

Unusual catalytic activity of iron containing mesoporous materials for synthesis of diphenylmethane

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Mesoporous ferrosilicates with various Si/Fe mole ratios have been prepared for the Friedel-Crafts alkylation reaction to synthesize diphenylmethane selectively under solvent-free reaction conditions. Mesoporous ferrosilicates (PS-1) have high BET specific surface area (*ca.* 1050 m² g⁻¹) and ordered pore structure. The incorporation of iron into the framework of mesoporous silica is characterized and confirmed by various techniques such as XRD, N₂-sorption and FTIR. The nitrogen sorption results show that the sample with Si/Fe mole ratio of 46 possesses improved textural properties as compared with 91 and 125 mole ratios. The catalytic activity of PS-1 catalysts has been tested in the Friedel-Crafts alkylation of aromatic compound for the selective synthesis of diphenylmethane. The results of the alkylation reaction indicate that the PS-1(46) catalyst shows higher activity as compare to other mesoporous ferrosilicates prepared under similar experimental conditions.

Keywords: Catalysts, Mesoporous catalysts, Alkylation, Friedel-Crafts alkylation, Benzylolation, Aromatics, Ferrosilicates, Diphenylmethane

Porous inorganic materials have several unique features and have found applications in separation, adsorption, biotechnology, and electronics¹. In recent years, mesoporous materials have also been the focus of green catalysis and alternative energy technologies such as fuel cells and solar cells². In general, mesoporous silica materials have been extensively used as a supported catalyst to improve stability and catalytic activity. The first mesoporous silica material with low bulk density has obtained by hydrolysis and condensation of tetraethoxysilane in the presence of cationic surfactants. The ordered porous structure with 1000 m² g⁻¹ surface area and pore volume up to around 1 cm³ g⁻¹ has been comprehensively studied and widely applied to many fields such as drug delivery, biosensors and catalysis. However, catalytic applications of the porous silica materials could be achieved through impregnation or substitution of the metal in the silica framework². The metal substituted porous materials with high surface area and large pore size have become alternative catalysts for the reactions involving large molecules that are unable to enter into channels of microporous materials. A remarkable advancement in the synthesis of mesoporous materials was made after the discovery of hydrothermally stable SBA-15 silica molecular sieves³. Among the various metal substituted porous

materials, iron containing mesoporous materials have attracted great interest because of their unique applications in catalysis^{4,5}. Iron containing MCM-41⁶, MCM-48⁷ and HMS⁸ mesoporous materials which are prepared under basic conditions have been widely investigated. Surprisingly, very few studies have focused on direct hydrothermal synthesis of mesoporous ferrosilicates under highly acidic conditions. Recently, iron containing mesoporous materials have been used effectively in various catalytic transformations for instance oxidation, phenol hydroxylation and ozonation of dimethylphthalate^{9,10}. On the other hand, environmentally responsible synthesis of fine chemicals through the development of green catalytic processes has garnered tremendous interest in recent years. In particular, diphenylmethane (DPM) and its derivatives are biologically active¹¹ and are very important as intermediates in pharmaceutical and fine chemical industry¹². Traditionally, soluble Lewis acids (AlCl₃, BF₃, TiCl₄, SnCl₄, FeCl₃, ZnCl₂, BiCl₃)¹³, strong protic acids (HF, H₃PO₄ and H₂SO₄)¹⁴ or Br₂/CCl₄¹⁵ are used as catalysts to prepare diphenylmethane derivatives. However, stoichiometric or higher amounts of catalyst and non-recyclability of these catalysts are some of the major disadvantages in large scale synthesis of diphenylmethane derivatives, and cause environmental and economical problems.

Moreover, due to homogeneous phases of most of these catalyst systems, separation of the products from reaction media is difficult. Also, these are moisture-sensitive and difficult to handle. To overcome the above drawbacks, there have been several attempts to use solid acid heterogeneous catalysts to replace the homogeneous catalysts such as zeolites¹⁶, sulfated ZrO_2 ¹⁷, Lewis acids on solid supports such as MCM-41, hydroxyapatite (HAP)¹⁸ and acidic ionic liquids¹⁹.

