



Synthesis, characterization and catalytic activity of copper incorporated and immobilized mesoporous MCM-41 in the single step amination of benzene

K.M. Parida*, Dharitri Rath, S.S. Dash

Institute of Minerals & Materials Technology, Bhubaneswar 751013, Orissa, India

ARTICLE INFO

Article history:

Received 6 October 2009
Received in revised form
18 November 2009
Accepted 18 November 2009
Available online 24 November 2009

Keywords:

Co-condensation
Impregnation
Aniline
Benzene
Amination

ABSTRACT

The paper reports the synthesis, surface and textural characterization of copper and amine modified MCM-41 and its application for the single step amination of benzene to aniline at 70 °C. Varying the amount of Cu different Cu/amine modified MCM-41 samples was synthesized by co-condensation and impregnation method. The samples were characterized by nitrogen adsorption–desorption, X-ray powder diffraction, Fourier-transform infrared spectroscopy (FT-IR), ²⁹Si magic-angle spinning (MAS) and ¹³C Nuclear Magnetic Resonance (NMR) and UV–vis diffuse reflectance spectroscopy (UV–vis DRS). X-ray diffraction patterns indicate that the modified materials retain the standard MCM-41 structure. FT-IR and DRS results indicated that Cu and amino groups are incorporated into the Si–O framework and frame wall respectively. NMR showed higher degree of condensation of materials in framework position. Cu-amine-MCM-41 samples showed significant catalytic activity for single step amination of benzene in acetic acid–water medium under mild reaction conditions using hydroxylamine as aminating agent. The Cu-amine-MCM-41 (Si/Cu = 20) showed highest benzene conversion (72.2%) and 100% selectivity for aniline.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of surfactant micelle-templated synthesis of mesoporous silica materials such as MCM-41/48, SBA-15 [1], MSU-n [2], KIT-1 [3], FSM-16 [4], many research efforts have been focused on the synthesis of organic/inorganic hybrid materials. This can be done by functionalizing the exterior and interior surfaces and controlling particle morphology. These organic/inorganic hybrid materials with active groups are unique as they offer potential advantages than the parent silica for various surface modifications. These materials are successfully utilized in separation, sensor design, catalysis and drug delivery.

The discovery of periodic, ordered mesoporous molecular sieves M41s received considerable attention in the heterogeneous catalysis area by applying these materials as support due to their high specific surface area (700–1500 m²/g) as well as their uniform pore size (1.5–10 nm). Many researchers have made their efforts to adopt the single site functionalization of MCM-41 related materials but there are very few reports and limited success is obtained on bifunctional groups [5–8]. Bifunctional mesoporous materials containing organic groups and transition metals can be used in dif-

ferent areas, where the organic groups play the role of providing improved hydrophobicity and the presence of metals provide the catalytic property [9,10]. Among the transition metals studied copper is particularly interesting due to its special redox properties and polarizability. So in the improved current state-of-art we can design a periodic mesoporous silica material having bifunctional sites of tunable pore size.

Among the aromatic amines, aniline is most widely used in industries. Traditionally aniline was produced through multiple chemical reactions. These routes have some disadvantages like unwanted waste production, use of very high temperature and pressure, time consumption etc. Single-step production of aniline via the direct amination of benzene, which significantly improves the atomic efficiency, is an attractive and challenging method from the viewpoint of both green chemistry and synthetic chemistry. The direct amination of benzene with ammonia in gas phase was carried out using Ni/NiO catalytic reactant or the group VIII metal catalysts [11,12]. But these methods suffer from the needs high temperature (from 100 °C to 1000 °C) and high pressure (from 10 atm to 1000 atm), relatively low aniline yield, and/or relatively low selectivity to aniline. Thus, we need enhancement of both the aniline yield and the selectivity.

Many attempts have been made to achieve liquid phase amination of benzene with hydroxylamine over transition metal redox catalysts [13–16]. The study of the direct amination of benzene with hydroxylamine will help in providing information for synthesizing aniline-like molecules with ammonia and hydrogen peroxide

* Corresponding author at: C&MC Department, Institute of Minerals & Materials Technology, (formerly RRL), Bhubaneswar 751013, Orissa, India.
Fax: +91 674 2581637.

E-mail address: paridakulamani@yahoo.com (K.M. Parida).

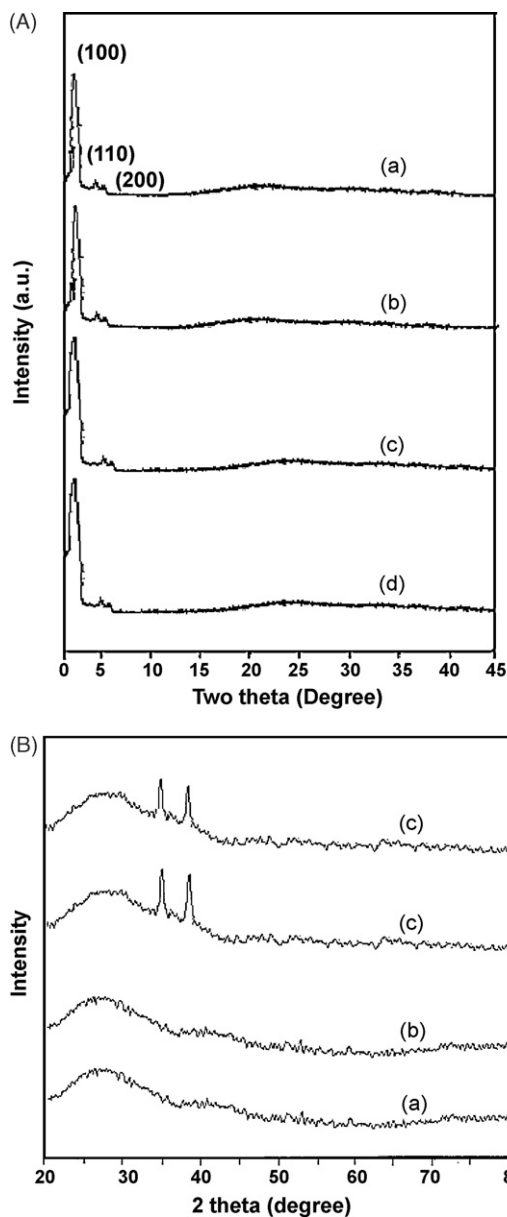


Fig. 1. (A) Low angle XRD patterns of MCM-41 (a), Cu-MCM-41 (20) (b), Cu-amine-MCM-41 (20) (c) and 4Cu/amine-MCM-41 (d). (B) High angle XRD patterns of MCM-41 (a), Cu-MCM-41 (20) (b), Cu-amine-MCM-41 (20) (c) and 4Cu/amine-MCM-41 (d).

in the future. Mantegazza et al. [17] reported the direct synthesis of hydroxylamine by the oxidation of ammonia with hydrogen peroxide in the presence of Ti-silicalite at low temperature under atmospheric pressure. With suitable selection of solvent, no potential deep oxidation of ammonia occurs, and no byproduct forms. Thus, it provided a potential benign supply of hydroxylamine for the amination of benzene.

