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Green Synthesis of Benzylated Aromatics Using Iron Loaded Mesoporous Materials

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Abstract: Syntheses of benzylated aromatics like diphenylmethane and its derivatives by the condensation of benzene or toluene or *o*-xylene with benzylchloride or 4-methylbenzylchloride in the presence of a catalytic amount of various iron loaded mesoporous solid acid catalysts such as Fe/Al-MCM-41 (Si/Al=25), Fe/Al-MCM-41 (Si/Al=50) and Fe/Al-MCM-41 (Si/Al=100) are reported.

Keywords: Green synthesis, Al-MCM-41, Benzylation, Mesoporous materials, Iron

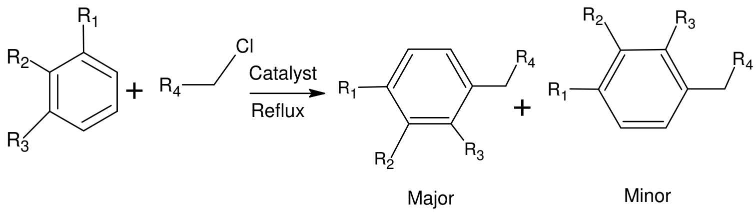
Introduction

The synthesis of M41S family of siliceous solids with sharply distributed pore diameter in the range of 20-100 Å have achieved the main goals in heterogeneous catalysis over the past two decades since it possessed the crystallinity and well-defined structure of zeolites in the mesoporous range[1-4] Iron loaded MCM-41 materials are remarkable for their molecular and electronic diversity and have quite significance in many areas *e.g*. catalysis, medicine, material science *etc*.

These iron loaded MCM-41 materials have received much attention because of their redox properties and unusual activity in alkylation and oxidation reactions[5-7] which is higher compared to conventional mineral acids[8], Lewis acids[9], ion exchange resins[10], mixed oxides[11] and iron supported zeolites, clay catalysts[12,13]. The use of iron loaded mesoporous materials as catalyst can also eliminate the hurdles like pore size constraint, recyclability, thermal and hydrothermal stability *etc*. posed by other support materials. In the past, benzylation of benzene has been carried over different iron containing mesoporous materials like Fe containing mesoporous silicate catalysts[14] and FeSBA-15[15] but so far no such work has been carried out over Fe/Al-MCM-41. Introduction of iron into the mesoporous material by wet impregnation technique showed high redox property than tetrahedrally coordinated Fe^{3+} located in the skeleton of the materials[16] which would be highly beneficial for the title reaction as it follows redox mechanism as confirmed by earlier report[14]. Iron loaded Al-MCM-41 catalyst prepared by wet impregnation was found to be the most effective catalyst in the sulfurisation of methanol involving redox mechanism than iron impregnated purely siliceous MCM-41[17].

Aromatic benzylation is a synthetically important transformation for the preparation of wide variety of benzyl aromatics, which are key intermediates in the multifaceted angle of industrial applications. Diphenylmethane and its derivatives are widely used as pharmaceuticals, petrochemicals, cosmetics, dyes, fine chemicals, insulators *etc*[18]., Mesoporous materials as support[19] and iron loaded mesoporous materials[20]as catalysts have proved to be highly active and efficient in our previous studies.

We report the results of synthesis of benzyl aromatics by using benzylchloride and substituted benzylchloride over this three different types of catalytic amounts of iron loaded MCM-41 like Fe/Al-MCM-41; Si/Al=25, Fe/Al-MCM-41; Si/Al=50 and Fe/Al-MCM-41; Si/Al=100 (Scheme 1). The effects of reaction parameter such as temperature and reaction times on reaction yields are also studied and the results are briefly discussed.



Scheme 1.

Compound I is Benzene if R_1, R_2 and R_3 = H or Toluene if R_1,R_2 = H and $R_3 = CH_3$ or Xylene if R_1= H ,R_2 and $R_3 = CH_3$.