In the present study, we report the direct synthesis of mesoporous ferrosilicates with varying iron content and coordination arrangement of iron ions in silica framework. The catalytic activity of the prepared mesoporous ferrosilicates has been tested by varying various factors such as time, temperature, Si/Fe mole ratio, catalyst amount and mole ratio of benzene to benzyl chloride in the benzylation of benzene as a model reaction under solvent-free conditions. In addition, the problems associated with the reported catalysts such as reaction time, conversion, selectivity, stability and reusability have been addressed by the development of a new and highly efficient catalyst system.

Materials and Methods

Synthesis of PS-1 catalytic materials

The mesoporous ferrosilicates with different iron content were synthesized using Brij 76 ($\text{C}_{18}\text{EO}_{10}$ polymer, mol. wt = 711) as a structure-directing agent. Tetraethoxysilane (TEOS) and iron nitrate hexahydrate were silicon and iron sources, respectively. In a typical synthesis, 6.0 g of Brij 76 was dissolved in 140 g of hydrochloric acid solution under vigorous stirring at 40 °C. To this mixture, 15.2 g of TEOS, followed by iron nitrate solution were added slowly. The resulting mixture was allowed to stir for 24 h. Then, the reaction mixture was heated at 100 °C for 24 h under static condition. The solid product formed was recovered by filtration, washed with water and then dried at 80 °C. After calcination at 550 °C for 10 h in presence of air, the obtained product was denoted as PS-1(x), where x represents Si/Fe mole ratio in the material.

Characterization of PS-1 catalytic materials

X-ray powder diffraction (XRD) patterns of all catalysts were recorded on Rigaku Ultima-IV diffractometer using Ni filtered Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 1° min^{-1} and a scan range of 0.7° – 80° at 40 kV and 30 mA. Both

low angle and wide angle XRD patterns of the samples were recorded to characterize the crystallinity and mesoporous ordering of the samples. The N_2 adsorption-desorption isotherms were recorded at 77 K using Quadrasorb-SI system after degasification under vacuum at 423 K for 12 h. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method in the P/P_0 range of 0.05–0.30. Average pore size was calculated by using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherm. The total pore volume was taken by a single point method at $P/P_0 = 0.99$. The FT-IR spectra of all samples were recorded on Perkin Elmer-Spectrum GX spectrometer in the range of 400–4000 cm^{-1} by using KBr pellets having 1 wt% of the sample.

Synthesis of diphenylmethane over PS-1 catalysts

The catalytic activity of PS-1 material was tested for Friedel-Crafts benzylation of aromatics in the temperature range of 35–100 °C under solvent-free conditions in liquid phase. In a typical reaction, the catalyst (15 mg) was taken in a dry round bottom pressure tube (15 mL), benzyl chloride (BC) (1.0 mmol) and aromatic substrates (BA) (7.5 mmol) were added at room temperature. The reaction mixture stirred at 80 °C for several minutes and the products were analyzed by HP 6890 series gas chromatography having flame ionization detector, with OVI-101 capillary column (0.32 i.d., 30 m length and 0.25 μm film thickness). The obtained products were further confirmed by GC-MS on a Shimadzu GCMS-QP 5050A instrument with a ZB-Wax capillary column (30 m length, 0.53 mm i.d. and 0.25 μm film thickness).

Results and Discussion

Characterisation of the catalysts

Figure 1 represents the XRD patterns of calcined PS-1 catalysts. As shown in the figure, all materials show three well resolved planes characteristic for three-dimensional pore structure of space group $P6_3/mmc$. The diffraction peaks of PS-1 materials shift to lower angle with increasing iron incorporation, which corresponds to an increased unit cell parameter value. These results confirm the formation of Fe-O-Si bond in the framework of PS-1 materials. The N_2 adsorption-desorption isotherms provide a method to determine surface area, pore size and pore volume. The textural properties of the PS-1 materials prepared at different Si/Fe mole ratios are

