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Room temperature efficacious synthesis of diphenylmethane over Fe/Al-MCM-41 catalysts

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ABSTRACT

Fe/Al-MCM-41 (Si/Al = 25, 50, 75 and 100) were synthesized. Their catalytic activity was evaluated towards benzylation of benzene with benzyl chloride in liquid phase. The catalytic activity of Fe/Al-MCM-41(25) was higher than the other catalysts. Diphenylmethane(DPM) was obtained as the major product with 100% selectivity and with 100% conversion of benzyl chloride under optimum condition. The effect of temperature and the feed ratio, on the activity of Fe/Al-MCM-41(25) and selectivity towards DPM was studied and a possible reaction mechanism was proposed.

1. Introduction

Homogeneous acid catalysts are normally employed in Friedel–Crafts alkylation, but they are not environmentally benign [1]. In addition catalyst recovery, reuse, waste disposal, corrosion etc are also the commonly encountered problems. In this context heterogeneous catalysts are advantageous. For the title reaction earlier studies indicated poor activity for the solid acid catalyst such as H–Y [2], H-ZSM-5 [2,3] and sulphated ZrO_2 [4] for the benzylation of benzene and other aromatic compounds. Clark et al. [5] reported high activity for thermally activated clayzic catalyst and the process has been commercialised. However, clayzic catalyst showed low selectivity (~ 80%) for diphenylmethane(DPM) [5]. Of late iron containing catalysts were rampantly studied for the Friedel–Crafts alkylation due to their high activity; some of the reported catalysts were $FeCl_3$/Mont K10 [6], sulphated $Fe2O_3$–ZrO_2 [4], Fe/MCM-41 [7–9], H–FeMFI zeolites [3], iron oxide nanoclusters loaded SBA-15 [9], Fe-SBA-15 [10], Fe mesoporous silicate catalyst [11,12], Fe-SBA-1 [13] and Fe^{3+} loaded SBA-15 [14]. All these iron catalysts required slightly higher temperature for catalyzing the reaction. Room temperature synthesis of DPM was reported on SO_4^{2-}/Al-MCM-41 [15] where the conversion of benzylchloride (BC) was 100% but the selectivity towards DPM was not 100%, and also over $AlCl_3$/MCM-41 [16] in which the conversion of BC was 100% with less than 100% selectivity towards DPM. Hence it is of interest to design a catalyst for the benzylation of benzene to give complete conversion of BC with 100% selectivity to the desired DPM product for industrial applications [17].

Up to our knowledge there are no detailed works on the benzylation of benzene over Fe/Al-MCM-41 catalysts. Aluminium present in the framework of MCM-41 catalysts activates extra framework iron thus enhancing the catalyst activity, acidity and thermal and hydrothermal stability [18–20]. In the present investigation Fe/Al-MCM-41 catalysts with different Si/Al were tested for the Friedel–Crafts benzylation of benzene. Fe/H–M, Fe/H–Y, Fe/H-ZSM-5 catalysts were also examined for this reaction in order to study the effect of pore size.

2. Experimental

Procedures to synthesize Fe/Al-MCM-41(27, 50, 75,100) and the experimental techniques to characterize the catalyst samples were described in detail elsewhere [21]. The physico-chemical characterization tests of the synthesized catalysts were similar to the previous report. H–M (Si/Al = 12), H–Y (Si/Al = 8) and H-ZSM-5 (Si/Al = 15), were procured from Sud Chemicals India Limited. These catalyst samples were impregnated with iron using a simple wet impregnation procedure as described elsewhere [20].

Liquid phase catalytic benzylation of benzene was carried out in a magnetically stirred 50 ml glass reactor fitted with a reflux condenser, a thermometer and a septum to withdraw the product samples. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, optimized amounts of benzene and BC (5: 1 mole ratio)

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were charged in to the reactor along with 0.1 g catalyst, and the products were analyzed using 9A model Shimadzu gas chromatograph equipped with flame ionization detector fitted with OV-101 column (2 m length). GC–MS analyses were performed on Shimadzu GC–MS–QP 5000 with a PE-5 capillary column.

