

Room temperature synthesis of diphenylmethane over novel mesoporous Lewis acid catalysts

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Abstract

Highly selective synthesis of diphenylmethane (DPM) was carried out by Friedel–Crafts benzylation of benzene using benzyl chloride (BC) as alkylating agent in the presence of a flow of nitrogen under liquid phase reaction conditions over novel mesoporous $\text{SO}_4^{2-}/\text{Al-MCM-41}$ catalysts with different Si/Al ratios. For these reactions, the influences of various reaction parameters, such as different catalysts, reaction temperature, time, mmol ratios of reactants and recyclability are discussed. With increasing the Si/Al ratios of $\text{SO}_4^{2-}/\text{Al-MCM-41}$ catalysts from 21 to 83, the conversion of BC and selectivity of DPM decreased because the number of Lewis acid sites in $\text{SO}_4^{2-}/\text{Al-MCM-41}$ catalysts are found to decrease almost linearly with increasing ratios of Si/Al. Further the catalytic results were compared with those obtained by using 0.8N sulfuric acid, different Si/Al ratios of Al-MCM-41, HY, H β , HM and H-ZSM-5 zeolites. From the comparison of the results, $\text{SO}_4^{2-}/\text{Al-MCM-41}(21)$ is found to be a highly active and recyclable heterogeneous catalyst for the highly selective synthesis of DPM. Thus, the selectivity of DPM in $\text{SO}_4^{2-}/\text{Al-MCM-41}(21)$ is higher than that in other $\text{SO}_4^{2-}/\text{Al-MCM-41}$ (Si/Al = 42 and 83), Al-MCM-41 (Si/Al = 21, 42 and 83), HY, H β , HM and H-ZSM-5.

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1. Introduction

Diphenylmethane (DPM) is considered important for its use in pharmaceutical and fine chemical industries [1]. They have been prepared typically by Friedel–Crafts benzylation reaction in liquid phase using strong Lewis acids, such as AlCl_3 , FeCl_3 and ZnCl_2 as catalysts [2]. These catalysts pose number of considerable problems in handling and disposal coming from the large amount of acidic effluents and difficulties in product isolation. Thus, there has been a strong need for the replacement of the homogeneous catalysts mentioned above by reusable and easily separable catalysts, i.e. heterogeneous solid catalysts having high activity in Friedel–Crafts type reactions. Earlier studies [3,4] on the highly acidic solid catalysts, such as the HY and H-ZSM-5 zeolites, showed poor benzylation reactivity and selectivity of DPM due to the diffusion limitation caused by the microporous networks.

The discovery of mesoporous material such as MCM-41 [5] has greatly extended the applicability of porous materials for catalysts in various organic reactions. Unfortunately, the acid strength of the MCM-41 resembles that of the amorphous silica-alumina rather than that of the more strongly acidic zeolite [6]. Several approaches have been proposed to increase the Lewis [7] and Bronsted acid [8,9] strength of the MCM-41. Selvaraj et al. reported the synthesis and characterization of the $\text{SO}_4^{2-}/\text{Al-MCM-41}$ with different Si/Al ratios for the production of neroline [10], dypnone [7] and 2-acetyl-6-methoxynaphthalene [11]. The catalysts were found to have higher surface areas, catalytic activities and reusability. Some researchers reported the synthesis of DPM over the mesoporous $\text{AlCl}_3/\text{Si-MCM-41}$ [12] and sulfated ZrO_2 [13].

Recently, there has been an increasing interest in developing processes with minimum environmental threats and maximum economic benefits. In that sense, a great demand to develop highly selective heterogeneous catalyst with large number of Lewis acid sites under mild reaction conditions without employing toxic materials. To the best of our knowledge, there are no reports on the heterogeneously catalysed Friedel–Crafts

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benzylation of benzene over $\text{SO}_4^{2-}/\text{Al-MCM-41}$. Herein we disclose a first time report on a DPM synthesis using novel $\text{SO}_4^{2-}/\text{Al-MCM-41}$ catalysts under the liquid-phase reaction conditions. The catalytic results are correlated and compared for 0.8N (N-normal) sulfuric acid solution and other solid catalysts such as different Si/Al ratios of Al-MCM-41, HY, H β , HM and H-ZSM-5.

