, time-10 min, catalyst/ benzyl chloride-0.152
o-xylene: benzyl alcohol -10:1, time-60 minutes, catalyst/benzyl alcohol-0.0859

Benzylating agent	Temperature (°C)	Conversion (%)	Selectivity (%)	
			<i>o</i> -product	<i>p</i> -product
Benzyl chloride	40	38.2	-	100
	50	60.5	-	100
	60	89.5	-	100
	70	99.7	-	100
	110	3.6	72.4	27.6
	120	14.3	53.3	46.7
Benzyl alcohol	130	32.6	57.4	42.6
	gentle reflux	93.0	84.0	16.0

cations could be ascribed to a different initiation of the reaction, for instance, homolytic rupture of C - Cl bond followed by oxidation of radical¹⁶.



With benzyl alcohol as the benzylating agent, the mechanism is probably purely ionic and hence the higher activation energy.

Effect of time

Effect of time on benzylation of *o*-xylene was studied. As the duration of the run was increased, the reaction went faster. When benzyl alcohol was the benzylating agent, the reaction showed gradual increase in rate with corresponding increase in time. Conversely, with benzyl chloride, in the first five minutes only a nominal product formation occurred, but a sharp leap in percentage conversion was observed after the first five minutes. This again is suggestive of a radical based initiation step. The reaction got completed in fifteen minutes with benzyl chloride whereas with benzyl alcohol 75 minutes was needed for complete conversion. Another interesting

point is that as the time goes on, the *o*- to *p*-product ratio increased from 1.1 to 9, indicative of the preferential formation of *p*-product in the initial stages. This is in accordance with the expectation, considering the steric hindrance at *o*-position. But as the reaction proceeded, the *o*-position became more susceptible to attack by the carbocation.

Effect of *o*-xylene to benzylating agent molar ratio

An inverse relationship was observed between *o*-xylene to benzylating agent molar ratio and conversion irrespective of the benzylating agent (Table 4). This can be explained as follows: the lower the reactant molar ratio, the higher the amount of benzylating agent and hence the increase in reaction rate. Again, at lower amounts of *o*-xylene, the *o*- to *p*-product ratio also increased.

Effect of catalyst concentration

Table 5 shows the effect of catalyst concentration on the benzylation of *o*-xylene. Increase in catalyst concentration, enhanced the percentage conversion and at a stage the reaction rate leveled off. Thus, only a small amount of catalyst was needed for the easy completion of the reaction. Again, increase in catalyst concentration boosted the *o*-product selectivity. With

Table 4—Effect of *o*-xylene: benzylating agent (BA) ratio temperature-50°C, time-10 min catalyst/ benzyl chloride-0.152 temperature-gentle reflux, time-60 minutes, catalyst/benzyl alcohol-0.0859

Benzylating agent	<i>o</i> -xylene : BA	Conversion (%)	Selectivity (%)	
			<i>o</i> -product	<i>p</i> -product
Benzyl chloride	5/1	95.6	5.2	94.8
	10/1	60.5	-	100
	15/1	37.1	-	100
	20/1	38.1	-	100
Benzyl alcohol	5/1	95.7	82.6	17.4
	10/1	93.0	84.0	16.0
	15/1	67.5	84.5	15.5
	20/1	27.8	70.1	29.9

Table 5—Effect of catalyst concentration temperature-50°C, *o*-xylene: benzyl chloride-10:1, time-10 min temperature-gentle reflux, *o*-xylene: benzyl alcohol-10:1, time-60 minutes,

Benzylating agent	Catalyst / BA	Conversion (%)	Selectivity (%)	
			<i>o</i> -product	<i>p</i> -product
Benzyl chloride	0.0758	30.6	-	100
	0.1515	60.5	-	100
	0.227	89.7	-	100
	0.303	72.4	16.2	83.8
Benzyl alcohol	0.0429	86.8	67.6	33.4
	0.0859	93.0	84.0	16.0
	0.1288	100	100	-
	0.1717	100	100	-