In our previous work [15] we have studied the effect of Mn towards the single step amination of benzene but herein, we have made a comparative study between the copper incorporated and immobilized mesoporous MCM-41 samples towards the reaction under mild experimental conditions. In the present study amine is used as the functional group which stabilized the catalyst and hence increased the catalytic activity. As catalytic properties of the transition metal modified amine functionalized MCM-41 depend on the structure, location and nature of the incorporated metal, we studied the details of the characterization of the material before

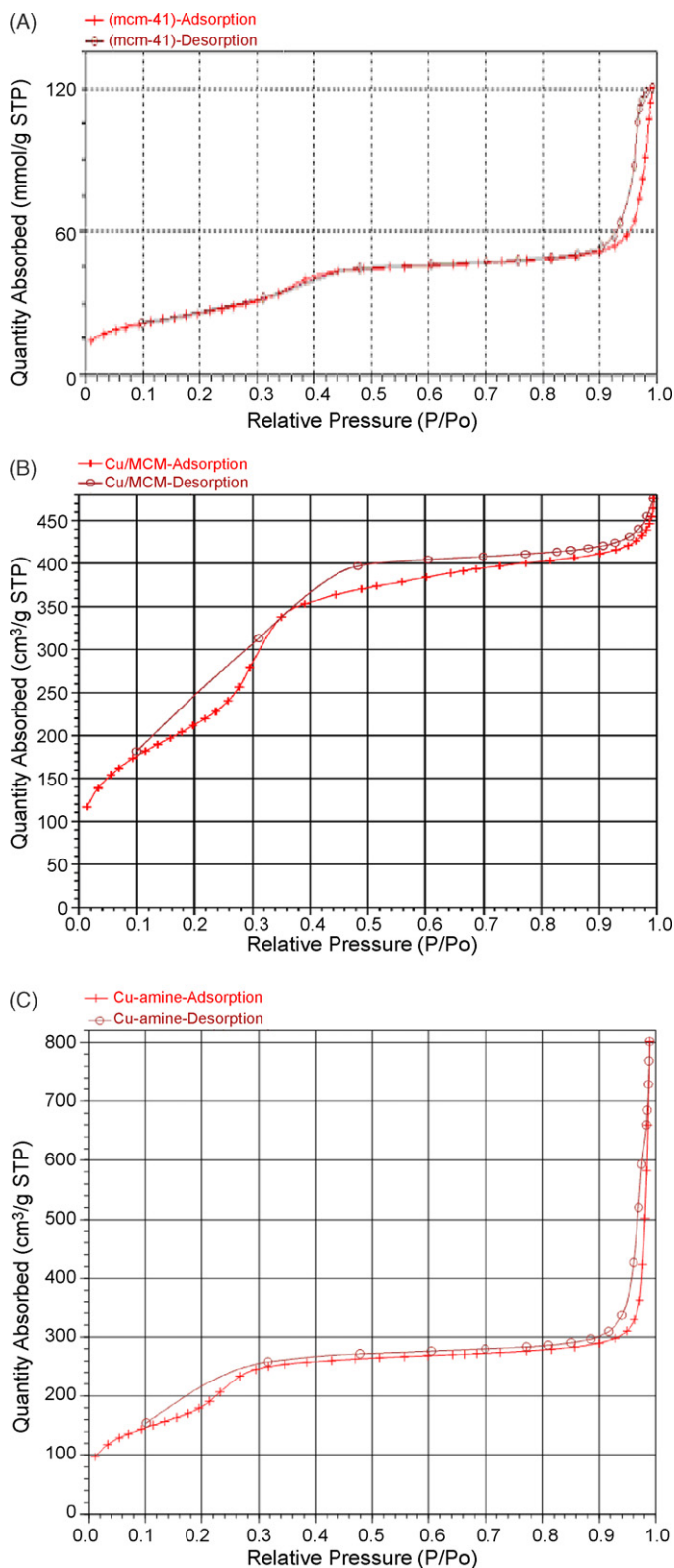


Fig. 2. (A) N_2 adsorption–desorption isotherms of MCM-41. (B) N_2 adsorption–desorption isotherms of Cu-MCM-41 (20). (C) N_2 adsorption–desorption isotherms of Cu-amine-MCM-41 (20).

Table 1
Surface properties of MCM-41 and modified MCM-41.

Sample code	BET surface area ^a (m ² /g)	Unit cell parameter ^b (Å)	Pore diameter (Å)	Pore volume ^d (cm ³ /g)	Wall thickness ^c (Å)
MCM-41	1380	43.1	25.5	1.28	17.6
Cu-MCM-41 (20)	960	46.8	24.9	1.04	21.9
^d Cu-amine-MCM-41 (40)	835	46.2	24.1	0.97	22.1
^d Cu-amine-MCM-41 (30)	814	47.5	23.9	0.90	23.6
^d Cu-amine-MCM-41 (20)	796	48.3	23.4	0.89	24.9
^d Cu-amine-MCM-41 (10)	773	48.5	22.9	0.87	25.6
^e 2Cu/amine-MCM-41	828	47.8	23.6	0.92	24.2
^e 4Cu/amine-MCM-41	805	48.1	23.3	0.88	24.8
^e 6Cu/amine-MCM-41	789	47.9	22.8	0.85	25.1
^e 8Cu/amine-MCM-41	742	48.6	22.1	0.79	26.5
^e 10Cu/amine-MCM-41	723	48.9	21.9	0.76	27

^a Values obtained from N₂ adsorption results.

^b Unit cell parameter = $2 \times d100/\sqrt{3}$ (from XRD).

^c Wall thickness (*t*) = unit cell parameter – pore size.

^d Samples prepared by co-condensation method.

^e Samples prepared by impregnation method.

performing the title reaction. The effects of reaction temperature, time, solvent, and catalyst concentration on conversion and products selectivity were also examined and the results are discussed thoroughly.