2. Experimental

2.1. Synthesis and physicochemical characterization of Al-MCM-41 and $\text{SO}_4^{2-}/\text{Al-MCM-41}$

The mesoporous Al-MCM-41 (Si/Al=21, 42 and 83) was synthesized using cetyltrimethylammonium bromide (CTABr) as template under hydrothermal conditions and also characterized using several sophisticated instrumental techniques according to the published method by Selvaraj et al [8,9]. The $\text{SO}_4^{2-}/\text{Al-MCM-41}(21)$ was prepared by impregnating 1 g of the calcined Al-MCM-41 with 50 mL of sulfuric acid (0.8N) with stirring at 500 rpm for 3 h in room temperature [10]. Then the sample was dried at 110 °C for 12 h. While the different $\text{SO}_4^{2-}/\text{Al-MCM-41}$ materials were synthesized in a similar manner using different Si/Al ratios of Al-MCM-41, 0.1 and 4N of sulfuric acid.

2.2. Commercial catalytic materials

H β (Si/Al=20, Strem), HY (Si/Al=2.9, PQ), H-mordenite (Si/Al=20, PQ) and H-ZSM-5 (Si/Al=30, PQ) were obtained from commercial sources. These catalysts were then calcined at 500 °C in air for 6 h before catalytic reaction.

2.3. Catalytic reaction

Synthesis of DPM was carried out in a 100 mL round-bottomed (RB) flask equipped with a reflux condenser and a magnetic stirrer under liquid phase reaction conditions. In a typical reaction procedure, benzene was mixed with BC and 0.2 g of catalyst in the presence of a flow of nitrogen in the RB. The mixture was then vigorously stirred for the desired time at different temperature. After the reaction, the samples was withdrawn periodically and analyzed by a Hewlett-Packard 6890 Gas Chromatograph fitted a flame ionization detector and a capillary column (50 m \times 0.2 mm) with methyl silicon gum. The products were confirmed by GC-MS.

2.4. Experimental for recyclable catalysts

After the initial use, the $\text{SO}_4^{2-}/\text{Al-MCM-41}$ usually suffers from the activity loss and hence the catalyst needs to be regenerated by calcination. In contrast, $\text{SO}_4^{2-}/\text{Al-MCM-41}$ is excellent catalyst for the Friedel–Crafts benzylation of benzene to DPM. It can be recycled by washing with dichloromethane and ethyl acetate at 40 °C followed by hot water to remove the organics and unreacted reactants. It was dried at 140 °C overnight. Fur-

ther the catalyst was washed at five times in a similar procedure. The recycled $\text{SO}_4^{2-}/\text{Al-MCM-41}$ catalyst was again prepared with a similar manner.

2.5. Leaching of sulfate experiment studies from $\text{SO}_4^{2-}/\text{Al-MCM-41}$

After the catalyst reaction, catalyst was equilibrated with distilled water for 1 week at 100 °C (pH < 5), and kept in water bath and the supernatant was checked for SO_4^{2-} with barium chloride using Nephelometer (Elico Limited, India). The experiment was repeated to verify reproducibility before reporting the results.

3. Results and discussion

3.1. Physicochemical properties of $\text{SO}_4^{2-}/\text{Al-MCM-41}$

The XRD patterns of both the Al-MCM-41 and $\text{SO}_4^{2-}/\text{Al-MCM-41}$ showed (Fig. 1) well-resolved reflections typical of the mesoporous MCM-41 structure [9,10]. The surface area, pore size and pore volume was estimated by the BET and BJH method using N_2 -adsorption measurements, and the results are shown in Table 1. Impregnation of the Al-MCM-41 with sulfuric acid resulted in the decreased crystallinity, *d*-spacing, unit cell parameter, surface area and pore diameter [10]. Particularly, the mesoporous structure in the high sulfate-containing Al-MCM-41 (4N- H_2SO_4 impregnated Al-MCM-41(21)) was collapsed [10]. We have concluded the following from the solid state NMR results (Fig. 2): (1) upon impregnation of SO_4^{2-} ion in the Al-MCM-41, the octahedral coordination of Al^{3+} ion became non-framework on the silica surface because of the SO_4^{2-} ion which are bonded to Si(IV) and (2) the strong Lewis acid sites were

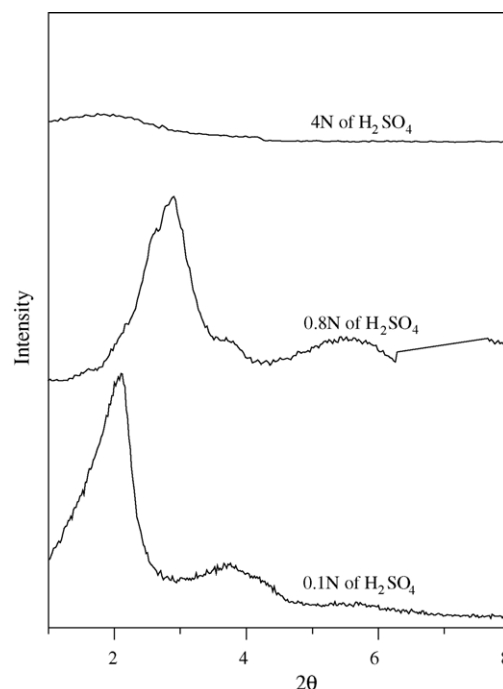


Fig. 1. X-ray diffraction patterns of $\text{SO}_4^{2-}/\text{Al-MCM-41}$ catalysts.

