Synthesis and Characterization of Silica–Polymer Nanocomposites Functionalized with Piperazine for the Synthesis of β -Nitro Alcohols

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Abstract In order to compare the activity and selectivity for the synthesis of β -nitro alcohols, piperazine was functionalized directly and after surface modification into the ordered mesoporous SBA-15 framework. The materials were characterized by powder X-ray diffraction, N₂-adsorption–desorption isotherm, FT-IR, SS-NMR and scanning electron microscopy. The catalyst synthesized via surface modification under solvent free conditions showed very high activity and selectivity of β -nitro alcohols compared to the one synthesized by direct functionalization of SBA-15. Finally the possible reaction pathways were explained mechanistically.

Keywords Mesoporous · Nitroaldol · Piperazine · Nanocomposites

1 Introduction

Heterogeneous catalysis plays an important role in the current industrial scenario because of its significant advantages in terms of easier product recovery, minimizing disposal problems, regeneration of active sites and for

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Present Address: A. Dubey Department of Chemistry, Maulana Azad National Institute of Technology, Bhopal, India environmental perspectives [1, 2]. However, due to the ever growing demand of the day to day products, hazardous homogeneous reagents (H₂SO₄, HF, NaOH, KOH, CH₃COOH and transition metal containing salts) are still in use as catalysts for many organic transformations. During the past few decades, many heterogeneous systems have been developed for acid catalyzed conversions compared to solid bases despite of having a decisive role in the synthesis of fine chemicals [3]. In fact 10-20% of the industrial processes such as isomerizations, additions, condensation, alkylations and cyclizations proceed selectively with higher rates by solid bases [4–7]. Hence, the development of new one step, green and recyclable solid base catalytic systems is strongly encouraged [8]. Among various heterogeneous catalysts, ordered mesoporous silica materials are getting tremendous attention due to their remarkable properties such as high surface area, tunable pore size (2-15 nm) and flexibility to incorporate organic and inorganic moieties within highly porous structures with high dispersion of active species [9]. Particularly mesoporous SBA-15 functionalized with organic moieties have been utilized effectively for many acid-base transformations [10]. Considering the solid base applications, amino-functionalized mesoporous silica materials were effectively designed either by grafting (post-synthetic) or co-condensation (direct during synthesis) methods to obtain organicinorganic hybrid materials for many catalytic conversions [11–14]. Particularly, the introduction of primary and secondary aliphatic amino groups on mesoporous silica materials has also been widely reported for nitroaldol condensation or Michael addition reactions [13, 15–17]. However, the limited scope and density of the functional groups achievable and relatively low hydrothermal stability of the siloxane bond under reactive conditions limit the practical utilization. Various methods were attempted to modify the surface properties of the silica framework and to achieve maximum selectivity of the products, but in almost all the methods, the resulting materials obtained were either non porous or disordered in nature [18, 19]. Very recently, the surface modified amino-functionalized ordered mesoporous silica were reported for Knoevenagel condensation [20].

Nitroaldol condensation is also a key reaction in the synthesis of β -nitroalkanols which are extensively important intermediates in variant organic transformations [21, 22]. β -nitroalkanols can further be converted to obtain 2-aminoalcohols for intermediates in chloroamphenicol, [23] ephedrine, norephedrine [24, 25], drugs like S-propanolol [26, 27] and to achieve amino sugars and ketones [28]. However, selective synthesis of β -nitroalcohols via nitroaldol condensation is quite challengeable because of its predominant dehydration to nitro alkenes that are susceptible for further polymerization. Moreover, the aldehydes in presence of strong base results in self condensation to give aldol product [29]. Therefore in order to overcome these difficulties, various primary and secondary amino groups were directly incorporated into MCM-41 materials [15, 16] yet piperazine as a secondary cyclic amine has not been functionalized on the surface modified SBA-15 materials synthesized via radical polymerization of monomers into the silica framework for nitroaldol condensation. In our earlier communication, we have reported the synthesis of new mesoporous polymersilica (KIT-6 with cubic Ia3d symmetry) composite materials through in situ radical controlled polymerization of vinylmonomers (styrene and vinyl ferrocene as a functional monomer) inside the silica mesopores for hydroxylation of phenol [30]. Therefore in the present paper, we report the synthesis and characterization of silica-polymer nanocomposites functionalized with piperazine for nitroaldol condensation and its comparison with direct functionalized SBA-15. The method of surface modification provides a powerful approach via ion-pair mechanism in controlling β -nitroalcohol selectivity almost exclusively.

