

# Benzylation of arenes in the presence of Montmorillonite K10 modified using aqueous and acetonitrile solutions of $\text{FeCl}_3$

S.G. Pai, A.R. Bajpai, A.B. Deshpande, S.D. Samant \*

*Organic Chemistry Research Laboratory, Department of Chemical Technology, University of Bombay, N.M. Parikh Marg, Matunga, Mumbai 400 019, India*

Received 6 January 1999; accepted 3 November 1999

## Abstract

Montmorillonite K10 was modified by treating it with  $\text{FeCl}_3$  dissolved in acetonitrile and water. The catalysts thus prepared were activated at different temperatures and were used for the reaction of benzyl chloride with various arenes. The reactions were carried out at different temperatures and it was found that the difference in the activity was marked when the reaction was carried out at  $40^\circ\text{C}$ . The maximum activity was associated with Montmorillonite K10 modified by  $\text{FeCl}_3$  in acetonitrile solution and activated at  $120^\circ\text{C}$ . © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Friedel–Crafts benzylation; Montmorillonite K10; Fe-impregnation; Benzyl chloride;  $\text{Fe}^{3+}$ -exchanged clay; Clay catalysis; Diaryl methanes

## 1. Introduction

Catalysis of organic reactions by inorganic solids is an important new dimension in preparative organic chemistry. The replacement of homogeneous catalysts by solid acids for the Friedel–Crafts alkylation is a challenging task. In recent years, we have witnessed the development of clay-supported Lewis acids as heterogeneous catalysts for Friedel–Crafts alkylation in a solution phase [1–3]. Laszlo prepared a series of catalysts by exchanging transition metal cations on Montmorillonite K10 in an aqueous medium and tested their efficiency for the

Friedel–Crafts reaction; in particular, the benzylation of arenes [4]. Among these catalysts, the superiority of  $\text{Fe}^{3+}$  cations over  $\text{Al}^{3+}$  cations was surprising; particularly on the background of the reversal of reactivity in their homogeneous counterparts [5]. It indicates that the clay is not merely an inert support, but shows a selective synergistic/antagonistic effect on the activity of the metal cations it supports. In this context, the presence of Fe in a clay seems to be a crucial factor [6]. Cseri et al. have proposed a radical mechanism, as against the conventional carbenium ion mechanism for the benzylation of benzene using benzyl chloride with reducible cations, like  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  on Montmorillonite K10; and has also shown that the  $\text{Fe}^{3+}$  content of the clay controlled the activity in iron-containing clays, in spite of their low acidity [6,7].

\* Corresponding author. Tel.: +91-022-4145616; fax: +91-022-4145614.

E-mail address: [ssd@udct.ernet.in](mailto:ssd@udct.ernet.in) (S.D. Samant).

It is also observed that the solvent used in the impregnation procedure plays an important role in determining the activity of the resultant catalyst. Though in an aqueous treatment  $\text{Fe}^{3+}$ -K10 is superior to  $\text{Zn}^{2+}$ -K10, 'clayzic' prepared by the impregnation of  $\text{ZnCl}_2$  from methanol is much superior to both of them [8].  $\text{FeCl}_3$  impregnated on Montmorillonite K10 from a methanolic solution has been investigated earlier, but surprisingly found to be very poor as compared to 'clayzic' when the reaction was carried out at room temperature [8]. The high activity of 'clayzic' may be due to the faster diffusion of the reactants onto the catalytic sites [9]. Also, the activation temperature has a profound influence on the catalytic activity of these catalysts [10].

It is well known that in water, trivalent and tetravalent metal halides undergo hydrolysis forming polymeric species. Obviously, large variation in the nature of the catalytic species on the surface can be envisaged with respect to the solvent used. Recently, we showed that  $\text{FeCl}_3$ -impregnated Montmorillonite K10 (K10-FeOO280) was an excellent catalyst for the Beckmann rearrangement for diaryl ketoximes [11]. We have also recently reported our results on the catalytic activity and regioselectivity due to a new catalyst, i.e.,  $\text{FeCl}_3$ -impregnated Montmorillonite K10, in the benzylation of various arenes [12]. The benzylation of benzenes and toluenes is interesting for the preparation of substitutes for polychlorobenzenes, which are used as dielectrics. Benzyl substituted phenols are useful as antioxidants [13]. This prompted us to revisit the benzylation of benzene using benzyl chloride in the presence of  $\text{FeCl}_3$ -modified Montmorillonite K10.