Table 1
Physicochemical characterization of $\text{SO}_4^{2-}/\text{Al-MCM-41}$ and Al-MCM-41

Catalysts	<i>d</i> -Spacing ^a (Å)	Unit cell parameter ^a <i>a</i> ₀ (Å)	Surface area ^b (m ² /g)	Pore size ^b <i>D</i> (Å)	Pore volume ^b (m ³ /g)	Wall thickness ^c (Å)
Al-MCM-41(21)	38.41	44.35	830	27.5	0.866	16.85
Al-MCM-41(42)	39.26	45.33	880	29.8	0.907	15.53
Al-MCM-41(83)	43.09	49.76	978	34.6	0.976	15.10
$\text{SO}_4^{2-}/\text{Al-MCM-41}$ (21)	35.31	40.77	725	25.9	0.85	14.87
$\text{SO}_4^{2-}/\text{Al-MCM-41}$ (42)	33.63	38.83	850	26.3	0.89	12.53
$\text{SO}_4^{2-}/\text{Al-MCM-41}$ (83)	32.75	37.05	950	27.4	0.91	9.65
$\text{SO}_4^{2-}/\text{Al-MCM-41}$ (21) ^d	43.7	50.4	810	26.8	0.810	23.6
$\text{SO}_4^{2-}/\text{Al-MCM-41}$ (21) ^e	–	–	230	–	–	–

^a Values obtained from XRD studies.

^b Values obtained from N₂ adsorption results.

^c Wall thickness (*t*) = Unit cell parameter (*a*₀) – pore size (*D*).

^d 0.1N H₂SO₄ was used.

^e 4N H₂SO₄ was used.

generated on the surface of the $\text{SO}_4^{2-}/\text{Al-MCM-41}$ due to the inductive effect of the sulfate group in the presence of octahedral aluminum ions (Fig. 3) from the sulfuric acid impregnation [10]. Above results (Lewis acid sites) were reconfirmed by the FTIR-pyridine analyses [10], and the results are shown in Table 2. While the uniformity of the $\text{SO}_4^{2-}/\text{Al-MCM-41}$ pore size was verified with TEM images [11], and pore size and hexagonal symmetry of the all sulfate-containing MCM-41 was found to be smaller than those of the Al-MCM-41 due to non-framework aluminum caused by impregnation of sulfate-ions [7].

3.2. Synthesis of DPM

The Friedal–Crafts benzylation of benzene using BC as alkylating agent in the presence of a flow of nitrogen for the synthesis

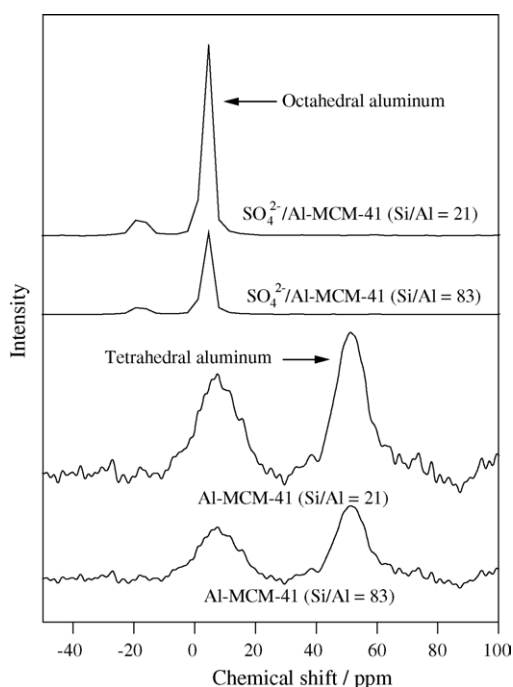


Fig. 2. ²⁷Al MAS-NMR spectra of calcined Al-MCM-41 and $\text{SO}_4^{2-}/\text{Al-MCM-41}$ catalysts.

of DPM (Fig. 4) was carried out with different optimal conditions such as different catalysts, reaction temperature, time, mmol ratios of reactants and recyclability reactions, and the all results are discussed below.