Compound II is Benzyl chloride if $R_4 = C_6H_5$ or 4-methylbenzyl chloride if R_4 = *p*-$CH_3C_6H_4$ Compound III is Diphenylmethane if R_1, R_2, R_3 = H, $R_4 = C_6H_5$ or 1-benzyl-4-methyl-benzene if R_1= CH_3, R_2 ,R_3= H, R_4= C_6H_5 or if R_1, R_2 ,R_3= H, R_4= *p*-$CH_3C_6H_4$ or ditolylmethane if R_1= CH_3, R_2 ,R_3= H, R_4 = *p*-$CH_3C_6H_4$ or 4-benzyl-1,2-dimethylbenzene if R_1,R_2 = CH_3, R_3= H, R_4= C_6H_5 or 3,4-dimethylphenyltolylmethane if R_1, R_2 = CH_3, R_3= H, R_4 = *p*-$CH_3C_6H_4$

Experimental

General

All chemicals were obtained from Merck and used as received. Fe/Al-MCM-41 (Si/Al=25), Fe/Al-MCM-41 (Si/Al=50) and Fe/Al-MCM-41 (Si/Al=100) were prepared according to the literature[16]. The synthesis procedure and characterisation of the catalyst used are discussed in detail in our previous report[20]. GC-MS analyses were performed on Shimadzu GC-MS-QP 5000 with a PE-5 capillary column; scan mode 40–400 amu. IR spectra were obtained with a Buck Scientific 500 spectrometer.^{1}H-NMR spectra were recorded on a Bruker 90 MHz FT-NMR.

Benzene (146.7 mmol) and benzylchloride (9.0 mmol) were taken in a 50 mL RB flask followed by catalyst (0.1 g). The reaction mixture was heated at reflux temperature (80°C for 4h.). The products were analyzed using gas chromatograph (Shimadzu model GC17A) equipped with flame ionization detector fitted with OV-101 column (2m length). After completion of the reaction, the catalyst was filtered off and dried. The quantity of Toluene (122.4 mmol), xylene (106.5mmol) and 4-methylbenzylchloride (7.5 mmol) were used in the respective reactions. All products were identified by comparison of their spectroscopic data with the data of the authentic samples.

Spectral data for selected samples

Diphenylmethane

^{1}H-NMR (CDCl3): 7.06-7.14 (m, 10 H, Ar-H), 3.81 (s, 2H, CH_2). MS: *m/z* 167 [M^+].

Ditolylmethane

^{1}H-NMR (CDCl3): 6.94 (d, 4H, Ar-H), 6.89 (d, 4H, Ar-H), 3.81 (s, 2H, CH_2), 2.35 (s, 6H, CH_3). MS: *m/z* 197 [M^+].

1-Benzyl-4-methylbenzene

^{1}H-NMR (CDCl3): 6.94-7.14(m, 9H, Ar-H), 3.81 (s, 2H,CH_2), 2.35 (s, 3H, CH_3). MS: *m/z* 182 [M^+].

4-Benzyl-1,2-dimethylbenzene

^{1}H-NMR (CDCl3): 6.74-7.14(m, 8H, Ar-H) , 3.81 (s, 2H,CH_2), 2.35 (s, 6H, CH_3). MS: *m/z* 197 [M^+].

3,4-Dimethylphenyltolylmethane

^{1}H-NMR (CDCl3): 6.74-7.94(m, 7H, Ar-H), 3.81 (s, 2H,CH_2), 2.35 (s, 9H, CH_3). MS: *m/z* 212 [M^+].