3. Results and discussion

3.1. Comparison of catalytic activities of different catalysts studied

Benzylation of benzene with BC over all the synthesized catalysts, Fe/H–M, Fe/H–Y and Fe/H-ZSM-5 were studied at room temperature for a duration of 4 h with the mole ratio of 5:1 M (benzene:BC) using 0.1 g catalyst. Equal aliquots of the samples were withdrawn at every 15 min and the results are presented in Fig. 1. Fig. 2 shows the percentage conversion of BC and the percentage selectivity towards DPM at the end of the 4 h. The major product was DPM and minor quantity of polyalkylates like dibenzylbenzene was also present. The BC conversion and DPM selectivity were higher over Fe/Al-MCM-41 (25, 50, 75 and 100) catalysts than the microporous Fe/H–Y, Fe/H–M, and Fe/H-ZSM-5 catalysts. The high selectivity of DPM might be due to the polar nature of the channel surface owing to the presence of the activated metal oxides in Fe/Al-MCM-41(25, 50, 75 and 100) catalysts [18,19,21]. The main product DPM due to its less polarity should be immediately expelled out of the pore as and when it was formed. Hence polyalkylation was found to be less. The catalytic activity of the iron containing mesoporous solid acid catalysts followed the trend, Fe/Al-MCM-41(25) > Fe/Al-MCM-41(50) > Fe/Al-MCM-41(75) > Fe/Al-MCM-41(100) which was also the trend of the acidity of the synthesized catalysts.

The catalytic activity of Fe/H–Y, Fe/H–M and Fe/H-ZSM-5 catalysts was low as shown in Figs. 1 and 2. This might be due to the small pore size which enabled least access to the reactant. Pore diameter of benzene is 5.8 [22] and that of H-ZSM-5 is 5.6 [23] and H–M, and H–Y in the range 5–7.5 [23]. Due to impregnation procedure their pores might be partly blocked by the iron oxide particles which are in agreement with the earlier studies [24,25]. The percentage conversion of BC was not observed to increase considerably above 210 min and hence Fe/H–Y, Fe/MOR, and Fe/H-ZSM-5 are not found to be suitable for this reaction.

3.2. Influence of reaction temperature

The liquid phase benzylation of benzene with BC over Fe/Al-MCM-41(25) was carried out at RT, 80 and 100 °C. The results of percentage conversion and percentage selectivity are shown in Fig. 3. As the temperature increased, the percentage conversion of BC also increased. Higher conversion at 80 and 100 °C was recorded than at RT, may be due to rejection of molecular association that aids dispersed adsorption of BC on the Fe sites. The selectivity to DPM decreased at higher temperatures, which might be due to Fe and aluminium ions present over the surface enters the pore as the temperature is increased, thereby increasing the dispersion and accessibility of the active sites hence favoring enhanced polyalkylation with increase in temperature. Hence room temperature is observed to be the best to obtain 100% selective DPM with 83.4% conversion of BC.

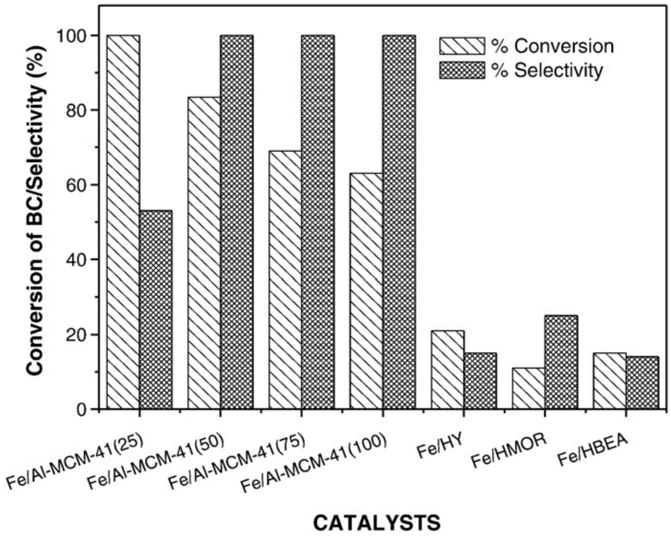


Fig. 2. Effect of different catalysts on percentage conversion of BC and selectivity towards DPM.

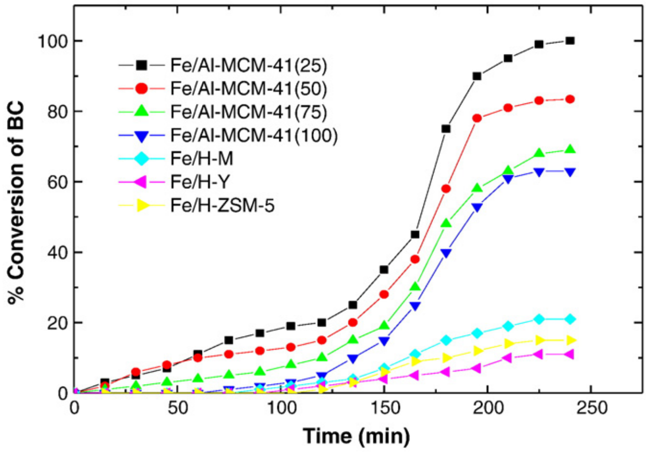


Fig. 1. Effect of time on stream on percentage conversion of BC over different catalysts.