2. Experimental

2.1. Material synthesis

The Cu incorporated MCM-41 was synthesized as follows: aqueous solutions of cetyltrimethyl ammonium bromide (CTAB), ammonium hydroxide and copper acetate Cu(CH₃COO)₂ are well mixed with tetraethyl orthosilicate (TEOS) to obtain a gel with a molar composition of 0.12CTAB:1TEOS:0.6NH₃:100H₂O:0.05Cu(CH₃COO)₂ to get the Si/Cu = 20 ratio. After stirring for 1 h, the gel is left at room temperature for 24 h. The products are filtered, washed with distilled water and then heated in a drying oven at 80 °C. The as-synthesized samples are calcined in air at 540 °C for 6 h.

Copper modified amine functionalized MCM-41 can be synthesized in two ways, co-condensation method and impregnation method

2.1.1. Co-condensation method

The mixture of cetyltrimethyl ammonium bromide (CTAB, 0.5 g, 5.49 mmol), 2 M of NaOH (aq) (7 ml, 14 mmol), and H₂O (480 g, 26.67 mmol) was heated at 80 °C for 30 min at a pH of 12.4. To this clear solution, tetraethyl ortho silicate (TEOS, 9.34 g, 44.8 mmol), aminopropyl triethoxy silane (APTES, 1.03 g, 5.75 mmol) and Cu(NO₃)₂·3H₂O (0.474–0.118 g for Si/Cu = 10–40) were added sequentially and rapidly. Following the addition, a light blue precipitation was observed after 3 min of stirring. The reaction temperature was maintained at 80 °C for 2 h. The products were isolated by a hot filtration, washed with sufficient amount of water and methanol and dried under vacuum. For each 1 g of as-synthesized material a mixture of 100 ml of ethanol and 1 ml of concentrated HCl was used for acid extraction at 80 °C for 6 h. Resulting surfactant removed solid products were filtered and washed with ethanol, and then dried at 60 °C. With the variation of copper amount we can get various wt% of Cu modified amine functionalized MCM-41. Further the samples are termed: Cu-amine-MCM-41 (*x*) (where *x* = Si/Cu = 10–40).

2.1.2. Impregnation method

The amine functionalized MCM-41 was synthesized by the above method without taking copper source. One gram of acid treated sample was suspended by 50 ml water in a beaker and then

aqueous solution of Cu(NO₃)₂·3H₂O (0.076–0.379 g) was added dropwise. The liquid phase was removed by a 4 h treatment at 50 °C in a rotary evaporator. Further the prepared samples are termed as *x*Cu/amine-MCM-41 (*x* varies from 2 wt% to 10 wt%).

2.2. Catalytic amination reaction

The catalytic amination reaction is carried out in a thermostatic two-necked round-bottomed flask at atmosphere pressure. In a typical experiment, 0.05 g of catalyst and 11.25 mmol of NH₂OH·HCl were loaded into the reaction flask containing 7.5 ml of 70 vol% acetic acid and stirred for about 20 min at room temperature. Then 1 ml benzene (11.25 mmol) was introduced, and the mixture was heated at 70 °C for 2 h. After the reaction was completed, the resulting mixture was cooled to room temperature and neutralized by a saturated solution of sodium bicarbonate. The organic compounds were extracted with ether and analyzed by gas chromatography (Shimadzu, GC-2010) on FID mode using a capillary column). M-toluidine was used as an internal standard to quantify the aniline produced (Scheme 1).

Decomposition of hydroxylamine was carried out at atmospheric pressure in argon with a flow rate of 25 ml/min. The gas product formed during the decomposition was analyzed by GC (3 mm × 2.3 mm Porapak Q column, TCD detector) after being dried by CaO.

2.3. Physico-chemical characterizations

Low angle XRD patterns of powdered samples were taken in the 2θ range of 1–30° at a rate of 2°/min in steps of 0.01° (Rigaku Miniflex set at 30 kV and 15 mA) using Cu Kα radiation. The high angle XRD patterns of powdered samples were taken in the 2θ range of 20–80° at a rate of 1.2°/min (Philips analytical 3710) using Cu Kα radiation.

The BET surface area, average pore diameter, mesopore distribution, total and micropore volume of all the samples were determined by multipoint N₂ adsorption–desorption method at liquid N₂ temperature (77 K) by an ASAP 2020 (Micromeritics). Prior to analyses, all the samples were degassed at 200 °C and 10^{−4} Torr pressure for 2 h to evacuate the physically adsorbed moisture. The mesopore structure was characterized by the distribution function of mesopore volume calculated by applying the Barrett–Joyner–Halenda (BJH) method.

The FT-IR spectra of the samples were recorded using JASCO FT-IR-5300 in KBr matrix in the range of 4000–400 cm^{−1}.

²⁹Si and ¹³C MAS NMR spectra of the samples were recorded on AV300 NMR spectrometer.

UV–visible DRS spectra of the samples were recorded in Varian Cary 100 Conc UV-visible spectrophotometer.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

PXRD patterns of MCM-41, Cu/MCM-41 and surfactant extracted copper modified organic amine functionalized mesoporous silica samples are shown in Fig. 1A. Regardless of organosilane and copper content all the samples show low angle peaks characteristics of mesoporous materials. The samples showed a typical mesoporous structure with three sharp peaks corresponding to Miller indices (1 0 0), (1 1 0) and (2 0 0). The prominent peak at 2θ ranging between 2° and 2.5° , corresponds to (1 0 0) plane, which is indicative of standard mesoporous silica. There is increase in d -spacing and unit cell parameter with the introduction of amine in the silica framework. This indicates that the organic groups get loaded into the frame wall position.

The copper modified MCM-41 sample (without organic amine) shows high angle XRD (Fig. 1B) peaks at $2\theta = 35.5^\circ$ and 38.7° , corresponding to monoclinic CuO (JCPDS 80-1917). But these high angle peaks are absent in Cu/amine modified samples. Thus the introduction of large organo spacers reduces the probability of formation of CuO.

3.1.2. Nitrogen adsorption–desorption isotherms

N_2 adsorption–desorption is a common method to characterize mesoporous materials, which can provide information about the specific surface area, average pore diameter and pore volume etc. BET surface area, pore size and pore volume for the synthesized materials are presented in Table 1.