Results and Discussion

At the onset, benzylation of benzene with benzylchloride was studied over all synthesized catalysts Fe/Al-MCM-41; Si/Al=25, Fe/Al-MCM-41; Si/Al=50 and Fe/Al-MCM-41; Si/Al=100. The products obtained are diphenylmethane (DPM) and the isomers of dibenzylbenzene (DBB) such as 1,2-DBB and 1,4-DBB. The results indicate that the nature of the catalyst plays an important role on their catalyticactivities. As shown in Table1, Fe/Al-MCM-41 (25) showed the highest activity and gave better yields. Although iron loading was found to be the same (10 wt. %) in all the synthesized catalysts higher conversion obtained over Fe/Al-MCM-41 (25) catalysts may be due to the high acidity of this catalyst[20]. The selectivity towards diphenylmethane was high over Fe/Al-MCM-41 (25) catalyst.

The effect of time on stream on the percentage of yields was studied and the results are given in Table 2 at all the temperatures for all the catalysts. The results indicated the increase in the yield increased with the reaction time. The percentage yield was found to be 100 % at 80°C and 110°C with comparatively highly acidic Fe/Al-MCM-41 (25) catalyst in the benzylation of benzene and 100% yield was obtained in the benzylation of toluene at 80°C and 110°C with Fe/Al-MCM-41 catalyst with Si /Al ratio 25 and 50.

Table 1. Catalytic activity of various catalysts in the benzylation of benzene with benzylchloride*

S.No.	Catalyst	Total Conversion, %	Selectivity, %		
			DPM	Isomers of DBB	
				1,2-DBB	1,4-DBB
1	Fe/ Al-MCM-41[a]	100	93	7	-
2	Fe/ Al-MCM-41[b]	98	95	3	-
3	Fe/ Al-MCM-41[c]	78	70	6	2

*Reaction conditions: Catalyst = 0.1g; Temperature:80°C ; [a] Si/Al=25; [b] Si/Al=50 ; [c] Si/Al=100

Table 2. Effect of temperature on the % yield of dibenzyl derivatives over various iron loaded catalysts

S.No.	Catalyst	Time, h	Yield, %[a]		
			50°C	80°C	110°C
1	Fe/ Al-MCM-41[a]	0.5	68	73	78
2	Fe/ Al-MCM-41[a]	1	77	81	85
3	Fe/ Al-MCM-41[a]	2	84	89	93
4	Fe/ Al-MCM-41[a]	3	89	97	98
5	Fe/ Al-MCM-41[a]	4	95	100	100
6	Fe/ Al-MCM-41[b]	0.5	63	67	69
7	Fe/ Al-MCM-41[b]	1	69	73	77
8	Fe/ Al-MCM-41[b]	2	73	78	82
9	Fe/ Al-MCM-41[b]	3	86	89	93
10	Fe/ Al-MCM-41[b]	4	93	98	99
11	Fe/ Al-MCM-41[c]	0.5	42	45	52
12	Fe/ Al-MCM-41[c]	1	51	56	58
13	Fe/ Al-MCM-41[c]	2	57	61	66
14	Fe/ Al-MCM-41[c]	3	65	72	75
15	Fe/ Al-MCM-41[c]	4	74	78	81
16	Fe/ Al-MCM-41[a]	0.5	59	62	68
17	Fe/ Al-MCM-41[a]	1	68	72	78
18	Fe/ Al-MCM-41[a]	2	75	79	84
19	Fe/ Al-MCM-41[a]	3	84	89	90
20	Fe/ Al-MCM-41[a]	4	89	100	100
21	Fe/ Al-MCM-41[b]	0.5	62	70	76
22	Fe/ Al-MCM-41[b]	1	69	75	80
23	Fe/ Al-MCM-41[b]	2	75	81	88
24	Fe/ Al-MCM-41[b]	3	89	91	93
25	Fe/ Al-MCM-41[b]	4	97	100	100
26	Fe/ Al-MCM-41[c]	0.5	64	72	78
27	Fe/ Al-MCM-41[c]	1	69	73	77
28	Fe/ Al-MCM-41[c]	2	73	78	82
29	Fe/ Al-MCM-41[c]	3	76	81	90
30	Fe/ Al-MCM-41[c]	4	86	89	93

[a] Yields were analysed by G.C.[a] Si/Al=25[b] Si/Al=50[c] Si/Al=100

The products were characterized using ^{1}H-NMR and GC-MS analysis. Analytical data were in accordance with those reported for authentic samples. Benzylation of toluene and xylene was also carried out at refluxing temperature using benzylchloride and 4-methylbenzylchloride and the results are summarized in Table 3.