The aim was to modify Montmorillonite K10 with  $\text{FeCl}_3$  in acetonitrile solution (K10-FeOO) and compare the catalyst with  $\text{Fe}^{3+}$ -exchanged Montmorillonite K10 (K10-FeAA). Along with this,  $\text{FeCl}_3$  was impregnated on Montmorillonite K10 using acetonitrile as a solvent and subsequently, the surface species were washed with water to exchange the ligands (K10-

FeOA). These procedures were expected to lead to different catalytic species on the surface of the catalyst. In addition to this, the effect of activation temperature on the catalytic activity was also investigated. To the best of our knowledge, this is the first report on the comparison of these types of catalysts.

$\text{FeCl}_3$  would be a normal dimeric species in an organic solvent. The solubility of  $\text{FeCl}_3$  in acetonitrile is high and the basicity of acetonitrile is poor, hence, acetonitrile was thought to be an ideal solvent for our purpose. Montmorillonite K10 was impregnated with  $\text{FeCl}_3$  in acetonitrile solution and the excess  $\text{FeCl}_3$  was removed by washing the catalyst with acetonitrile (K10-FeOO). In another procedure,  $\text{FeCl}_3$  was impregnated on K10 as given above, but the doped clay was washed thoroughly with deionised water to exchange ligandic Cl by OH (K10-FeOA). Similarly,  $\text{FeCl}_3$  was exchanged with K10 in its aqueous solution and the clay was thoroughly washed with deionised water (K10-FeAA). For comparison, Montmorillonite K10 was modified as per the procedure of Laszlo and Mathy [4] and Cseri et al. [6,7], to prepare  $\text{Fe}^{3+}$ -K10. The clays were activated at 120°C, 280°C and 550°C, which were selected on the basis of differential scanning calorimetry (DSC) results, to see the effect of different catalytic sites formed on the surface (the activation temperature is mentioned after the name of the catalyst).

## 2. Catalyst preparation

Montmorillonite K10 was obtained from Aldrich and Fluka (manufactured by Sud-Chemie). The Chemical composition (wt.%) of the clay (main elements) was  $\text{Al}_2\text{O}_3$ : 14.6;  $\text{SiO}_2$ : 67.6;  $\text{Fe}_2\text{O}_3$ : 2.9;  $\text{MgO}$ : 1.8. The BET surface area  $220 \pm 20 \text{ m}^2/\text{g}$  and microporous volume:  $0.1 \text{ m}^3/\text{g}$ .

$\text{Fe}^{3+}$ -K10 catalyst was prepared by the reported procedure [7].

**K10–FeOO catalyst:** FeCl<sub>3</sub> (15 g) was dissolved in dry acetonitrile (60 ml) and Montmorillonite K10 (10 g) was added over a period of 10 min. The resulting slurry was stirred at room temperature for 5 h. The clay was then filtered, washed with acetonitrile (10 ml), and then with benzene (60 ml).

**K10–FeOA catalyst:** FeCl<sub>3</sub> (15 g) was dissolved in dry acetonitrile (60 ml) and Montmorillonite K10 (10 g) was added over a period of 10 min. The resulting slurry was stirred at room temperature for 5 h. The clay was then filtered and washed with deionised water till free from Cl<sup>−</sup> ions (AgNO<sub>3</sub> test).

**K10–FeAA catalyst:** FeCl<sub>3</sub> (15 g) was dissolved in deionised water (60 ml) and Montmorillonite K10 (10 g) was added over a period of 10 min. The resulting slurry was stirred at room temperature for 5 h. The clay was then filtered and washed with deionised water till free from Cl<sup>−</sup> ions.

Each catalyst was activated at 120°C, 280°C and 550°C for a period of 5 h, e.g., K10–FeOO was activated at 120°C, 280°C and 550°C to obtain K10–FeOO120, K10–FeOO280 and K10–FeOO550 catalysts, respectively.

The catalysts were then preserved in a vacuum desiccator and used when necessary after activation at 120°C overnight (except K10–FeOO8).

### 2.1. Catalyst characterization

The BET surface area measurements (Table 1) indicated no appreciable change in the surface area of the three catalysts prepared (K10–FeOO, K10–FeOA and K10–FeAA) by different methods. The elemental analysis of the three catalysts (Table 1) indicated that K10–FeOO had a slightly higher Fe content than the other two catalysts K10–FeOA and K10–FeAA.

In order to decide about the activation temperature, the catalysts were analysed by DSC. In the DSC of K10–FeOO (Fig. 1a), an exotherm is observed at about 104°C, which is due to the liberation of HCl, indicating some kind of bond

Table 1  
Surface area and elemental analysis of the K10–Fe catalysts prepared

Catalyst	Surface area (m <sup>2</sup> /g)	Elemental analysis (%)		
		Fe	Al	Mg
K10–FeOO	222 ± 20	4.6	8.94	0.85
K10–FeOA	239 ± 20	3.27	8.98	0.85
K10–FeAA	190 ± 20	3.19	8.55	0.80

formation on the surface of the clay. At around 158°C, similar to that for K10 (Fig. 1d), there is an endotherm, indicating the removal of physisorbed water from the surface of the catalyst. At about 80°C, the removal of physisorbed water is complete. The sharp endotherm at 550°C was possibly due to the formation of iron silicates. The DSCs of K10–FeOA, K10–FeAA and Montmorillonite K10 (Fig. 1b and c), do not show the exothermic peak at 104°C. Based on these results, the catalysts were activated at 120°C, 280°C and 550°C.