3.3. Effect of different catalysts for synthesis of DPM

The Friedal–Crafts benzylation of benzene using BC in the presence of a flow of nitrogen for the synthesis of DPM was carried out over H-ZSM-5, HM, H β , HY, Al-MCM-41(21),

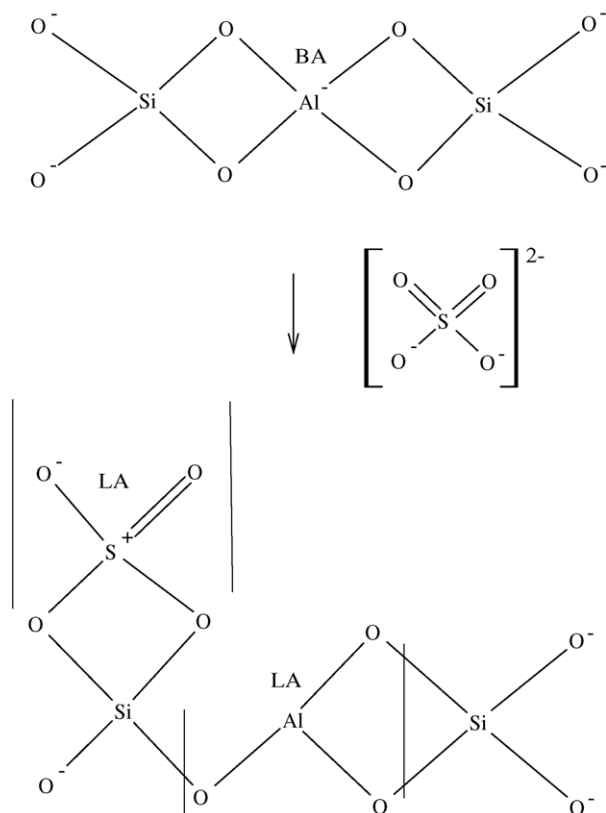


Fig. 3. Scheme proposed for the sulfate-containing Al-MCM-41 material showing possible Lewis acid sites (LA, Lewis acid sites and BA, Bronsted acid sites).

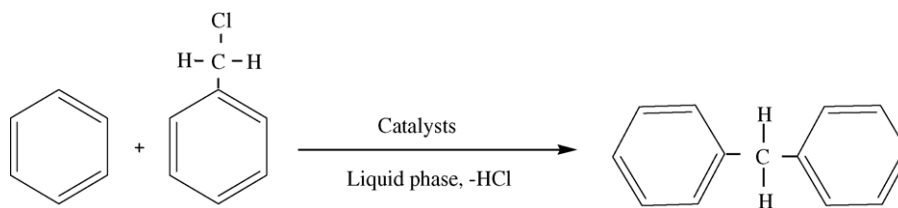


Fig. 4. Scheme of benzylation of benzene reaction.

Table 2

Bronsted acidity and Lewis acidity of the $\text{SO}_4^{2-}/\text{Al-MCM-41}$ and Al-MCM-41 samples measured by FTIR spectroscopy combined with pyridine adsorption and desorption at different temperatures

Catalysts	Total acidity from TPD-pyridine studies (mmol pyridine g^{-1})	Bronsted acidity ($\mu\text{mol pyridine g}^{-1}$) ^a				Lewis acidity ($\mu\text{mol pyridine g}^{-1}$) ^a			
		R ^b	100 ^c	200 ^c	300 ^c	R ^c	100 ^c	200 ^c	300 ^c
Al-MCM-41(21)	0.099	23.8	18.3	12.3	11.3	11.9	10.3	8.3	6.3
Al-MCM-41(42)	0.092	18.5	15.3	10.4	10.1	9.25	8.5	6.7	4.2
Al-MCM-41(83)	0.052	12.4	10.4	4.5	4.0	6.20	5.40	4.5	3.2
$\text{SO}_4^{2-}/\text{Al-MCM-41}(21)$	0.501	20.3	18.4	16.5	8.3	88.3	85.3	70.3	65.3
$\text{SO}_4^{2-}/\text{Al-MCM-41}(42)$	0.403	18.3	14.3	11.5	6.5	50.2	47.2	37.3	25.3
$\text{SO}_4^{2-}/\text{Al-MCM-41}(83)$	0.302	10.3	8.2	5.8	3.3	30.6	28	25.3	23.4
$\text{SO}_4^{2-}/\text{Al-MCM-41}(21)^{\text{d}}$	0.100	22.6	15.3	10.5	9.3	42.3	35.3	30.3	27.3
$\text{SO}_4^{2-}/\text{Al-MCM-41}(21)^{\text{e}}$	0.800	9.3	7.2	6.3	4.3	90.3	86.3	84.5	78.1

Total acidity measured by TPD-pyridine.