3.3. Reaction scheme

A reaction scheme is suggested (Scheme 1) to account for the formation of the products. Co-ordination of BC on Fe sites might weaken and ultimately break the CH_2–Cl bond. The resulting benzyl cation can react with benzene electrophilically to yield the products.

Free radical was not considered favourable, even though this catalyst has got redox properties. If there is formation of any free radical intermediate, diphenylethane might also be produced as one of the major products, since the benzyl radical are highly reactive. But the product diphenylethane was not observed in this study. Since the

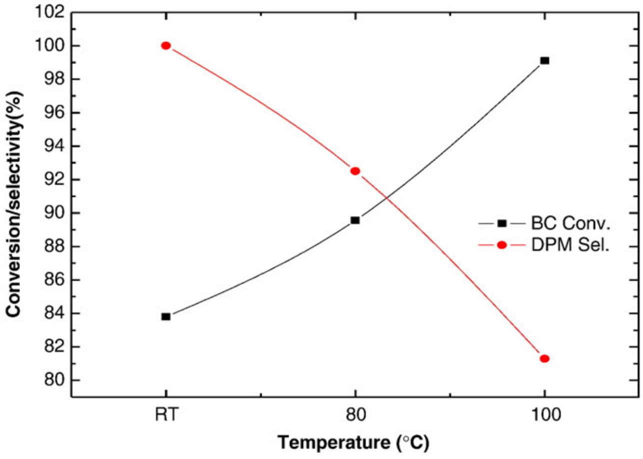
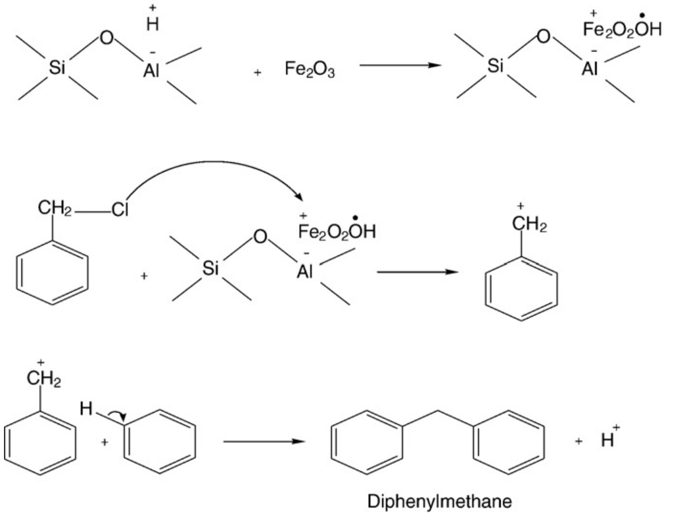


Fig. 3. Effect of temperature on the conversion of BC and selectivity towards DPM over Fe/Al-MCM-41(25) catalyst.



Scheme 1. Mechanism of benzylation of benzene with BC.

metal oxides are of nanodimensions, those should have high surface free energy sufficient enough to activate BC by Lewis acid base interaction without subsequent change in its valency. Activation of benzene was required to be present for benzylation based on alkylation of benzene in ZSM-5 [7]. But this supporting evidence seems to be contradicting as the formed DPM would produce large sterric congestion within its pores. Hence we are much reluctant to apply activation of benzene by the metal oxide. If the said activation really exists over metal oxide, there might be tremendous ring deactivation because of high charge transfer between the ring and the Lewis acid sites.

The released HCl in this electrophilic alkylation can greatly activate Fe_2O_3 for the subsequent activation of BC. During ion exchange Fe^{3+} should have undergone hydrolysis producing $Fe(OH)_2^{2+}$, $Fe(OH)_2^{+}$ and $Fe(OH)_3$ [26] species. $Fe(OH)_3$ decomposes to form $Fe_2O_3^{+}$ and $Fe(OH)_2^{+}$ forms FeO^{+}. The later species remains as charge compensating ion for the framework '—'ve charge of Al species. It can act as Lewis acid site to catalyse benzylation. It could have reacted with BC and yielded benzyl cation which in turn would have reacted with benzene to produce diphenylmethane DPM. Hence the ionic mechanism is more probable for this reaction. Enhanced activation by HCl is also evident by the enhanced conversion at the end of 4 h, in comparison to conversion at the end 2 h (Fig. 1) over each catalyst.