In order to assess the morphological changes associated with the method of preparation of catalyst and the activation temperatures, SEM studies were performed on the three catalysts prepared, and also on the catalyst K10–FeOO activated at different temperatures. No significant morphological changes were observed on the surface of the catalyst.

### 2.2. Reactions

Ten substrates were investigated at various temperatures, as specified, using a batch reactor (Scheme 1).

Each reaction was carried out in a 25-ml round bottom flask equipped with reflux condenser, magnetic stirring and a CaCl<sub>2</sub> guard tube. The catalyst (0.1 g) was heated at 120°C overnight for activation in the reaction flask itself in open air. An arene (10 ml) and benzyl chloride (0.23 ml, 2 mmol) were added and the flask heated in a thermostated oil bath at the required temperature.

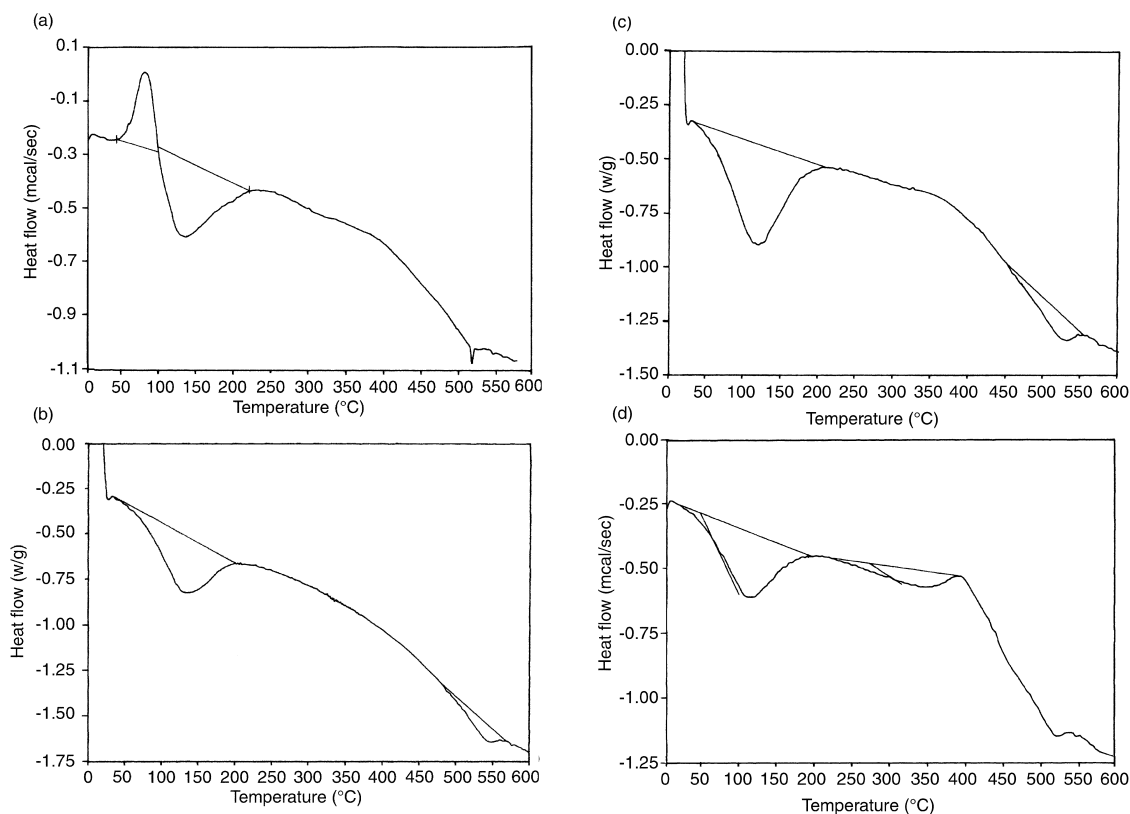


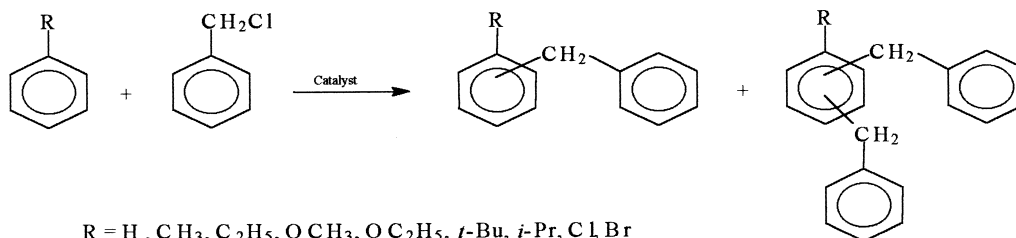
Fig. 1. (a) DSC curve for K10-FeOO. (b) DSC curve for K10-FeOA. (c) DSC curve for K10-FeAA. (d) DSC curve for Montmorillonite K10.