^a Values obtained from FTIR-pyridine studies.

^b Room temperature ($^{\circ}\text{C}$).

^c Temperature ($^{\circ}\text{C}$).

^d 0.1N H_2SO_4 was used.

^e 4N H_2SO_4 was used.

Al-MCM-41(42), Al-MCM-41(83), $\text{SO}_4^{2-}/\text{Al-MCM-41}(21)$, $\text{SO}_4^{2-}/\text{Al-MCM-41}(42)$, $\text{SO}_4^{2-}/\text{Al-MCM-41}(83)$ and 0.8N H_2SO_4 as catalysts and their results are shown in Table 3. The order of catalytic activity for the selectivity of DPM was found to be $\text{SO}_4^{2-}/\text{Al-MCM-41}(21) > \text{SO}_4^{2-}/\text{Al-MCM-41}(42) > \text{SO}_4^{2-}/\text{Al-MCM-41}(83) > \text{HY} > \text{Al-MCM-41}(21) > \text{H}\beta > \text{Al-MCM-41}(42) > \text{Al-MCM-41}(83) > 0.8\text{N } \text{H}_2\text{SO}_4 > \text{HM} >$

H-ZSM-5. Above results on the catalyst acid strength is based on the FTIR and TPD analysis of the adsorbed pyridine [10,14,15]. The mesoporous $\text{SO}_4^{2-}/\text{Al-MCM-41}(21)$ (pore size = 25.9 Å), $\text{SO}_4^{2-}/\text{Al-MCM-41}(42)$ (pore size = 26.3 Å) and $\text{SO}_4^{2-}/\text{Al-MCM-41}(83)$ (pore size = 27.4 Å) shows high catalytic activity for the formation of high selectivity of DPM in room temperature with no diffusional constraint. But the

Table 3

Benzylation of benzene over various types of catalysts

Catalysts	Si/Al ratio	Reaction time (h)	Conversion of BC (%) ^a	DPM selectivity (%)	Sulfate-ions content per gram of catalyst surface after reaction (%)
$\text{SO}_4^{2-}/\text{Al-MCM-41}(21)$	21	4	100	99.1	1.999
$\text{SO}_4^{2-}/\text{Al-MCM-41}(42)$	42	4	96.1	85.3	1.987
$\text{SO}_4^{2-}/\text{Al-MCM-41}(83)$	83	4	90.5	78.3	1.986
Al-MCM-41(21) ^b	21	6	82.2	62.9	–
Al-MCM-41(42) ^b	42	6	72.4	53.4	–
Al-MCM-41(83) ^b	83	6	65.3	48.3	–
0.8N H_2SO_4	–	4	64.2	48.1	–
$\text{SO}_4^{2-}/\text{Al-MCM-41}(21)^{\text{c}}$	21	4	85.4	73.2	0.249
$\text{SO}_4^{2-}/\text{Al-MCM-41}(21)^{\text{d}}$	21	4	67.4	59.1	9.987
H β^{b}	20	6	63.1	55.3	–
HY ^b	2.9	6	56.3	65.3	–
H-ZSM-5 ^b	30	6	2.9	2.9	–
HM ^b	20	6	5.2	7.2	–

Reaction conditions: 0.2 g of catalyst; 90 mmol of benzene and 10 mmol (9:1) of benzyl chloride were introduced into batch reactor and stirred at room temperature under a flow of nitrogen.

^a Conversion of BC is defined as a total percentage of BC transformed into product.

^b Reaction temperature of 80 $^{\circ}\text{C}$.

^c 0.1N of H_2SO_4 was used.

^d 4N of H_2SO_4 was used.