As shown in Fig. 2 (A and B) MCM-41 and Cu/amine modified MCM-41 exhibited characteristic type IV BET isotherms consistent with the presence of cylindrical meso-scale pores. It is observed that there are three different well-defined stages in the isotherm. The initial increase in nitrogen uptake at low P/P_0 may be due to monolayer adsorption on the pore walls, a sharp steep increase at intermediate P/P_0 may indicate the capillary condensation in the mesopores and a plateau portion at higher P/P_0 associated with multilayer adsorption on the external surface of the materials. Both the catalysts show a characteristic step around $P/P_0 \approx 0.3$ indicating the mesoporous nature of the materials [18]. MCM-41 sample exhibits isotherm with well-developed step in the relative pressure range ≈ 0.32 , characteristic of capillary condensation into uniform mesopores. A hysteresis of H_3 type was observed for the modified samples. This is due to N_2 condensation and evaporation with interparticles.

Fig. 3 (A and B) shows the BJH pore size distribution of MCM-41 and Cu/amine modified MCM-41. From the figure one can see that all the samples possess good mesoporous structural ordering and a narrow pore size distribution. The surface area of parent MCM-41 was $1380 \text{ m}^2/\text{g}$; this value gradually decreased with the increase in metal and amine loading. The pore diameter and volume decrease with increase in Cu loading.

3.1.3. FT-IR

The FT-IR spectra of MCM-41, amine modified MCM-41 and Cu/amine modified MCM-41 samples are shown in Fig. 4. The characteristic band at $1080\text{--}1090 \text{ cm}^{-1}$ is due to the Si–O stretching in Si–O–Si structure, which is seen in all the figures. The absorption band due to H–O–H bending vibration in water is at $1620\text{--}1640 \text{ cm}^{-1}$. The spectra showed a broad band around $3100\text{--}3600 \text{ cm}^{-1}$, which is due to adsorbed water molecules. Cu/amine modified sample shows the N–H bending vibration at

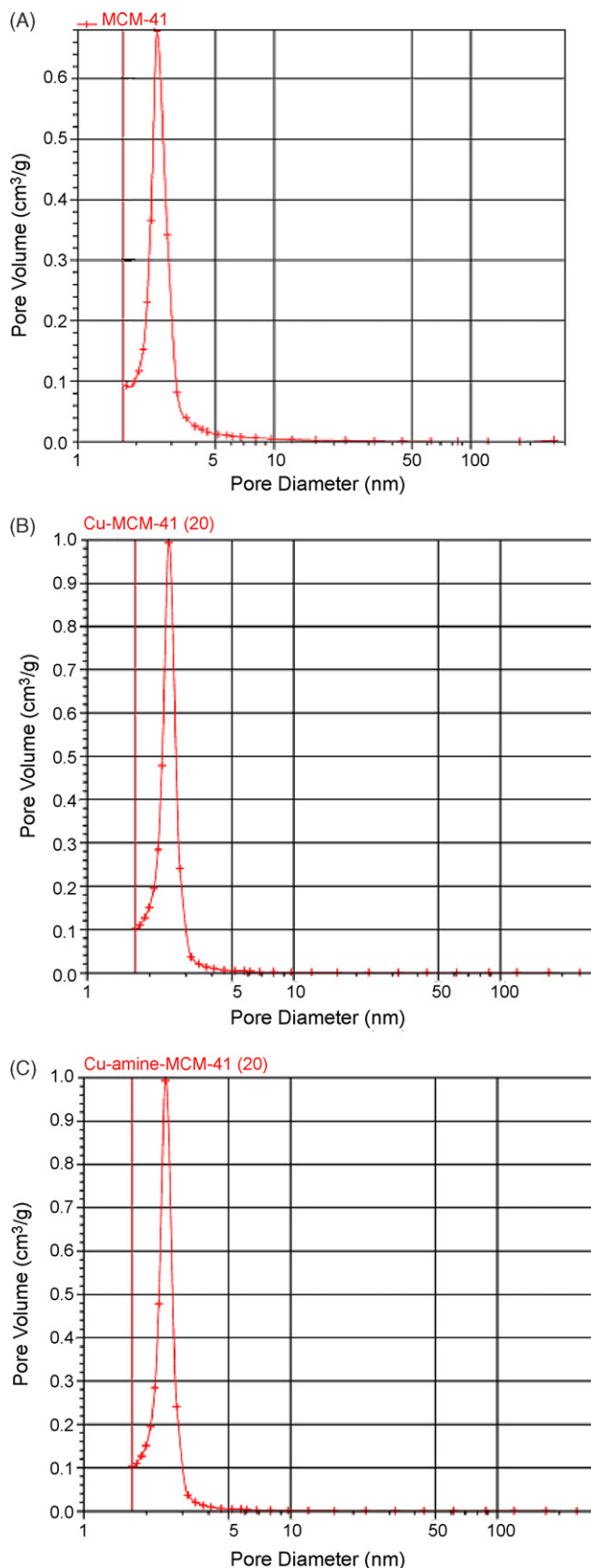


Fig. 3. (A) BJH pore size distribution curves of MCM-41. (B) BJH pore size distribution curves of Cu-MCM-41 (20). (C) BJH pore size distribution curves of Cu-amine-MCM-41 (20).

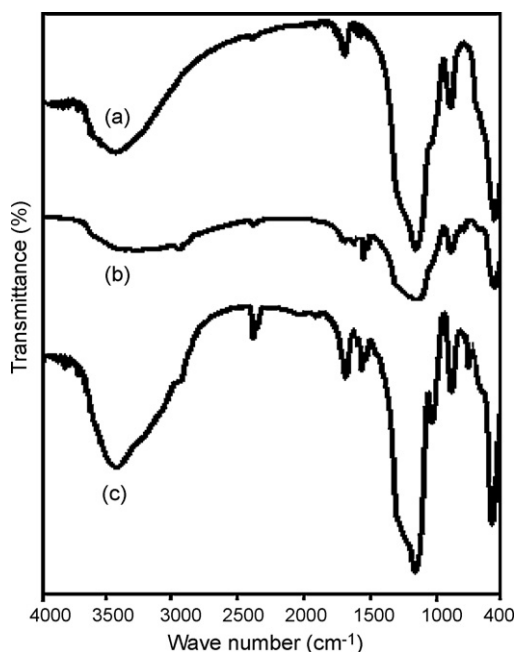


Fig. 4. FT-IR spectra of MCM-41 (a), amine-MCM-41 (b) and Cu-amine-MCM-41 (c).

682 cm^{-1} and $-\text{NH}_2$ symmetric bending vibration at 1525 cm^{-1} . But these two peaks should be at 690 cm^{-1} and 1532 cm^{-1} respectively. The shifting in peak position towards lower wave number is due to bonding of Cu metal with the amine group. Neat MCM-41 is lacking these two peaks. The characteristic band of asymmetric vibration of the $-\text{CH}_2-$ groups of the propyl chain in the silylating agent is at 2935 cm^{-1} , which is present in both the amine modified MCM-41 and the Cu/amine modified MCM-41.