The products were analysed by GC using a Chemito 2865 Gas Chromatograph (5% SE-30, 1.5 mts) equipped with a flame ionisation detector. The temperature program followed was: 40°C–3 min–5°C/min–70°C–10 min–20°C/min–250°C.

GC–MS were recorded on a Hewlett-Packard GCD series Gas Chromatograph G1800A equipped with an electron capture detector.

### 3. Results

Previous workers have carried out the benzylation of arenes at 80°C. However, as the Friedel–Crafts reaction is kinetically controlled, the reaction of benzyl chloride with benzene was carried out at 40°C, 60°C and 80°C and for each reaction, the percentage conversion of benzyl chloride was studied (Table 2).



Scheme 1.

Table 2

Percentage of conversion of benzyl chloride after 60 min in the reaction of benzyl chloride with benzene at different temperatures in the presence of different K10–Fe catalysts

Figures in the parentheses indicate the reaction time in minutes.

Catalyst	Temperature		
	40°C	60°C	80°C
K10–FeOO120	100	100 (20)	100 (< 5)
K10–FeOO280	12	100	100 (15)
K10–FeOO550	– <sup>a</sup>	–	100 (15)
K10–FeOA120	96	100 (30)	100 (5)
K10–FeOA280	68	100 (20)	100 (8)
K10–FeOA550	–	17	100 (30)
K10–FeAA120	48	99	100 (15)
K10–FeAA280	62	100	100 (5)
K10–FeAA550	–	100	100
Fe <sup>3+</sup> –K10 <sup>b</sup>	14	94	100

<sup>a</sup>In this case, only about 8% conversion is obtained even after 8 h.

<sup>b</sup>Catalyst was prepared by the reported procedure [5].

### 3.1. Effect of activation temperature

In general, it was found that at any reaction temperature, as the activation temperature is increased, the rate of reaction decreased. This effect was pronounced when the reaction was carried out under the kinetic domain at 40°C, while it was less significant at 80°C.

### 3.2. Effect of work-up procedure

It was observed that the solvent used for the preparation of the catalyst had a profound effect on the catalytic activity particularly when the reaction was carried out at 40°C. Reactions

were also carried out using the untreated clay (Montmorillonite K10) and a model HCl treated clay (Filtrol-24) at 40°C to get an idea about the efficacy of the work-up procedure. Montmorillonite K10 could bring about only 2% conversion of benzyl chloride whereas Filtrol-24 gave 6% conversion of benzyl chloride after 1 h. Among all these catalysts, K10–FeOO120 was the best.

### 3.3. Selectivity for monobenylation

For each reaction, the conversion of benzyl chloride was first calculated from the standard of benzyl chloride, after the stipulated time. It was found that in the reaction monobenzylated product was formed along with the three isomers of dibenzylated product. No other compound was detectable (GC). In evaluating the mass balance and the product distribution using the authentic sample of the monobenzylated product, the percentage of the monobenzylated product formed was determined. As monobenylation referred to 1:1 stoichiometry of the arene and benzyl chloride, the remaining quantity of benzyl chloride was expected to be consumed for the dibenylation. On the basis of the relative intensities of the three isomeric peaks of the dibenzylated products and knowing the amount of benzyl chloride used up in the dibenylation, the isomer distribution was determined.

Among all the catalysts (Table 2), K10–FeOO120 was found to be the best, hence, the

Table 3

Mono- and di-benzylations of benzene at 100% conversion of benzyl chloride in the reaction of benzene with benzyl chloride at different temperatures in the presence of K10–FeOO120

Reaction temperature	Time for 100% conversion of benzyl chloride (min)	Monobenylation (%)	Dibenylation (%)		
			<i>o</i> -	<i>m</i> -	<i>p</i> -
40°C	60	96.8	2.0	0.5	0.7
60°C	20	93.7	2.3	0.7	3.3
80°C	5	93.6	2.3	0.8	3.3
80°C	120 <sup>a</sup>	93.4	2.4	0.8	3.4

<sup>a</sup>The reaction was continued for a longer time (120 min), in order to investigate the effect of equilibrium.

reaction was carried out in the presence of K10–FeOO120 at different temperatures and the proportions of monobenylation and dibenylation were noted at 100% conversion of benzyl chloride (Table 3). At 40°C, there was 96.8% monobenylation and 3.2% dibenylation. As the reaction temperature increased, there was a slight decrease in the selectivity towards monobenylation. In order to investigate the effect of equilibrium at 80°C, the reaction was continued for a longer time (120 min), when negligible change in the product-spread was observed.