selectivity of DPM in the $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ is higher than that of other $\text{SO}_4^{2-}/\text{Al-MCM-41}$ due to the higher number of acid sites on its surface by increasing octahedral aluminum [10]. When Al-MCM-41 was impregnated with 0.8N H_2SO_4 , the selectivity of DPM increased from 48.1 to 99.1 mol%, a much higher value than the case of using sulfuric acid solution (64.2%, BC conversion) itself as a catalyst at room temperature. This indicates that the sulfuric acid modification of the Al-MCM-41(21) enhances both catalytic activity and catalyst acidity. In order to verify this, the $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ was first stirred and washed in de-ionized water and then the filtrate was analyzed by atomic absorption spectroscopy (AAS). The resulting filtrate was found to contain aluminum cation. Furthermore, the resulting catalyst exhibited a significant decrease in BC conversion, from 99.1 to 40.1%. We believe that the non-framework aluminum existing in the intrachannel space is supposed to increase the catalyst activity due to the increase of Lewis acidity [10]. The BC conversion and DPM selectivity of the 0.8N H_2SO_4 -sulfated Al-MCM-41(21) was higher than those of the 0.1N and 4N H_2SO_4 -sulfated Al-MCM-41(21) due to the higher catalytic activity. But, the selectivity was found to be very lower for the 4N H_2SO_4 -sulfated Al-MCM-41(21) because of the collapsed pore structure of the catalyst (Table 3). A very low percentage of conversion and selectivity was observed at room temperature (27 °C) for 8 h (the values are not shown in Table 3) over different Si/Al ratios of Al-MCM-41, HY, HM and H-ZSM-5, but, the selectivity is found to be higher for reactions at 80 °C for 6 h exhibiting the values (selectivity) in the following order: $\text{HY} > \text{Al-MCM-41(21)} > \text{H}\beta > \text{Al-MCM-41(42)} > \text{Al-MCM-41(83)} > \text{HM} > \text{H-ZSM-5}$ as shown in Table 3. The conversion and selectivity in Al-MCM-41(21) is higher than that in other Al-MCM-41 catalysts due to the higher number acid sites on its surface. Zeolite H β is found to be more active (63.1% BC conversion) compared to the HY (56.3% BC conversion). However, in terms of selectivity, H β is found to be less selective (55.3%) than HY (65.3%) in the reaction. The higher selectivity of HY might be explained on the basis of its strong acidity and slightly larger pore opening size (7.4 Å) than H β (7.6, 5.4 Å) while geometrical constraints produced by H β did not allow the formation of bulkier products in the small channels, and, hence a higher selectivity of DPM is achieved over HY rather than H β zeolite. HM and H-ZSM-5, in spite of its strong acidity achieved by several researchers, but, it is found to be less active in the reaction. The small pore size of the HM (7.1 Å) and H-ZSM-5 (5.4 Å) zeolites imposes diffusion control through which the bulky product DPM cannot diffuse out with the formation of the small amount of the product probably through a surface reaction. From the comparison of all catalytic results, $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ is found to be a highly active and novel heterogeneous catalyst for the highly selective synthesis of DPM at room temperature for 4 h. It is evident that the pore size and acid strength of the catalyst plays a major role during the synthesis of DPM, a large molecule while the important relation is between pore size and molecular size of the reactant/product. The pore size of the catalyst must be accessible to reactant and product molecules in order to take part in the reaction. Thus, the effect of temperature, time,

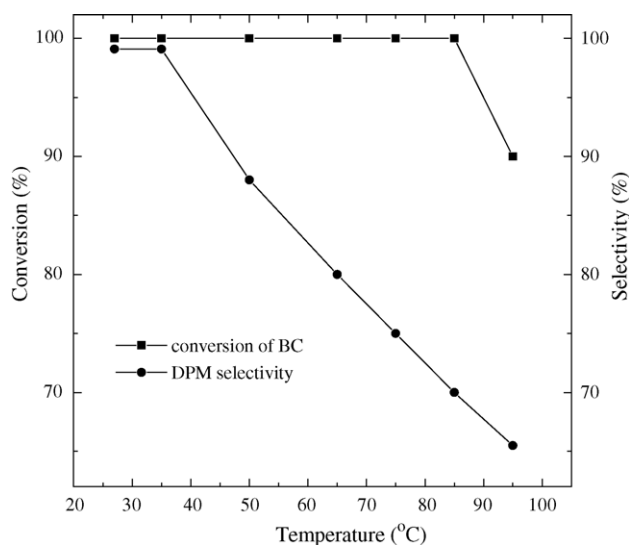


Fig. 5. Variation of conversion of BC and selectivity of DPM with different reaction temperature over $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$.

the mmol ratios of reactants and recyclability were studied on $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$.

3.4. Effect of reaction temperature

The synthesis of DPM was carried out with different reaction temperature from room temperature to 95 °C with 9:1 mmol ratio of BC to benzene in the presence of a flow of nitrogen for 4 h over $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ catalyst and as given in Fig. 5. The conversion of BC is to remain constant upto 85 °C, but the conversion of BC at higher reaction temperature (>85 °C) and also selectivity of DPM from 35 to 95 °C decreased because of the formation of consecutive alkylation products (the isomers of dibenzylbenzene (DBB) such as 1,4-DBB, 1,3-DBB and 1,2-DBB). From the above catalytic results, the optimum reaction temperature was found to be room temperature for highly selective synthesis of DPM.