3.1.4. ^{29}Si MAS NMR

The NMR spectra of parent MCM-41, amine modified MCM-41 and Cu/amine modified MCM-41 are shown in Fig. 5. Solid-state ^{29}Si NMR experiments employing magic-angle spinning (MAS) with cross polarization (CP) has been shown to be a reliable mean to characterize various silicate materials. Peaks in the “T” region are contributed by Si atoms of the trialkoxy silane while those in the “Q” region arise from Si atoms of TEOS. Presence of T^2 and T^3 functionalities confirmed the existence of the covalent linkage between the organic groups and the silica surface.

Resonances around -60.77 ppm and -68.33 ppm represented silicon atoms in positions $[(=\text{SiO})_2\text{Si}(\text{OH})\text{R}]$ and $[(=\text{SiO})_3\text{SiR}]$, which are denoted as T^2 and T^3 respectively. The resonance lines at -110.66 , -101.59 and -93.73 representing Q^4 [siloxane, $(=\text{SiO})_4\text{Si}$], Q^3 [single silanol, $(=\text{SiO})_3\text{SiOH}$] and Q^2 [geminal silanol, $(=\text{SiO}_2)_2\text{Si}(\text{OH})_2$] are also observed [19] in case of Cu/amine functionalized MCM-41.

Parent MCM-41 sample shows the presence of resonance peaks from -95 ppm to -110 ppm, indicating a range of Si–O–Si bond angles. The sample contains a large amount of Q^3 sites indicating the reduced framework cross-linking. $(\text{Q}^2 + \text{Q}^3)/\text{Q}^4$ ratio indicates the presence of silanol groups residing on the support surface. This value for amine-modified and Cu/amine modified MCM-41 samples is less than that of the parent MCM-41. Hence it indicates that the materials have few residual silanol groups with a greater degree of condensation and hydrothermal stability than that of parent sample. The decrease in Q^2 and Q^3 signals after organo functionalization suggests that the condensation proceeds by the simultaneous co-condensation of the TEOS and the organosilanes at the structure directing interface.

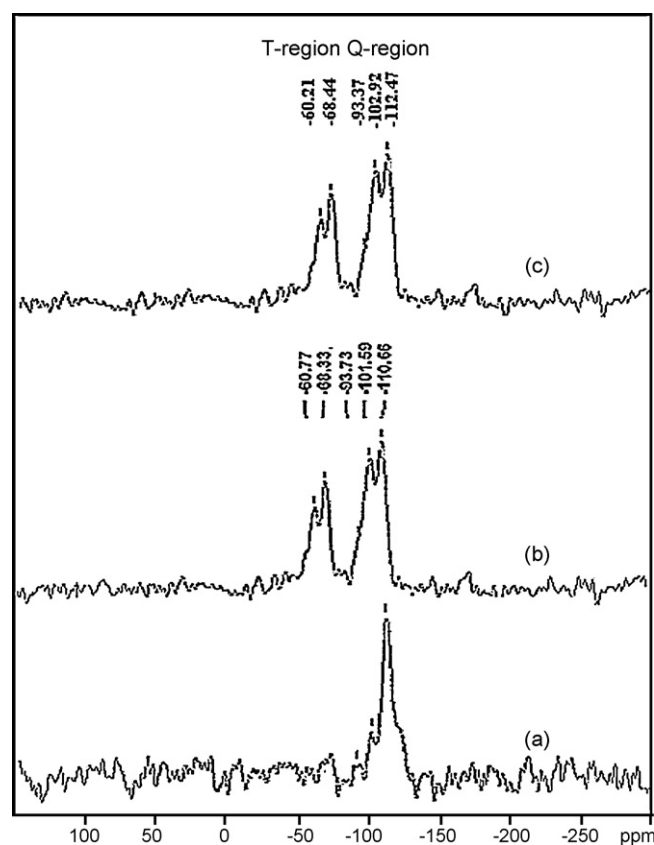


Fig. 5. ^{29}Si MAS NMR spectra of MCM-41 (a), amine-MCM-41 (b) and Cu-amine-MCM-41 (c).

The surface coverage of the mesopores with organic amine could be estimated as $\text{SC} = (\text{T}^2 + \text{T}^3)/(\text{T}^2 + \text{T}^3 + \text{Q}^2 + \text{Q}^3)$. The surface coverage of Cu-amine-MCM-41 (20) modified sample is calculated as 39%. These results suggested that the organoalkoxy silanes with hydrophobic functional groups could better orient themselves around the water/micelle interface and intercalate these groups to the hydrophobic regions of the CTAB micelles during the co-condensation reactions.

3.1.5. ^{13}C MAS NMR

The ^{13}C NMR spectra of amine modified MCM-41 and Cu/amine modified MCM-41 are shown in Fig. 6. ^{13}C CP MAS NMR spectra show the presence of functionalized organic groups inside the MCM-41 pore channels and the absence of surfactant species after solvent extraction process. Absence of signals at 15 ppm and 58 ppm, assigned to the $\text{SiO}-\text{CH}_2-\text{CH}_3$ species, and in the range 50–70 ppm, for surfactant groups, indicates that the hydrolysis of the organosilane monomers is complete and the surfactant is completely removed from the MCM-41 pore channels. ^{13}C NMR spectra show three peaks at 44.18 ppm, 22.45 ppm and 10.86 ppm corresponding to the carbon atom of the propyl chain starting from the carbon attached to the amine group. There is no much change in the peak values with the modification of copper.