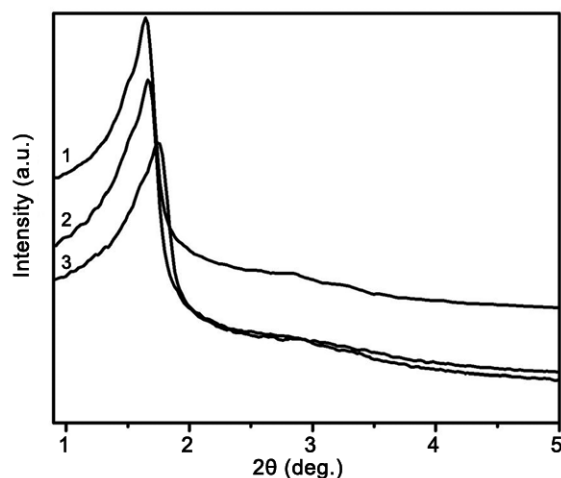


Fig. 1—XRD patterns of PS-1 catalysts. [1, PS-1(46); 2, PS-1(91); 3, PS-1(125)].

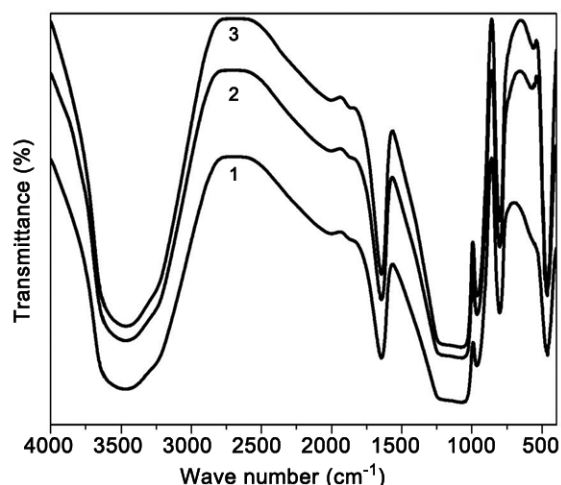


Fig. 2—FT-IR analysis of PS-1 catalysts. [1, PS-1(46); 2, PS-1(91); 3, PS-1(125)].

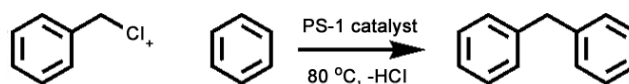
Table 1—Textural properties of PS-1 materials prepared at different Si/Fe mole ratios

Sample	a_0 (nm)	A_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p (cm^3/g)	dp, BJH (nm) ads.
PS-1(46)	6.49	1116	1.0	3.9
PS-1(91)	6.34	1077	0.89	3.5
PS-1(125)	6.22	1028	0.80	3.4
NPS	5.91	890	0.64	3.0

depicted in Table 1. All materials exhibit specific surface area more than $1000 \text{ m}^2/\text{g}$. The specific surface area of PS-1 materials increases from 1028–1116 m^2/g and pore volume increases 0.8–1.0 cm^3/g with increasing Fe content (Table 1). Moreover, a systematic increase in diameter from 3.4–3.9 nm is observed with increase of Fe content in PS-1 materials. It has also been found that the textural properties of PS-1 materials are higher than that of pure silica NPS material. The FT-IR spectra of PS-1 materials are shown in Fig. 2. The bands at 3476 cm^{-1} and 1643 cm^{-1} are attributed to the $-\text{OH}$ groups (surface silanols and adsorbed water molecules). The peak at 571 cm^{-1} is assigned to the tetrahedral bending of the Si–O bond with a knocking effect of the molecules. The high intense band at around 965 cm^{-1} is indexed as due to Si–OH in silica framework. In addition, the bands corresponding to metallosilicates are been at 801 cm^{-1} , 965 cm^{-1} , and 1650 cm^{-1} , highlighting the formation of surface modified porous silica framework¹².