3.5. Effect of reactants ratio

The synthesis of DPM was carried out at room temperature with various mmol ratios of reactants for 4 h in the presence of a flow of nitrogen over $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$, and the results are shown in Table 4. A decrease in conversion of BC and selectivity of DPM was observed at 1:1, 1:2 and 5:2 mmol ratio of BC

Table 4
Benzylation of benzene over different mmol ratios of benzene and BC over $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$

Benzene/BC mmol ratio	BC conversion (%)	DPM selectivity (%)
1:1	25.4	15.8
1:2	50.5	42.4
5:2	85.3	75.4
9:1	100	99.1

Reaction conditions: 0.2 g of $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ catalyst; reaction temperature = 27 °C (room temperature); reaction time = 4 h.

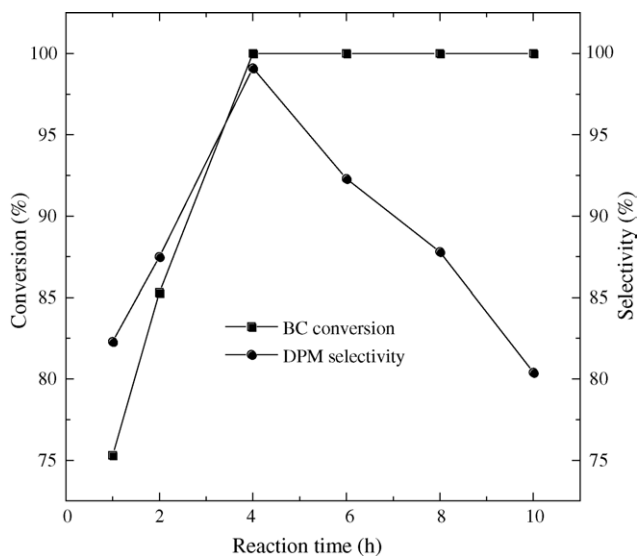


Fig. 6. Variation of conversion of BC and selectivity of DPM with different time over $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$.

to benzene. This may be due to insufficient quantity of the reactants to react with each other. But, an increase in conversion of BC and selectivity of DPM was observed in the 9:1 mmol ratio of BC to benzene at the same reaction conditions. This may be due to equilibrating of each reactant quantity on the acid sites of the inner side surface of catalyst. Further experiments were carried out and also reconfirmed to obtain DPM with maximum selectivity as shown in Table 4.

3.6. Effect of reaction time

The variation of reaction time on the Friedal–Crafts benzylation of benzene was studied in the range of 1–10 h at room temperature with 9:1 mmol ratio of BC to benzene over $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$, and the results are shown in Fig. 6. The conversion of BC and selectivity of DPM increased with increasing reaction time upto 4 h because the contact time is decreased between reactants and active sites of the catalyst. Further the reaction time is increased; the conversion is to remain constant, but the selectivity of DPM decreased because of the formation of consecutive alkylation products (the isomers of dibenzylbenzene (DBB) such as 1,4-DBB, 1,3-DBB and 1,2-DBB) due to very high contact time. From the above results, the optimum reaction time was found to be 4 h for highly selective synthesis of DPM.

3.7. Recyclability of the catalysts

$\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ and $\text{SO}_4^{2-}/\text{Al-MCM-41(83)}$ catalysts was reused for the Friedal–Crafts benzylation of benzene. The reaction was carried out at room temperature for 4 h with 9:1 mmol ratio of BC to benzene for the highly selective synthesis of DPM, and the results have been depicted in Fig. 7. No loss of catalytic activity and Al-ions were observed after 4 runs in $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$. Instead, its conversion of BC and selectivity of DPM is to remain constant with each cycling $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$. But, the conversion and selectivity

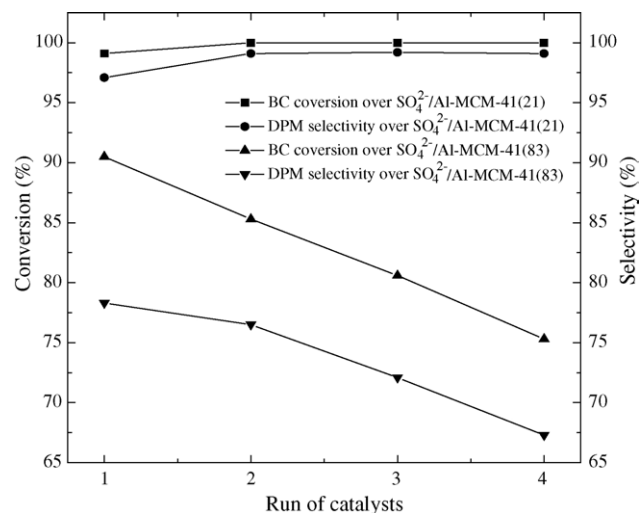


Fig. 7. Variation with run of the catalysts with conversion of BC and selectivity of DPM over $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ and $\text{SO}_4^{2-}/\text{Al-MCM-41(83)}$.