2 Experimental Methods

2.1 Synthesis of SBA-15

All the chemicals were procured from Sigma-Aldrich and used without further purification. The synthesis of SBA-15 is carried out using Pluronic (P123) (EO₂₀PO₇₀EO₂₀, MW = 5800, Aldrich) and TEOS as the surfactant and silica source, respectively. In a typical synthesis batch with TEOS, 3 g of P123 was dissolved in 100 g of distilled water and 5.9 g of conc. HCl (35%). After stirring for 1 h, 7.3 g of TEOS (ACROS, 98%) was added at 35 °C maintaining the molar ratio of P123: H₂O: HCl: TEOS ratio as 1: 5562.9: 86.29: 42.51 and stirring for 24 h. Subsequently the mixture was heated for 24 h at 100 °C under static conditions in a closed polypropylene bottle. The solid product obtained after the hydrothermal treatment was filtered and dried at 80 °C. The template was removed by calcinations at 550 °C for 6 h.

2.2 Synthesis of Direct Functionalized SBA-Piperazine Catalyst (SBA/PP)

Piperazine was incorporated via post-synthetic grafting technique. Typically, 10 mL of 3-chloropropyltriethoxvsilane (CPTS) was mixed with 1 g of SBA-15 under inert atmosphere in dry toluene (20 mL) under stirring conditions (Fig. 1). The product SBA/CPTS was filtered and exhaustively washed with ethanol in Soxhlet extractor for 24 h. SBA-15 functionalized with CPTS was dried under vacuum and used further for functionalization with piperazine. Typically, 1 g of SBA/CPTS was mixed with 1 g of piperazine in 15 mL of triethylamine (acts as a neutralizing agent for HCl generated during the functionalization) and refluxed for 24 h under stirring conditions. Finally piperazine functionalized SBA-15 was filtrated and washing thoroughly with dil HCl and water. The functionalization of SBA-15 with piperazine was further confirmed by ninhydrin test that changed the color of solid from white to pink. The sample was named as SBA/PP.



Fig. 1 Direct functionalization of SBA-15 with piperazine (SBA/PP)

2.3 Synthesis of SBA-15/Polymer Nanocomposites (SBA-PS)

The synthesis methodology of SBA/PS (Fig. 2) involves the incorporation of vinyl monomers (4-chloromethylstyrene and divinyl benzene), cross linkers and radical initiators into the SBA-15 mesopore walls via the wet-impregnation method and equilibrated under reduced pressure to achieve a uniform distribution similar to our previous report [30]. The monomers adsorbed on the mesopore walls were subsequently polymerized with controlled temperature programmed heating.

Typically, for 10 wt% polymer loading, 0.0827 g of 4-chloromethylstyrene (CS) (80 mol %), 0.0175 g divinylbenzene (20 mol %), 0.0065 g of AIBN, a, a-9-azoisobutyronitrile (3% relative to the total vinyl group) were dissolved into 2 mL of solvent (dichloromethane). The resulting mixture is impregnated uniformly into the SBA-15 framework. After impregnating the solution, the sample was heated to 40 °C to remove the dichloromethane and subjected to freeze-vacuum-thaw to remove the residual solvent and air. The sample was sealed in a Pyrex tube and subjected to controlled temperature programming for polymerization. The temperature scheme follows 45 °C for 24 h, 60 °C for 4 h, 100 °C, 120 °C and 150 °C for 1 h. Finally the polymer was washed with ethanol to remove the adsorbed monomers. Similarly 30 and 20 wt% polymer loading over SBA-15 was carried out. The sample was named as SBA-x PS where x stands for wt% polymer loading. The role of 4-chloromethylstyrene is to make the nature of the surface more hydrophobic and functionalize piperazine by replacing chloro groups in polymer.

2.4 Functionalization of SBA-PS with Piperazine (SBA/PS/PP)

In a typical synthesis of SBA/PS/piperazine, 1 g of SBAxPS was refluxed with 420 mg of piperazine in presence of 10 mL of triethylamine for 24 h. The solid was filtered and washed well initially with dil HCl and then thoroughly with water to remove unreacted piperazine. Finally the samples were named as SBA-xPS/PP where PP stands for piperazine.