3.1.6. UV-vis DRS

UV-vis diffuse reflectance spectra of the Cu-MCM-41 and Cu/amine modified samples (modified by both co-condensation and impregnation method) are shown in Fig. 7. The DR spectra of the samples prepared by co-condensation method show three main bands; first one is around 270 nm, second one is at 320 nm and the last one is around 430 nm. The first two bands around 270 nm and 320 nm corresponding to the ligand to metal ($\text{O} \rightarrow \text{Cu}^{2+}$ and

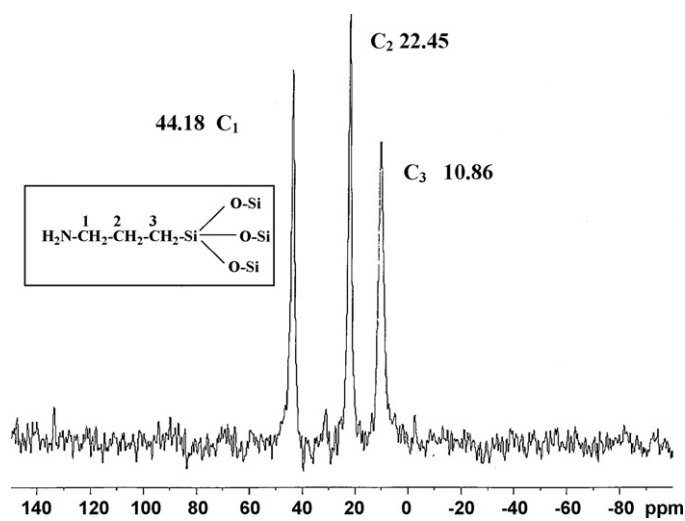


Fig. 6. ^{13}C MAS NMR of amine-MCM-41.

$\text{N} \rightarrow \text{Cu}^{2+}$ respectively) charge transfer (LMCT) spectra. The band around 430 nm is due to the d–d transition ($t_{2g} \rightarrow e_g$) for the divalent Cu ions (Cu^{2+}) in octahedral coordination.

The second peak corresponding to $\text{N} \rightarrow \text{Cu}^{2+}$ is absent in Cu/MCM-41 sample. This sample is having another peak at 450 nm which has been assigned to the formation of Cu^{1+} three-dimensional clusters in the CuO matrix [20].

Cu/amine modified samples prepared by impregnation method shows two sharp bands at 318 nm and 425 nm and a weak band at 270 nm. This may be due to the fact that in impregnation method most of the metal is present as a coordinate bonding with the $-\text{NH}_2$ group of the functional group and rarely the metal is sited inside the silica framework.

3.2. Catalytic amination reaction

All the Cu loaded organic amine functionalized MCM-41 were tested for direct amination of benzene to aniline in acidic medium at 70°C and atmospheric pressure and the results are summarized in Table 2. Conversion of benzene, selectivity for aniline and hydroxylamine are also given in this table. MCM-41 and Cu/MCM-41 (20) gave 5.6% and 42.5% benzene conversion with 55% and 78% aniline selectivity respectively. Cu/amine loaded MCM-41 samples shows higher conversion than parent MCM-41 and Cu/MCM-41 indicating

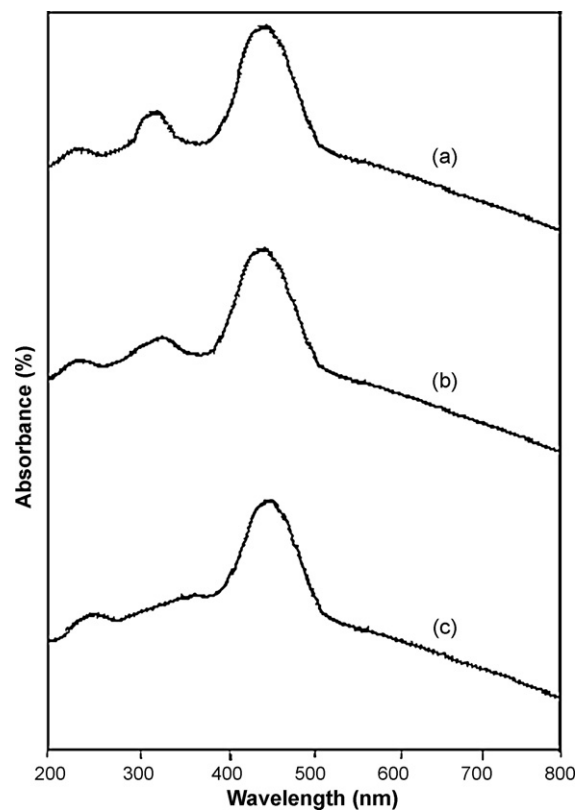


Fig. 7. UV-vis DRS figures of Cu-amine-MCM-41 (20) (a), 4Cu/amine-MCM-41 (20) (b) and Cu-MCM-41 (20) (c).

the influence of Cu/amine in the reaction. The enhanced activity is due to (i) the wormhole-like channel morphology obtained which may facilitate an enhanced access for the benzene molecules to the active copper sites, (ii) the better hydrophobicity relations between the NH_2OH and catalyst and (iii) the absence of CuO clusters, which create all the active copper sites available for the substrate molecules.

Further it is observed that Cu/amine samples prepared by co-condensation method gives higher catalytic activity compared to samples prepared by impregnation method due to uniform distribution of Cu in the silica framework. Benzene conversion and aniline selectively increases with decrease in Si/Cu ratio up to 20 and then decreases with further rise in Cu amount. The highest ben-

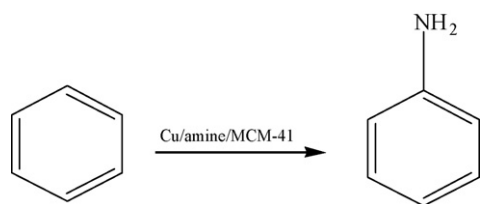
Table 2
Effect of various catalysts on single step amination of benzene.

Catalyst	Benzene conversion (%)	Selectivity (%)		Hydroxyl amine	
		Aniline	Others	Conversion (%)	Selectivity ^a (%)
MCM-41	5.6	55	45	43	13
Cu/MCM-41 (20)	42.5	78	22	57.6	73.7
^b Cu-amine-MCM-41 (40)	11.7	68	32	51.4	22.6
^b Cu-amine-MCM-41 (30)	26.1	80	20	64.1	40.6
^b Cu-amine-MCM-41 (20)	72.2	100	–	88.6	81.5
^b Cu-amine-MCM-41 (10)	53.5	82	18	71.8	74.4
^c 2Cu/amine-MCM-41	59.3	93	7	69.2	49.5
^c 4Cu/amine-MCM-41	55.9	86	14	61.3	58.4
^c 6Cu/amine-MCM-41	54.8	96	4	74.5	80.0
^c 8Cu/amine-MCM-41	41.2	92	8	55.8	73.8
^c 10Cu/amine-MCM-41	32.3	90	10	51.5	62.6
^b Cu-diamine-MCM-41 (20)	79.6	100	–	89.3	89.1
^b Cu-triamine-MCM-41 (20)	86.3	100	–	91.7	94.0

^a Selectivity (SE) of $\text{NH}_2\text{OH} = \text{NH}_2\text{OH}$ consumption for aniline formation/total consumption of NH_2OH .