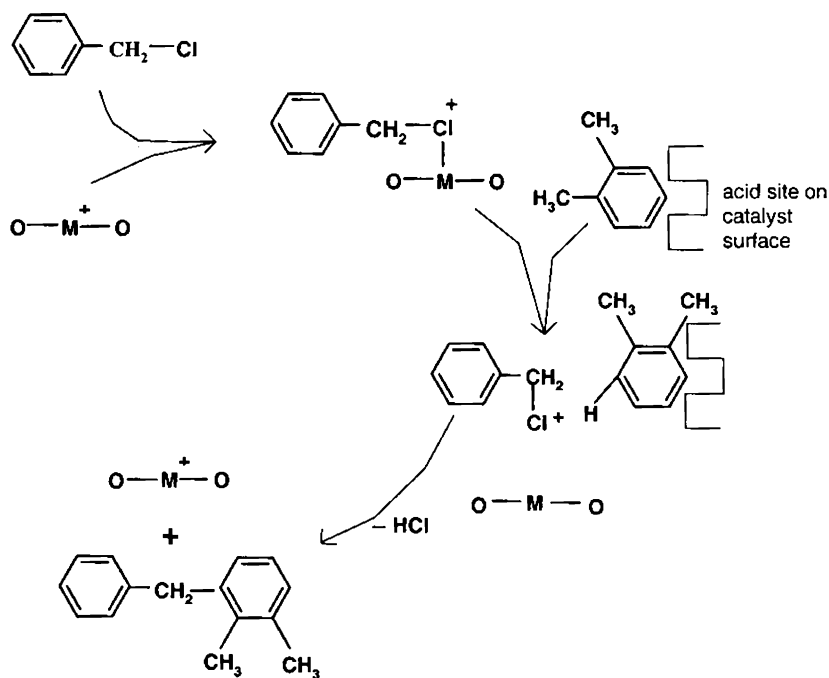


Fig. 4—Plausible mechanism for *o*-product formation over acidic sites on the solid acid.

benzyl chloride, high concentration of catalyst resulted in deviation from cent percent *p*-product selectivity.

The trend in *o*-product selectivity leads to the conclusion that *o*- and *p*-product formation occurs by two different mechanisms. For *p*-product, the generally accepted mechanism for Friedel-Crafts alkylations and acylations in which, the benzyl carbocation formed by the interaction with catalyst surface attacking the unadsorbed substrate molecules, forming product¹⁷ is appropriate. *Ortho* product formation is more difficult in this case due to the hindrance of three bulky functional groups attached at adjacent positions in the same ring. Nevertheless, increase in reaction time, catalyst concentration and decrease in reactant molar ratio favours *o*-product formation.

Therefore, for *o*-product formation, we propose a new mechanism in which the *p*-position of *o*-xylene is locked from attack by benzyl cations. *O*-xylene has two electron releasing groups and this causes an accumulation of a slight negative charge in the ring. Thus, *o*-xylene gets adsorbed to acidic sites on the catalyst surface, preferably at *para* position, considering steric factors. The *p*-position being blocked, the benzyl cation attacks the *o*-position. This is depicted in Fig. 4.

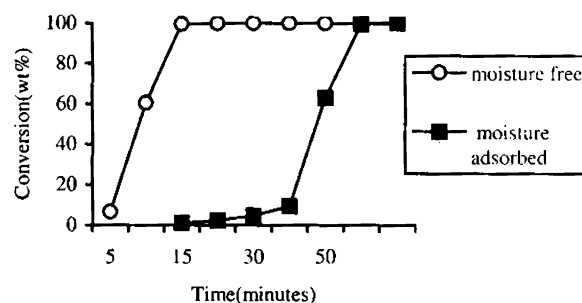


Fig. 5—Effect of moisture

At lower reaction times, the attack by benzyl cation occurs before the adsorption of *o*-xylene molecules to catalyst surface. Thus, shorter reaction times may be the reason for the cent percent *p*-product selectivity when benzyl chloride is the benzylating agent. Again at higher *o*-xylene concentrations, the benzyl cation attacks the *p*-position of the unadsorbed *o*-xylene molecules, which are greater in number. Higher catalyst concentrations lead to greater adsorption of substrate molecules at the catalyst surface and hence better *o*-product selectivity. Thus different

mechanisms for *o*- and *p*-product formation based on the adsorption of the *o*-xylene on the catalyst molecule clearly gives an explanation for the preferential formation of *p*-product when benzyl chloride is used as the benzylating agent and *o*-product when benzyl alcohol is used.