When K10–FeOO activated at different temperatures was used for the reactions at 40°C and 80°C, it was observed that as the activation temperature increased, the selectivity towards monobenylation decreased from K10–FeOO80 to K10–FeOO165, increased to some extent with K10–FeOO280 and then decreased drastically with K10–FeOO550.

The benzylation of different arenes with benzyl chloride was carried out at 40°C and the product mixtures were analysed for mono- and di-benzylated products (Table 5).

As the conversion of benzyl chloride was low in the case of substrates other than benzene and toluene at 40°C, the reaction was studied at 80°C for the substrates (Table 6). At 80°C, the reaction gave quantitative yields with almost all the substrates within 15 min. The significant observation, however, was that even at this temperature; dibenylation was low with K10–FeOO120 as the catalyst.

#### 4. Discussion

It is known that when Montmorillonite K10 is treated with an aqueous solution of a metal salt, ion-exchange takes place and in the earlier work, attention had been focused on the exchange of the metal ions with the clay in the aqueous solutions only [4,6,7]. It has been

demonstrated that Fe<sup>3+</sup>-exchanged Montmorillonite K10 was the best catalyst for benzylation [4]. The concentration of FeCl<sub>3</sub> in water employed by the earlier worker was 1 M and the clay was equilibrated for 24 h. We found a linear relationship between the amount of Fe<sup>3+</sup> deposited and the amount of clay, both in the acetonitrile solution as well as in the aqueous solutions (Fig. 2a and b). The amount of Fe exchanged/doped was found to be optimum within 5 h; hence, further equilibration was not necessary.

The solvent had no effect on the surface area of the catalyst. The elemental analysis of the resulting catalyst showed that in the case of the K10–FeOO, the Fe content was slightly higher than that in the case of the other two catalysts.

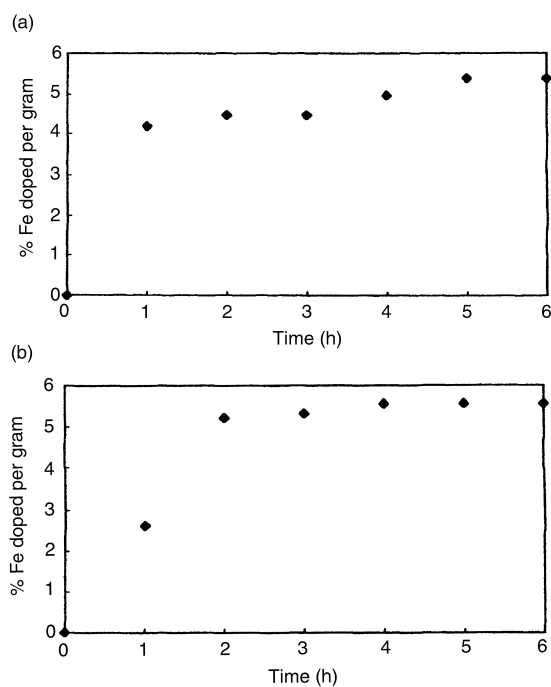


Fig. 2. (a) Amount of Fe\* doped on Montmorillonite K10, from acetonitrile solution. \*10 g of clay equilibrated with 15 g of FeCl<sub>3</sub> in 60 ml acetonitrile and Fe detected by back titration of the mother liquor. (b) Amount of Fe\* doped on Montmorillonite K10, from aqueous solution. \*10 g of clay equilibrated with 15 g of FeCl<sub>3</sub> in 60 ml deionised water and Fe detected by back titration of the mother liquor.

However, the increase in the conversion of benzyl chloride due to this catalyst was much more than what could be anticipated on the basis of the iron content alone. This effect was clearly seen when the results of K10–FeOO were compared with those of K10–FeAA (any activation temperature), and when the reaction was carried out at 40°C. This led us to believe that the active species were different in both the cases.