^b Samples prepared by co-condensation method.

^c Samples prepared by impregnation method: temperature = 70°C , benzene = 11.25 mmol, catalyst amount = 0.05 g, acetic acid = 7.5 ml (70 vol%), NH_2OH = 11.25 mmol, time = 2 h.



Scheme 1. Schematic presentation of amination of benzene.

zene conversion of 72.2% and 100% aniline selectivity is observed using Cu/amine-MCM-41 (20) catalyst. Further increase in copper content on Cu/amine-MCM-41 may block some pores of MCM-41 which results in decrease in benzene conversion.

Free-radical mechanisms have been proposed for amination reactions using N-chloroalkylamines, hydroxylamine-*o*-sulfonic acid and alkylhydroxylamines as the aminating agents catalyzed by redox metal ions such as Ti^{3+} , Fe^{2+} , and Cu^+ [21]. Kuznetsova et al. [22] proposed a free-radical mechanism, considering the protonated amino radical ($\cdot NH_3^+$) as the active aminating species for the amination of benzene. The catalyst interacts with hydroxylamine in acidic medium and generates protonated amino ($\cdot NH_3^+$) radical by reduction of hydroxylamine. Then the protonated amino radicals react with benzene to give protonated aminocyclohexadienyl intermediates. Then the unstable intermediate is oxidized by catalyst to give aniline along with regeneration of catalyst. The detailed mechanism of amination reaction is given in Scheme 2.

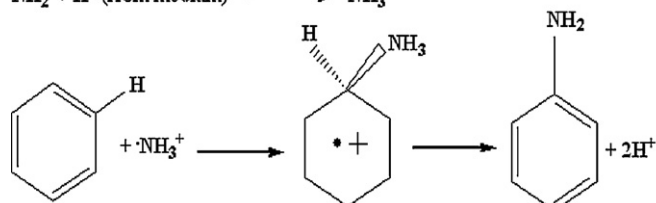
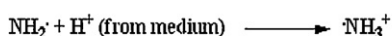
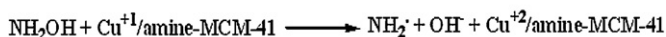
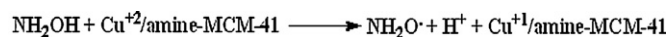
The total amount of hydroxylamine consumed, including catalytic process and disproportionation reaction, is equivalent to the amount of N_2O released in the process. Such total consumption of hydroxylamine was analyzed and is included in Table 2.

In order to study the effect of various amines the present reaction is studied using the Cu/diamine-MCM-41 (20) and Cu/triamine-MCM-41 (20). MCM-41 is modified with Cu and N-[3-(trimethoxysilyl)-propyl] ethylene diamine to get Cu/diamine-MCM-41 (20) and with N-[3-(trimethoxysilyl)-propyl] diethylene triamine to get Cu/triamine-MCM-41 (20). Cu/diamine-MCM-41 (20) and Cu/triamine-MCM-41 (20) gave 79.6% and 86.3% benzene conversion respectively. In case of triamine modified samples the leaching effect of Cu is very much reduced compared to other samples. So the catalytic activity of Cu is enhanced.

The influences of various reaction parameters such as different reaction times, temperature, solvents, amount of hydroxylamine and catalyst loadings have been investigated by taking Cu-amine-MCM-41 (20) as catalyst to optimize the reaction conditions.

3.2.1. Effect of solvent

Different solvents such as acetone, acetonitrile, acetic acid, water and acetic acid–water medium were tried for amination



Scheme 2. Schematic presentation of mechanism for amination of benzene.

Table 3

Effect of various solvents on single step amination of benzene.

Solvent	Benzene conversion (%)	Selectivity (%)	
		Aniline	Others
Acetone	5.5	59	41
Acetonitrile	11	66	34
Acetic acid	19	69	31
Water	52	78	22
70% acetic acid	72.2	100	0

Temperature = 70 °C, benzene = 11.25 mmol, catalyst amount = 0.05 g, $NH_2OH = 11.25$ mmol, time = 2 h.

of benzene using and results are given in Table 3. Only 5.5%, 11%, 19% and 52% of benzene conversion observed in acetone, acetonitrile, water and acetic acid medium respectively. Acetic acid–water medium as solvent gives highest benzene conversion (72.2%), indicating some influence of acidic medium for generation of $\cdot NH_3^+$ radicals. The pKa of $\cdot NH_3^+$ is 3.75 [19], which indicates that in a relatively acidic medium $\cdot NH_3^+$ rather than the neutral amino radical predominates. The effect of acetic acid concentration on amination of benzene and hydroxylamine selectivity is shown in Fig. 8. With the increase in acetic acid concentration up to 70 vol%, the percentage of benzene conversion and aniline selectivity increased but a reverse effect is observed with further increase in acetic acid concentration. This may be due to 70 vol% acetic acid exhibits good solubility and favorable acidity for the highest decomposition of hydroxylamine, thus giving highest conversion of benzene and 100% selectivity for aniline. The selectivity of hydroxylamine for aniline formation increases with an increase in acetic acid concentration up to 70 vol% and decreases thereafter with further rise in acetic acid concentration. This may be due to decrease of the reduction of Cu^{2+} to Cu^+ in strongly acidic medium [20].

3.2.2. Effect of reaction temperature

The effect of reaction temperature on amination of benzene was studied and experimental results are shown in Fig. 9. Neither hydroxylamine decomposition nor aniline formation was observed up to 40 °C of reaction temperature, suggesting that the amination

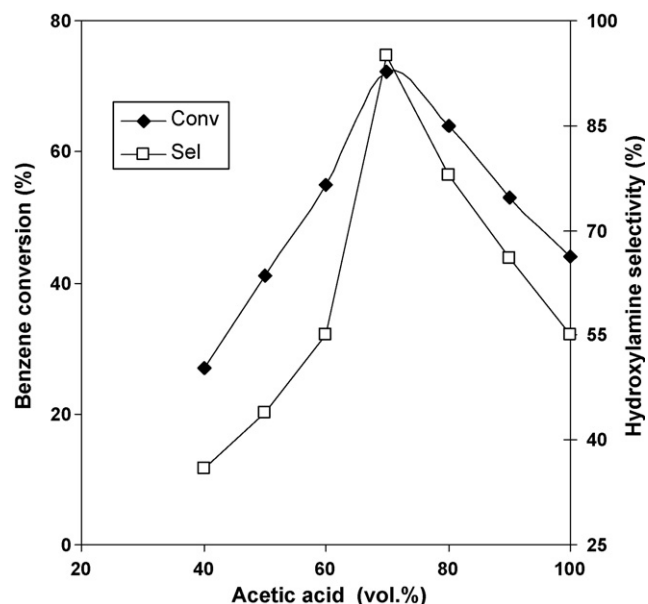


Fig. 8. Influence of acetic acid concentration on amination of benzene. Acetic acid = 7.5 ml, benzene = 11.25 mmol, catalyst amount = 0.05 g, $NH_2OH = 11.25$ mmol, time = 2 h.