3.4. Influence of catalyst concentration

Table 1 displays the conversion of BC and product distribution after 4 h of the reaction time, as a function different catalysts weights over Fe/Al-MCM-41(25). The BC conversion and the selectivity of DPM was 100% when the catalyst used constituted the weight of 0.3 and 0.5 g. The percentage yield of DPM varies linearly with the concentration of the catalyst. The selectivity of DPM reduced at 0.5 g of catalyst, which might be due to the exposure of the reactant and product to larger number of active sites than required which facilitates polyalkylation.

3.5. Influence of benzene to BC mole ratio

Table 1 exhibits the effect of benzene/BC mole ratio on the catalytic activity of Fe/Al-MCM-41(25) at room temperature using a catalyst weight of 0.3 g. The ratios were changed by keeping the amount of benzene which is taken comparatively in excess to be constant. The data at RT showed that at higher catalyst weight (0.3 g), the percentage conversion of BC remained to be 100% regardless of the change in B:BC mole ratio until 5:1.5(B:BC), but at 5:2(B:BCl), the selectivity toward DPM was reduced. In order to get better understanding, 0.1 g of the highly active Fe/Al-MCM-41 was investigated for various mole ratios of the reactant.

Table 1
Study of effects of catalyst loading, reactant mole ratio and recyclability at RT on conversion of BC and product selectivity over Fe/Al-MCM-41(25) catalyst.

Contents	BC conversion (%)	Selectivity of products (%)	
		DPM	Others
Catalyst loading (g)			
0.1[a]	83.4	100.0	–
0.3[a]	100.0	100.0	–
0.5[a]	100.0	98.7	1.3
Mole ratio			
5:0.5[b]	100.0	100.0	–
5:1[b]	100.0	100.0	–
5:1.5[b]	100.0	100.0	–
5:2[b]	100.0	98.6	1.4
5:0.5[c]	100.0	100.0	–
5:1[c]	83.4	100.0	–
5:1.5[c]	62.7	100.0	–
5:2[c]	56.2	100.0	–
Recyclability			
Fresh[a,c]	83.4	100.0	–
First cycle[a,d]	83.1	100.0	–
Second cycle[a,e]	83.0	100.0	–

Reaction conditions: temperature = RT, time = 4 h.

[a] Mole ratio = 5:1(B:BC).
[b] Catalyst weight = 0.3 g.
[c] Catalyst weight = 0.1 g.
[d] Catalyst weight = 0. 99 g.
[e] Catalyst weight = 0.98 g.

The results given in Table 1 showed that at lower concentration of BC 5:0.5(B:BCl), the percentage conversion of BC was 100% with 100% selectivity towards the desired product. When the mole ratio is varied by increasing the concentration of BC, the percentage conversion of BC decreased significantly with 100% selectivity towards DPM which might be due to the less availability of active sites at lower catalyst weight. Hence B:BC mole ratio of 5:1.5 with 0.3 g was taken as the optimum one since higher concentration of BC and its 100% conversion should give greater quantity of 100% selective DPM.

3.6. Recycling of the catalyst

Fe/Al-MCM-41(25) used in the benzylation of benzene was recycled two times in order to check its activity, stability and reusability. The results are shown in the Table 1. After completion of the reaction on fresh catalyst, the catalyst was filtered from the reaction mixture using a Whatmann filter paper, washed with acetone and air dried. It was incinerated to obtain the catalyst at 823 K for 4 h in the presence of air. The weight of the catalyst measured after calcination in the first and second cycle was 0.99 and 0.98 g respectively. The activity of the Fe/Al-MCM-41(25) decreases progressively but slightly with increase in the number of cycles. The selectivity towards the desired product was 100%.

4. Conclusions

It is proved that Fe/Al-MCM-41(25) is highly efficacious towards the benzylation of benzene. At room temperature with B:BCl(5:1.5), over 0.3 g of Fe/Al-MCM-41(25) catalyst we can obtain a high yield of DPM with 100 % selectivity and 100% conversion of BC. Free radical mechanism was not suitable for this reaction since we didn't obtain diphenylethane as one of the products. The highly active Fe/Al-MCM-41 catalysts can be applied to many other acid catalyzed reactions.

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