2.5 Nitroaldol Reaction

The catalytic activity studies were carried out in the liquid phase. 3 mmol of *p*-nitrobenzaldehyde and 5 mL of nitro ethane were mixed at 65 °C (Scheme 1). The desired amount of the catalyst (10-500 mg) was added to the reaction mixture under inert atmosphere under stirring conditions and the reaction was monitored for 24 h. The products of the reaction were identified by gas chromatography after considering the response factors of the authentic samples using n-decane as internal standard. After the completion of reaction, catalyst was filtered and washed with solvent. Product was isolated using column chromatography using ethyl acetate: Hexane (2%). The reaction product was identified and characterized by ¹H-NMR and FT-IR (Figure 4S, Supplementary Information (SI)). The melting point of the sample was also in agreement with the literature.

2.6 Characterization Methods

Powder X-ray diffraction (PXRD) pattern was recorded on Hecus X-ray systems S3 Model using Cu K α radiation

Et₂N

С

SBA/PS/PP

Fig. 2 SBA-15 polymer nanocomposites (SBA-PS) functionalized with piperazine



Scheme 1 Nitroaldol condensation

(k = 1.5404 A) from 0–10°. Nitrogen adsorption–desorption isotherms were measured by using Micromeritics ASAP 2020 analyzer at –196 °C. The specific surface area was calculated by the BET method and the pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) method from the desorption isotherm of the sample. SSNMR ¹³C of samples were recorded on AV500S-500 MHz high resolution multinuclear FT-NMR spectrometer. The IR spectra of samples (as KBr pellets) were recorded using a Shimadzu FTIR spectrophotometer in the range of 400–4000 cm⁻¹. SEM images were recorded on Digital scanning electron microscope-JSM 6100 (JEOL).

The number of basic sites on the catalyst surface was determined by Hammett indicators including bromthymol blue (H = 7.1), phenol red (H = 7.4), cresol purple (H = 8.3), thymol blue (H = 8.9), phenolphthalein (H = 9.7), and alizarine yellow (H = 11.0). Soluble basicity was also determined by stirring 500 mg of SBA/PP and SBA/PS/PP with 0.02 M HCl solution for 12 h and finally unadsorbed H⁺ ions were titrated with Na₂CO₃.

3 Results and Discussions

3.1 Synthesis and Characterization of Piperazine Functionalized SBA-15

3.1.1 PXRD

PXRD pattern of the samples at low angles (Fig. 3) shows the diffraction pattern similar to SBA-15 sample. The diffraction at (100), (110), and (200) planes can be indexed to reflections comprising of hexagonal p6 mm space group indicating that the materials possess the ordered mesoporous structure and piperazine has been uniformly incorporated into the framework. A careful examination of the spectrum showed the increase in the intensity of the base peak in SBA-(10)PS/PP catalyst compared to the SBA/PP catalyst due to the polymer formation inside the mesopores of silica materials resulting in an increase in the apparent density of the mesopore walls [31].



Fig. 3 PXRD pattern of a SBA-(10)PS/PP and b SBA/PP catalysts

3.1.2 N₂ Sorption Studies

 N_2 adsorption isotherms were measured at -196 °C using a Quantachrome AS-1MP volumetric adsorption analyzer. Before the adsorption measurements, all samples were out gassed for 12 h at 80 °C in the degas port of the adsorption analyzer. The nitrogen adsorption-desorption isotherm (Fig. 4) of the catalysts showed a type IV adsorption isotherm according to the IUPAC classification with H1 hysterisis loop indicative of mesoporous nature of the samples [9]. The shapes of the isotherms are slightly deviated from the parallel shape due to the strain generated in the mesopores of SBA-15 during the incorporation of piperzine moiety. The surface area, pore volume and pore diameter decreased with the incorporation of piperazine, indicating that the piperazine has been incorporated inside the SBA-framework. All the structural parameters of the catalysts are included in Table 1.

3.1.3 ¹³C CP-MAS NMR

The incorporation of piperazine into the silica framework was further confirmed by ¹³C CPMAS SS NMR. The spectrum of SBA/PS (Fig. 5) shows peaks at 128, 139 and 120 ppm indicating the presence of aromatic carbons of the



Fig. 4 $\,N_2\text{-}adsorption\text{-}desorption$ isotherm of a SBA-(10)PS/PP and b SBA/PP

polymer resulted from the monomers chloromethyl styrene and divinyl benzene [32]. The peak at 25 ppm shows the presence of the carbon directly linked to mesoporous silica $(-CH_2-Si)$ [33]. Furthermore piperazine linkage to polymeric chain was indicated by sharp peak at 48.3 ppm (CH₂ piperazine) [34]. The intensities of peaks were not recognized fully because of the different concentration of piperazine in SBA/PP and SBA-(10) PS/PP catalysts. However, the peaks obtained were sharper in direct

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functionalized piperazine [34, 35] compared to the polymeric derived SBA-PS/PP catalysts (Fig 1S, SI).