Effect of leaching

Fe in the clay can be reduced and this has every chance of combining with Cl^- ions from benzyl chloride, forming FeCl_3 . Hence, the effect of leaching of iron was studied by continuing the reaction for 5 minutes, after filtering off the catalyst. The percentage conversion increased from 60.5 to 65.6 showing that the reaction is not completely heterogeneous. On addition of thiocyanate ions, the reaction mixture gave blood red colour, confirming the presence of leached out iron ions. This effect was not found when benzyl alcohol was the benzylating agent, signifying the heterogeneity of the reaction.

Effect of moisture

The Lewis acid catalysts usually used for Friedel-Crafts alkylations are moisture sensitive. In order to test the effect of moisture on catalyst performance, the catalyst and the substrate were saturated with water vapor, by keeping them over deionised water in a dessicator for two days. The reaction was carried out as usual. An induction period of 30 min was observed, when there was no or nominal reaction (Fig.5). After that, the reaction proceeds as in moisture free conditions. This induction period is suggestive of water molecules occupying the active sites prior to reaction, from where the Cl^- ions displace them. With benzyl alcohol, only dibenzyl ether was formed even after 3 hours signifying that benzyl alcohol was unable to displace the water molecules from the active sites.

Conclusion

Pillaring with Fe, Al and mixed Fe-Al species on montmorillonites yielded catalysts with enhanced basal spacing and high surface area and pore volumes. FTIR spectra and XRD profile confirmed the presence of incorporated transition metals. Excellent catalytic activity was shown towards benzylation of *o*-xylene with exclusive selectivity for the monoalkylated

products. The activities could be well correlated with the amount of strong acid sites obtained from NH_3 -TPD. Fe pillared samples showed maximum activity, indicative of a radical based initiation step. Studies on various reaction variables were suggestive of the operation of two different mechanisms for the production of the isomeric products. For Fe containing samples, leaching of Fe was noticed, pointing towards the slightly homogenic nature of the reaction. Presence of moisture produced an induction period for the initiation of the reaction.

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References

- 1 Pinnavia T J, *Science*, 220 (1983).
- 2 Figueras F, *Catal Rev Sci Eng*, 30 (3) (1988) 457.
- 3 Klopogge J T, *J Por Mat* 5 (1998) 5.
- 4 Gil A, Gandia L M & Vicente M A, *Catal Rev Sci Eng*, 42 (2000) 145.
- 5 Bahranowski K, Gazior M, Kielski A, Podobinski J, Serwicka E M, Vastikian L A & Wodnicka K, *Clays Clay Min*, 46 (1998) 98.
- 6 Yang R T & Long R Q, *Appl Catal B* 24 (2000) 13.
- 7 Yang R T, Tharappiwattananon N & Long R Q, *Appl Catal B* 19, (1998) 289.
- 8 Commanduer R, Berger N, Jay P & Kervannal J, EP 0 442 (1991) 986.
- 9 Ratnaswamy P, Singh A P & Sharma S, *Appl Catal A*, 135 (1996) 25.
- 10 Choudhary V R, Jana S K & Kiran B P, *J Catal*, 192 (2000) 257.
- 11 Izumi Y, Natsuma N, Takamine H, Tamaoki J & Urabe K, *Bull chem Soc Japan*, 62 (1989) 159.
- 12 Thorat T S, Khumbar P S & Yadav G D, *Tetrahedron lett*, 34 (1993) 529.
- 13 Lenarda M, Storaro L, Pellegrini G, Piovesan L & Ganzerla R, *J molec Cat A Chem*, 145 (1999) 237.
- 14 He N, Bao S & Xu Q, *Appl Cat A Gen*, 169 (1998) 29.
- 15 Choudhary B M, Kantam M L, Sateesh M, Rao K K & Santhi P L, *Appl Catal A Gen*, 149 (1997) 257.
- 16 Cseri T, Bekassy S, Figueras F & Rizner S, *J molec Cat A Chem*, 98 (1995) 101.
- 17 Jacob B, Sugunan S & Singh A P, *J molec Cat A Chem*, 139 (1999) 43.