decreased only in $\text{SO}_4^{2-}/\text{Al-MCM-41(83)}$ with each cycling at the same reaction conditions. This may be due to decreasing the catalytic activity along with acid sites on the surface of the catalyst. It was verified that the reaction did not occur in the absence of catalyst. Also, the sulfate ion in recycled samples confirmed that $\text{SO}_4^{2-}/\text{Al-MCM-41}$ was resistant to leaching under reaction conditions tested in this study.

3.8. Leaching of sulfate from $\text{SO}_4^{2-}/\text{Al-MCM-41}$

From the experiments on leaching studies carried out using SO_4^{2-} impregnated Al-MCM-41 it was observed no leaching of SO_4^{2-} from the catalyst after the catalytic reaction.

4. Conclusions

The synthesis of DPM was carried out over Al-MCM-41, $\text{SO}_4^{2-}/\text{Al-MCM-41}$, 0.8N H_2SO_4 and different types of zeolites as catalysts. A decrease in BC conversion and DPM selectivity in the Al-MCM-41 and $\text{SO}_4^{2-}/\text{Al-MCM-41}$ was observed with increasing Si/Al ratios at different reaction temperature. Further the conversion and selectivity results were compared with those obtained by using 0.8N sulfuric acid, 0.1N and 4N H_2SO_4 -sulfated Al-MCM-41(21), different Si/Al ratios of Al-MCM-41, HY, H β , HM and H-ZSM-5 zeolites. From the comparison of the results, finally, $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ is found to be a highly active and recyclable heterogeneous catalyst when it is compared to the above catalyst for the highly selective synthesis of DPM. In the context, the $\text{SO}_4^{2-}/\text{Al-MCM-41(21)}$ is found to be more suitable for the Friedal–Crafts benzylation of benzene to highly selective synthesis of DPM.

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References

- [1] U. Beck, A.G. Bayer, Ullmann's Encyclopedia of Industrial Chemistry, vol. A13, Weinheim, New York, 1985, p. 260.
- [2] G.A. Olah, Friedel–Crafts Chemistry, Wiley, New York, 1973.
- [3] B. Coq, V. Gourves, F. Figueras, Appl. Catal. A. 100 (1993) 69.
- [4] V.R. Choudhary, S.K. Jana, B.P. Kiran, Catal. Lett. 59 (1999) 217.
- [5] (a) C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vashuli, J.S. Beck, Nature 359 (1992) 710;
(b) A. Corma, M.T. Navarro, J. Perez-Pariente, Chem. Commun. 2 (1994) 147;
(c) J.S. Reddy, A. Sayari, Chem. Commun. 21 (1995) 2231.
- [6] R. Mokaya, W. Jones, Z. Luan, M.D. Alba, J. Kilinowski, Catal. Lett. 37 (1996) 113.
- [7] M. Selvaraj, P.K. Sinha, A. Pandurangan, Micropor. Mesopor. Mater. 70 (2004) 81.
- [8] M. Selvaraj, A. Panurangan, K.S. Seshadri, P.K. Sinha, V. Krishnasamy, K.B. Lal, Appl. Catal. A: Gen. 242 (2003) 347.
- [9] M. Selvaraj, B.R. Min, Y.G. Shul, T.G. Lee, Micropor. Mesopor. Mater. 74 (2004) 143.
- [10] M. Selvaraj, P.K. Sinha, K.S. Seshadri, A. Pandurangan, Appl. Catal. A: Gen. 265 (2004) 75.
- [11] M. Selvaraj, K. Lee, K.S. Yoo, T.G. Lee, Micropor. Mesopor. Mater. 81 (2005) 343.
- [12] X. Hu, G.K. Chuah, S. Jaenicke, Appl. Catal. A 217 (2001) 1.
- [13] N. Katada, J. Endo, K. Notsu, N. Yasunobu, N. Naito, M. Niwa, J. Phys. Chem. B 104 (2000) 10321.
- [14] J. Medina-Valtieira, O. Zaldivar, M.A. Sanchez, J.A. Montoya, J. Navarrete, J.A. de los Reyes, Appl. Catal. A: Gen. 166 (1998) 387.
- [15] J. Medina-Valtieira, M.A. Sanchez, J.A. Montoya, J. Navarrete, J.A. de los Reyes, Appl. Catal. A: Gen. 158 (1997) 1.