In the DSC of K10–FeOO, the exotherm at 104°C could be attributed to the liberation of HCl, leading to the formation of a bond on the surface, possibly an Fe–O bond. The catalyst was found to evolve HCl on heating. The endotherm between 123°C and 260°C is due the removal of physisorbed water. This can be inferred by the comparison of the DSC with the DSC of Montmorillonite K10. It has been proven that calcination results in a gradual removal of water that converts Brønsted acidic centers to Lewis acidic centers [14]. At about 280°C, the removal of physisorbed water is complete. There is a sharp endotherm at 550°C, which possibly indicates the formation of iron silicate on the surface of the catalyst. This may explain the sharp decrease in the activity of the catalyst at this temperature (K10–FeOO550). In the DSCs of K10–FeOA and K10–FeAA, the most important observation is that the exotherm at around 110°C is absent. It may suggest that in this process, no bond formation has taken place like that in the case of K10–FeOO catalyst. The endothermic peaks are observed at around 130°C. They are due to the removal of chemisorbed water. This indicates that there is a simple ion exchange on the surface.

From the scanning electron microscopy results, it was clear that the surface morphology of the catalysts do not change with respect to the procedure of preparation and the activation temperature.

Taking into account the changes visible in the DSCs, the clays were activated at 120°C, 280°C and 550°C and used as catalysts in the reaction of various substituted arenes with benzyl chloride.

It was observed that K10–FeOO is more active than the other two types of catalysts. Moreover, with increase in the activation temperature, the activity of the catalyst decreases dramatically; the difference is particularly marked in the reactions carried out at a low temperature, 40°C, e.g., the catalyst K10–FeOO calcined at 550°C could bring about only 8% conversion at 40°C, even after 8 h of the reaction. K10–FeAA catalyst shows a different behavior. At 40°C, with K10–FeAA120, the rate of the reaction is initially high and about 46% conversion is observed within the first 15 min, but the conversion remains at 55% even after 5 h. The activation of the catalyst at 280°C brings about an increase in the activity, but calcination at 550°C decreases the activity substantially.

From the results, it appears that the active species on the surface of the catalysts, particularly the ligandic structure, is the same for K10–FeOO and K10–FeOA catalysts. Thus, both the catalysts activated at 120°C give very high conversion at 40°C. However, the species might be different for K10–FeAA catalyst where mere cation exchange has taken place. As against the K10–FeOO catalyst, K10–FeOA catalyst is expected to have lesser number of Cl<sup>−</sup> ligands. When the K10–FeOO catalyst is heated, as has been noticed in the DSC, there is evolution of HCl resulting in the formation of Fe–O bonds and the activity sharply decreases from K10–FeOO120 to K10–FeOO550. Such a sharp decline is not observed in the case of K10–FeOA catalyst.

The Friedel–Crafts reaction is a kinetically controlled reaction and, hence, the kinetic influence can be best seen at a low temperature. For the benzylation of benzene using benzyl chloride, most of the earlier workers have carried out the reactions at 80°C; the boiling point of benzene, which may favor the thermodynamic control. To see these effects clearly, the reaction was carried out at 40°C, 60°C and 80°C. The benzylation of benzene with benzyl chloride is expected to give both monobenzylation as well as dibenzylation, though earlier workers have

reported only monobenylation [6–8]. Hence, the catalytic activity can be best evaluated not only in terms of the percentage of conversion of benzyl chloride, but also in terms of the selectivity towards monobenylation.

When the reaction is carried out at 80°C, we found that all the catalysts are effective and gave 100% conversion within 30 min. Some of them, e.g., K10–FeOO120, K10–FeOA280 and K10–FeAA280 show 100% conversion within 5 min. Thus, the comparison of the catalysts is not meaningful at 80°C. This could be due to fast kinetics culminating into rapid equilibration. On the other hand, when the reaction is carried out at 40°C, the catalyst showed marked difference in all the cases, the catalysts activated at 550°C are totally ineffective, possibly due to the collapse of the active structure on the clay surface to iron silicates. K10–FeOO catalyst differed markedly from the K10–FeAA catalyst possibly due to the different catalytic species present, in the case of K10–FeOO and K10–FeOA, the possible initial catalytic species being the same, higher conversion is obtained for a catalyst activated at 120°C. The activity decreases as the activation temperature increases in the case of K10–FeOO catalyst. This can be explained on the basis of the change in the active sites with lower acidity. On the other hand, in the case of K10–FeAA, the catalyst activated at 280°C is more active than the one activated at 120°C.

This is in consonance with the reported observation of increased Lewis acidity at the cost of Brønsted acidity as the activation temperature increases [14]. Considering the classical mechanism for the present reaction, the Lewis acidity appears to be crucial.

Thus, it is found that among all the catalysts, K10–FeOO120 is the best one. The important observation is that the product spread does not change significantly when the reaction is carried out for a prolonged time (Table 4). It indicates that even at 80°C, thermodynamic equilibration is not significant. When this catalyst is used and the reaction is carried out for the substrates, at 40°C and 80°C, the, *para*- selectivity is found to be higher than the *ortho*- selectivity (Tables 5 and 6), the formation of the *meta*- isomer being negligible.