Fe/Al-MCM-41 catalysts were found to be highly selective toward the benzylation of substituted benzenes. This study confirms the exclusive and selective formation of *para* isomers for the benzylation of toluene and xylene using benzylchloride and 4-methylbenzylchloride (Table 3). 1-Benzyl-4-methylbenzene was the product obtained in both the benzylation reactions of toluene with benzyl chloride and benzene with 4-methyl benzyl chloride howeve, higher yield of 1-benzyl-4-methylbenzene was obtained in the former than the latter. This demonstrates the less ability of 4-methylbenzylchloride than benzylchloride as an alkylating agent due to the presence of electron donating methyl group. Better yields were obtained when only one CH_3 group was present in the substrate with benzylchloride was used as benzylating agent but when two CH_3 groups were present in the substrate, the percentage yield was found to be less with both the benzylating agents. This result is opposite to that expected according to the classical mechanism of the Friedel-Crafts acid catalysed benzylation reaction where the benzylation of an aromatic compound is facilitated if one or more electron donating groups are present in the aromatic ring[21]. A similar effect has also been reported on the acetylation of 2-methoxynaphthalene with acetic anhydride over dealuminated HY zeolites[22].

Table 3. Synthesis of diphenylmethane derivatives over various iron loaded catalysts at reflux condition[*]

S.No.	R_1	R_2	R_3	R_4	Catalyst	Total Conversion [d], %
1	H	H	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[a]	85
2	H	H	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[b]	81
3	H	H	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[c]	76
4	CH_3	H	H	$C_6H_5CH_2$-	Fe/ Al-MCM-41[a]	100
5	CH_3	H	H	$C_6H_5CH_2$-	Fe/ Al-MCM-41[b]	100
6	CH_3	H	H	$C_6H_5CH_2$-	Fe/ Al-MCM-41[c]	81
7	CH_3	H	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[a]	84
8	CH_3	H	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[b]	79
9	CH_3	H	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[c]	69
10	CH_3	CH_3	H	$C_6H_5CH_2$-	Fe/ Al-MCM-41[a]	79
11	CH_3	CH_3	H	$C_6H_5CH_2$-	Fe/ Al-MCM-41[b]	65
12	CH_3	CH_3	H	$C_6H_5CH_2$-	Fe/ Al-MCM-41[c]	47
13	CH_3	CH_3	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[a]	57
14	CH_3	CH_3	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[b]	50
15	CH_3	CH_3	H	*p*-CH_3 $C_6H_5CH_2$-	Fe/ Al-MCM-41[c]	36

[*]Reaction conditions: Catalyst = 0.1 g; reaction time = 4 h[a] Si/Al=25[b] Si/Al=50[c] Si/Al=100
[d] $(C_6H_5CH_2\text{-})_2CH_2$ isomers, exclusive 100 % selectivity of *para* isomers in each case

Catalyst reusability

The catalyst was separated from the reaction using simple filtration technique, washed with acetone, air dried and used for subsequent two runs of the reaction process. The results were consistent for all the consequent runs

Conclusions

Thus, iron loaded MCM-41 catalysts can be used as efficient catalysts for the synthesis of benzyl aromatics and therefore Fe/Al-MCM-41 could be a convenient substitute for hazardous Friedel-Crafts catalysts like $FeCl_3$ and $AlCl_3$. The Fe/Al-MCM-41 catalysts are recyclable, heterogeneous, environmentally benign solid acid catalysts possessing desirable properties such as high thermal and hydrothermal stability which are the prerequisite in the area of green chemistry. This study provides a green and selective route for the alkylation of aromatics.

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