3.1.4 FT-IR and Bascity Studies

The FT-IR spectrum (Fig. 6) showed a broad peak around 3500 cm^{-1} in all the samples confirming the presence of N–H stretching of secondary amine (piperazine) incorporated into the mesoporous SBA-15 framework.

Basicity of the catalyst was calulated by Hamett indicator method and found in range of $8.3 < H_0 < 11$. The number of basic sites was also determined by the titration method; 200 mg of the varied catalyst prepared were stirred with 10 mL of 0.02 mol/L of HCl for 12 h and the solution was filtered from the catalyst. The residual H⁺ ions were titrated with 0.02 mol/L of Na₂CO₃ to obtain the amount of HCl adsorbed on the piperazine functionalized SBA-15. The basicity of SBA-PP catalysts was found to be lower compared to the SBA-PS/PP catalysts (Fig 2S, (SI)). This may be due to the better dispersion of the piperazine moiety after the surface modification in polymeric derived catalysts.

3.1.5 SEM

The SEM images (Fig. 7) of SBA/PS/PP (10%) and after piperazine incorporation in SBA-(10%) PS/PP showed the rod shape particles with relatively 1 μ m uniform size.

Table 1 Structural parameters of the catalysts

	-	•			
Entry	Materials	Surface area (m ² /g)	Pore volume (cm^3/g)	Pore size BJH _{Ads} (nm)	Piperazine ^a (%)
1.	SBA-15	678	1.2	8.2	0
2.	SBA/PP	76	0.16	7.7	7.5
3.	SBA/(10)PS/PP	294	0.32	5.1	4.2

^a The amount of piperazine added per gram of the catalyst





Fig. 6 FT-IR spectra of piperazine (PP), SBA/PP and SBA-(10) PS/ PP catalysts

 Table 2
 Effect of different catalyst on the conversion of nitroalcohol conversion

Catalyst	Conversion ^a (%)	Product selectivity (%)		
		A	В	С
Piperazine	63	72	17	11
Polystyrene-PP	52	70	15	15
SBA-15	0	0	0	0
SBA-NH ₂	75	7	90	3
SBA/PP	70	85	12	2
SBA-(30)PS/PP	80	96	4	0
SBA-(20)PS/PP	85	98	2	0
SBA-(10)PS/PP	92	98	2	0

Conditions: 3 mmol (p-nitrobenzaldehyde), 5 mL (nitroethane), temp-65 °C, time (24 h) and catalyst wt (200 mg)

^a Conversion is based on total products



Fig. 7 SEM image of SBA-(10)PS/PP catalyst

These rod shaped structures are uniformly dispersed on ordered mesoporous silica material resulting in better activity and selectivity of the β -nitroalcohols.

3.2 Catalytic Studies

3.2.1 Effect of the Different Catalysts

Table 2 showed the total conversion and the selectivity of the desired product (A) for nitroaldol condensation (Scheme 1). Careful analysis of the results revealed very high conversion of the products (92%) with 98% selectivity of the product (A) on SBA-(10) PS/PP catalyst. The catalytic activity decreased with increase in the percentage loading of the monomers up to 30%. Comparatively lower activity (70%) and selectivity (85%) of the desired product (A) was obtained over direct functionalized SBA/PP catalysts. This may be due to the higher surface area and better dispersion of the active centers inside the surface modified catalyst compared to the direct grafted catalyst (Fig. 7). It is to be mentioned here that only 63% conversion of the products and 72% selectivity of the desired product was obtained on pure piperazine (homogeneous) indicating the effect of heterogenization of piperazine on the surface modified silica framework in controlling the overall selectivity of the product(s). The higher product selectivity of the nitroalcohol is in agreement with earlier reports wherein the secondary amine preferentially gives nitroalcohol over nitrioalkene [15, 16]. The best catalyst SBA-(10) PS/PP was selected for further studies. The variation of the catalyst weight on the conversion of the products showed increasing trend with respect to both SBA/PP and SBA-(10) PS/PP catalyst. Hence catalyst weight of 200 mg is selected for further catalytic studies.