K10–FeOO120 is the best catalyst for this reaction. Using this catalyst, the benzylation of benzene was carried out at 40°C, 60°C and 80°C, until 100% conversion of benzyl chloride was achieved, and in each reaction, monobenylation and dibenylation were noted (Table 3). It is observed that the reaction does give a small amount of dibenzylated product even at 40°C. As the reaction temperature increases, dibenylation increases. At 80°C, 6.6% dibenylation is observed. As expected in the dibenzylated product *para*-disubstituted product is more than the *ortho*-disubstituted one.

Table 4

Mono- and dibenzylation of benzene at 100% conversion of benzyl chloride (or as specified) in the reaction of benzene with benzyl chloride at different temperatures

Catalyst	Temperature									
	40°C					80°C				
	Time	Mono	Di			Time	Mono	Di		
<i>o</i> -			<i>m</i> -	<i>p</i> -	<i>o</i> -			<i>m</i> -	<i>p</i> -	
K10–FeOO80 <sup>ab</sup>	90	100	–	–	–	10	96.1	1.5	0.5	1.9
K10–FeOO120	60	96.8	2.0	0.5	0.7	5	93.6	2.3	0.8	3.3
K10–FeOO165	60	94.9	1.9	0.6	2.6	5	95.6	1.6	0.6	2.2
K10–FeOO280	420	97.0	1.2	–	1.8	12	98.9	0.6	–	0.5
K10–FeOO550	–	–	–	–	–	16	89.2	8	1.5	5.5

<sup>a</sup>Complete conversion is not obtained after 90 min at 40°C.

<sup>b</sup>Was used without activation at 120°C.



To study the effect of activation temperature on the mono- and di-benzylations, K10–FeOO catalysts activated at different temperatures were employed and the reaction was carried out at 40°C and 80°C (Table 4). The results show that the selectivity of K10–FeOO for monobenylation is maximum when K10–FeOO80 is used and the reaction is carried out at 40°C. As the activation temperature increases, the catalytic activity decreases and a small amount of the dibenzylated product is formed, the percentage of which increases with the increase in the activation temperature.

In the benzylation of substituted benzenes, it appears that the conversion in the case of benzenes with a substituent having a lone pair is low possibly due to the complexation of such groups with the catalyst, decreasing the reactivity of the substrate (Table 5). Maximum conversion is obtained in the case of benzene and toluene. In all the cases, the selectivity for monobenylation is very high.

Comparing the results of monobenylation at 40°C and 80°C, it is found that at 40°C, no or negligible *meta*- isomer is formed in any of the substrates and there a very high selectivity for the *para*- isomer (Table 5). At 80°C, however, the selectivity decreases (Table 6). Particularly

Table 5

Conversion of benzyl chloride and selectivity in the benzylation of different arenes with benzyl chloride using K10–FeOO120 as catalyst after 1 h at 40°C

<sup>1</sup>H NMR were recorded on a 300 MHz (VXR 300S) in CDCl<sub>3</sub>. GC–MS were recorded on a Hewlett-Packard GCD G1800A series Gas Chromatograph equipped with an ECD and the percentage of the monobenzylated and dibenzylated product was calculated assuming that the mass spectrograph detector gave equal response for both products [14] and are uncorrected.

Substrate	Percentage of conversion	Monobenylation			Dibenylation
		<i>o</i> -	<i>m</i> -	<i>p</i> -	
Benzene	100	(97) <sup>a</sup>			3
Toluene	100	44.5	6.1	48.3	1.1
Anisole	49	48.5	–	51.5	–
Ethylbenzene	69	47.5	–	52.5	–
Cumene	64	35	–	65	–

<sup>a</sup>Only one isomer.

Table 6

Conversion and selectivity in the benzylation of arenes with benzyl chloride using K10–FeOO120 as catalyst after 15 min at 80°C

<sup>1</sup>H NMR were recorded on a 300 MHz (VXR 300 S) in CDCl<sub>3</sub>. GC–MS were recorded on a Hewlett-Packard GCD G1800A series Gas Chromatograph equipped with an ECD and the percentage of the monobenzylated and dibenzylated product was calculated assuming that the mass spectrograph detector gave equal response for both products [14] and are uncorrected.

Substrate	Percentage of conversion	Monobenylation			Dibenylation
		<i>o</i> -	<i>m</i> -	<i>p</i> -	
Benzene <sup>a</sup>	100	(93.6) <sup>b</sup>			6.4
Toluene <sup>a</sup>	100	45.2	8.1	45.3	1.4
Ethylbenzene	100	49	–	51	–
Cumene	100	30.5	13.9	55.7	–
Propylbenzene	94	49	–	51	–
<i>Tert</i> -butylbenzene	100	30.4	–	54.1	15.5
Anisole	100	49	–	51	–
Phenetole	100	45.6	–	50.5	3.9
Chlorobenzene	100	41.5	1.7	56.8	–
Bromobenzene	93	35.5	–	48.5	16

<sup>a</sup>Complete conversion of benzyl chloride obtained in 5 min.