Catalytic activity

In order to determine the best reaction conditions, the catalytic activity of PS-1 materials was tested for



Synthesis of diphenylmethane using PS-1 catalysts

Scheme 1

Friedel-Crafts benzylation on benzene (Scheme 1) under solvent-free condition by using 25 mg of the catalyst, benzyl chloride (1.0 mmol) and aromatic substrate (7.5 mmol) and the results are shown in Fig. 3. It is observed that in the absence of the catalyst, the reaction does not proceed, which signifies the importance of PS-1 catalysts. Of the PS-1(46), PS-1(91) and PS-1(125) catalysts tested for the reaction, PS-1(46) shows the highest conversion under solvent-free conditions, which indicates that with high Fe content, high conversion (100%) of benzyl chloride was observed (reaction was completed in 15 min). The catalytic activity results are strongly supported by the textural properties of PS-1 materials as shown in Table 1. The effect of reaction temperature was studied for the synthesis of DPM over PS-1(46) catalyst in the range of 35–100 °C. The conversion of BC increased from 42% to 76%, when the temperature was increased from 35 °C to 50 °C. At 80 °C, the conversion of BC suddenly increased to 100%. At all temperatures, 100% selectivity for the synthesis of DPM was observed. The conversion and selectivity remained constant with further increase in the reaction temperature to 100 °C. The effect of varying BA:BC mole ratio from 2.5–10 on synthesis of DPM was studied at 80 °C over PS-1(46). The conversion of BC increased with increasing BA:BC mole ratio from 2.5–7.5; maximum conversion was observed at BA:BC molar ratio of 7.5.

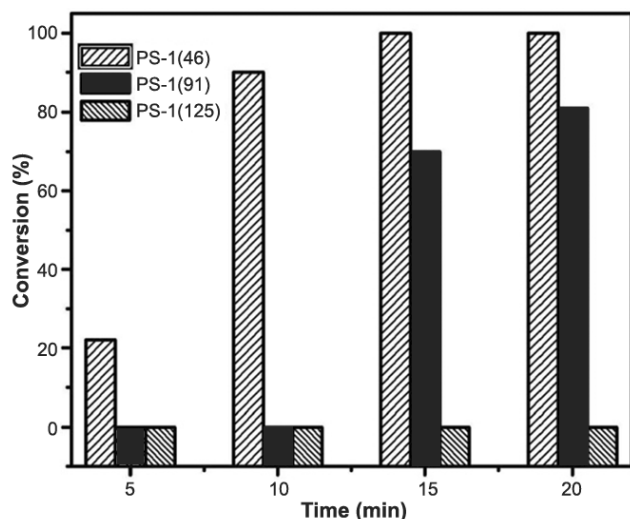


Fig. 3—Effect of Si/Fe ratio of PS-1 catalysts for the synthesis of diphenylmethane.

Interestingly, the selectivity of mono alkylated product DPM remains same for all the molar ratios, which indicates that the selectivity of DPM is independent of the reactants molar ratios under optimized reaction conditions. The effect of weight of the catalyst added 5–25 mg in the reaction mixture is also investigated to optimize the catalytic activity of PS-1(46). The conversion of BC increased from 38% to 100% with an increase in the amount of PS-1(46) catalyst from 5 to 20 mg in the reaction mixture. The complete conversion of BC was observed when the amount of catalyst used in the mixture is 20 mg. The selectivity of the DPM remains unchanged. At the above optimized conditions, the effect of time was also studied from 10 to 30 min. The synthesis of DPM was completed in 15 min of reaction time. Finally, the reusability of the catalyst was tested for the benzylation of benzene over PS-1(46) catalyst under optimized reaction conditions. The catalyst is separated by filtration after the reaction and re-run under similar reaction conditions. Even after the catalyst was reused for four reaction cycles, it showed maximum performance without significant loss of its catalytic activity, which reveals that the PS-1(46) catalyst is stable, robust and reusable.

Conclusions

In summary, we have explored a highly efficient, economical and eco-friendly protocol for the synthesis of diphenylmethane under solvent-free conditions with 100% selectivity and conversion using highly ordered mesoporous ferrosilicates. This reaction can be performed under aerobic conditions without use of specialized equipments. The catalyst is stable, robust

and maintains high selectivity of diphenylmethane (100%) even after several reaction cycles.

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