3.2.2 Effect of the Solvent

To further optimize the nitroaldol condensation of pnitrobenzaldehyde with nitroethane, different solvents were chosen to see the influence on total conversion of the products. A careful examination of solvents under study (Table 3) indicates that solvent free conditions are the best conditions to carry out reaction selectively with high conversions. Higher conversion in nitro ethane is attributed to its high dielectric constant 28.06 [36, 37] which helps to stabilize the transition state as well enhance the solubility of p-nitrobenzaldehyde (dielectric constant-20). The conversion and selectivity in other solvents depends on how reluctantly nitronoate ion is generated and stabilized by these solvents (Scheme 2).

3.2.3 Effect of the Reaction Temperature

Figure 8 showed the effect of temperature on the conversion and selectivity of nitro alcohol. The results concluded that the conversion of the products and the selectivity of nitro alcohol product increased with increase in the

Solvents	SBA/PP	SBA/PP Product sele. (%)		SBA-(10)PS/PP	SBA-(10)PS/PP Product sele. (%)	
	Conv. (%)			Conversion (%)		
		A	В		A	В
Nitroethane	70	85	12	93	98	2
Ethanol	60	80	14	68	96	3
Chloroform	46	90	5	60	97	3
Tetrahydrofuran	35	82	10	38	96	3
Acetonitrile	25	84	7	26	98	2
Methanol	20	80	15	25	98	2

Table 3 Effect of different solvents on the conversion and selectivity of the nitroalcohol (conditions as in Table 2)



Scheme 2 Stability of nitronoate ion



Fig. 8 Variation of conversion and selectivity of β -nitroalcohol with temperature (conditions as in Table 2)

temperature up to 65 °C and then decreased with further increase in temperature. This decrease in the selectivity of nitro alcohol product (A) may be due to the formation of nitroalkene via dehydration of nitro alcohol at higher temperature. Hence the best temperature 65 °C was chosen for further catalytic activity studies.

3.2.4 Time-on-Stream Studies

Very interesting observations were seen on the conversion of the products with time. The initial kinetics of the reaction was faster in SBA-(10) PS/PP catalyst compared to SBA/PP catalysts indicating the influence of the surface



Fig. 9 Variation of conversion and selectivity of β -nitroalcohol with time (conditions as in Table 2)

modification (Fig. 9). Secondly, the slight color change (colorless to brown) was observed in SBA/PP catalysts during the progress of the reaction indicating that the reactant molecules might be adsorbing on to the surface of silica and may be blocking the active sites of the catalyst, resulting in lowering the conversion of the products. However, no such color change was noted in the polymer grafted catalyst with the progress of the reaction indicating that the surface modification helps to avoid the adsorptions of the reactant molecules and hence enhancing the conversion of products [16]. The catalyst after the completion of the reaction was washed thoroughly with nitroethane, solvents and with water. The catalyst was dried and still the color change of the catalyst was observed in SBA/PP catalysts.

3.2.5 Plausible Mechanism

Mechanistically, we believe that piperazine functionalized SBA-15 both via direct and after surface modification selectively gives nitro alcohol via ion-pair mechanism [17, 22]. However, in direct functionalized piperazine, the formation of minor product nitroalkene (B, Scheme 3) was also observed. This selectivity difference resulting in the



Scheme 3 Plausible mechanism

formation of nitroalkene may be due to the presence of residual silanol groups that remained after the silylation with chloropropyltriethoxysilane and hence follows the reaction pathway II [38]. Comparatively, the surface modified piperazine, totally cap's the silanol group and preferentially favors the reaction by pathway I in generating selectively nitro alcohol product (A). The melting point of the product was found to be 90 °C (Literature melting point 91–93 °C) [26].

3.2.6 Reusability

In order to see the reusability of the catalysts SBA-(10) PS/ PP, the catalyst after first cycle was filtered, washed thoroughly with chloroform, acetone and finally with water, dried at 150 °C in the air oven and subjected to fresh reaction under identical reaction conditions. No difference in the activity and selectivity was observed up to three cylcles however, slight decrease in the conversion was noted afterwards. The decrease in the activity after third cycle might be due to blockage of the active sites of the catalyst by nitroethane which is highly polar in nature. Similarly leaching of the active centres, piperazine (SI, 1.2), during the course of reaction (Fig 3S, SI) was also tested by several blank experiments [39, 40].

4 Conclusions

We have synthesized piperazine functionalized SBA-15 nanocomposites by different routes and compared the structure- activity relationship for nitroaldol condensation. The selectivity of the product is fairly controlled by surface modification process via polymerization of monomers inside the silica framework. The degree of surface modification by different methods may pave the role for better organic transformations.

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