<sup>b</sup>Only one isomer.

in the case of linear alkylated benzenes such as toluene, ethyl benzene and propyl benzene, there is a marked selectivity towards monobenylation without any trace of dibenylation. Also, the amount of *para*-benzylated product obtained in all the cases is higher. Moreover, no *meta*- product is obtained in the case of such arenes. The benzylation in general was found to be a very fast reaction, so that the reaction was mainly governed by the kinetics rather than the thermodynamics. Equilibration of the products did not take place over such a short reaction time. Due to the fast kinetics of the reaction, the product distribution was expected to be governed by the electronic factors and statistical consideration. Hence, the *ortho*- selectivity was not significantly reduced from benzene to *tert*-butyl benzene.

We noticed that alkyl aryl ethers were less reactive than alkyl arenes. It may be explained as follows: Alkyl aryl ethers may strongly anchor on the catalyst surface through O-atom with Lewis acidic sites. Similar observation has

been reported earlier in the reaction of anisole and benzyl chloride [15]. This behaviour thus decreases the reactivity of alkyl aryl ethers in Friedel–Crafts and related reactions on clay surfaces. The reaction appears to be a surface reaction, proceeding through adsorption/complexation of the aromatic substrate and benzyl chloride on the clay surface and not taking place through any electrophilic species in the solution. In that event, we believed that in the case of substrates like anisole, higher *ortho*-selectivity was obvious. In the case of other substituents, devoid of any lone pair containing groups, the adsorption may take place by keeping the ring parallel to the surface of clay, through a loose  $\pi$ -complex formation. Reactivity of the ring in such a case is unaltered, and obviously, the benzylation may take place at all the different sites and the regioselection would be governed by the bulk of the substituent.

It is reported that the penetration of polar molecules into the interstitial space of the clay is related to the ratio of the dipole moment to molecular size [16]. Thus, in the case of polar molecules like halogenated benzenes, the rate of reaction depends on the rate of diffusion of the reactant molecules into the interstitial spaces. The reaction is thus diffusion controlled and the size of the halogen has an important bearing on the diffusion and in turn on the rate of the reaction. The slow diffusion of bromobenzene in comparison with chlorobenzene may also suggest a higher residence time for the former and, obviously, more chances of it to undergo dibenylation.

## 5. Conclusion

When Montmorillonite K10 is treated with  $\text{FeCl}_3$  in acetonitrile and aqueous solutions, different catalysts are obtained, which contain different catalytic species. In the former case, initial impregnation of  $\text{FeCl}_3$  takes place, which on heating leads to the Fe–O bond formation on the surface. In the case of an aqueous treat-

ment, simple ion-exchange takes place, and as the catalyst is activated at higher and higher temperature, there is a gradual conversion of Brønsted acidic sites into Lewis acidic sites. In the benzylation of arenes using benzyl chloride, the catalytic activity of all the catalysts decreases dramatically at 550°C, possibly due to collapse of the clay structure. When the catalyst prepared from an acetonitrile solution is washed with water, substantial amount of  $\text{Cl}^-$  is found to be washed away resulting in the decrease in activity.

Thus, the solvent used for the preparation of the K10–Fe catalyst has a profound effect on the catalytic activity of the resulting catalyst in the benzylation of benzene using benzyl chloride. The most effective catalyst is the one prepared using acetonitrile as a solvent. As the calcination temperature increases, the activity of any type of catalyst decreases. This change is marked in the case of reactions carried out under the kinetic domain at a low temperature, i.e., 40°C. The catalyst calcined at 550°C was totally ineffective at 40°C. Though all the catalysts are active at 80°C, K10–FeOO120 is the best catalyst in terms of selectivity and reactivity, when the reaction is carried out at 40°C.

Thus, it is observed that the catalyst K10–FeOO120 prepared by the impregnation of  $\text{FeCl}_3$  on Montmorillonite K10 is a superior catalyst as compared to  $\text{Fe}^{3+}$ –K10 prepared by ion-exchange.

## Acknowledgements

The authors are grateful to the Indo-French Center for the Promotion of Advanced Research, New Delhi, for a research grant (Project No, 1106-2), to Dr. Figueras, Lyon, France, for providing the surface area and elemental analysis, and to the Regional Sophisticated Instrumentation Center, IIT, Bombay, for providing the  $^1\text{H}$  NMR and the mass spectra.

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