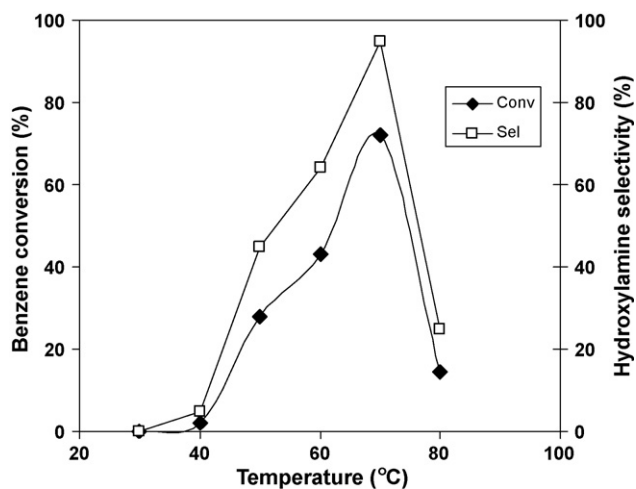


Fig. 9. Influence of temperature on amination of benzene. Acetic acid = 7.5 ml (70 vol%), benzene = 11.25 mmol, catalyst amount = 0.05 g, NH_2OH = 11.25 mmol, time = 2 h.

process is associated with the decomposition of hydroxylamine. With the increase in reaction temperature from 50 °C to 70 °C, benzene conversion increased from 28% to 72.2%. The selectivity of hydroxylamine for aniline formation increases from 45% to 95% with the increase in temperature from 50 °C to 70 °C. With further increase in reaction temperature a sharp fall on benzene conversion as well as selectivity of hydroxylamine is observed. The sharp decrease in conversion of benzene to aniline at 80 °C may be due to vaporization of benzene and accelerated decomposition of hydroxylamine, resulting in loss of active aminating species.

3.2.3. Effect of time

The effect of reaction time on amination reaction is shown in Fig. 10. As the time increased from 0.5 h to 2 h, benzene conversion and hydroxylamine selectivity increases from 15% to 72.2% and 40% to 95% respectively. Further reaction time increases from 2 h to 3 h selectivity of hydroxylamine increases from 95% to 97% indicating aniline yield increases marginally. Therefore 2 h is sufficient for carrying out amination of benzene.

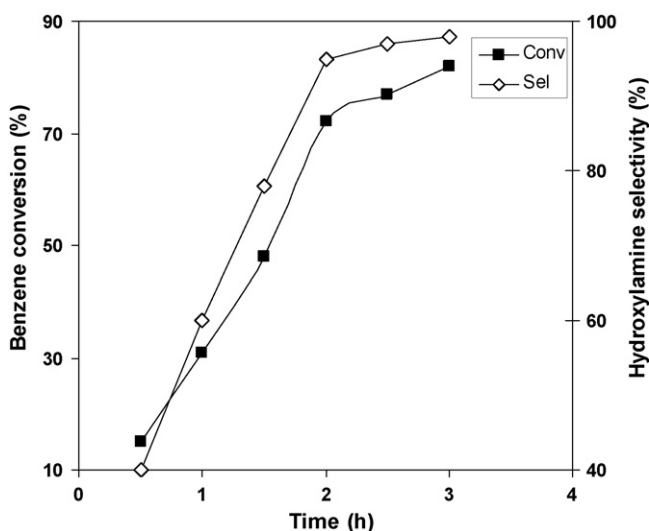


Fig. 10. Influence of time on amination of benzene. Temperature = 70 °C, benzene = 11.25 mmol, catalyst amount = 0.05 g, acetic acid = 7.5 ml (70 vol%), NH_2OH = 11.25 mmol.

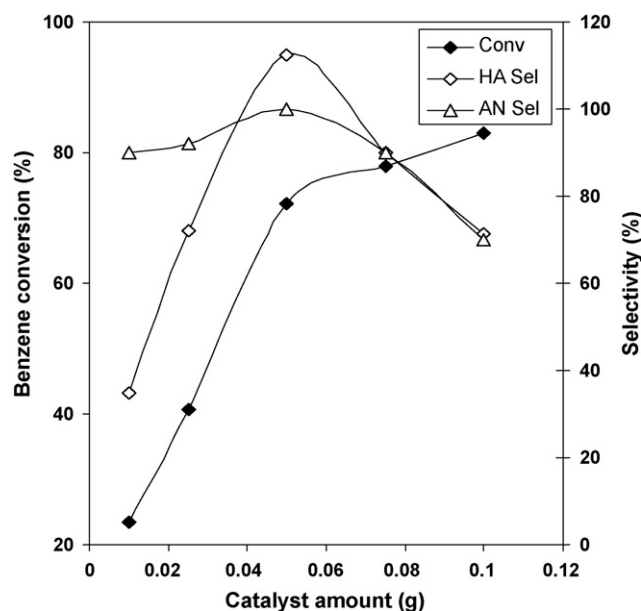


Fig. 11. Influence of catalyst amount. Temperature = 70 °C, benzene = 11.25 mmol, acetic acid = 7.5 ml (70 vol%), NH_2OH = 11.25 mmol, time = 2 h.

3.2.4. Effect of hydroxylamine amount

The variation of percentage of conversion of benzene with the amount of hydroxylamine was studied and results are shown in Fig. 11. As the molar ratio of NH_2OH /benzene increased from 0.5 to 1, the conversion of benzene, selectivity of aniline and selectivity of hydroxylamine increases from 42% to 72.2%, 75% to 100% and 78% to 95% respectively. On further increase in molar ratio of NH_2OH /benzene to 2, the benzene conversion increased slightly from 72.2% to 79% but the selectivity aniline and hydroxylamine decreases from 100% to 69% and 95% to 77% respectively. This may be due to formation of more side products i.e. chlorobenzene, phenol and biphenyl etc. A relatively larger initial concentration of hydroxylamine in the solution led to an accelerated decomposition of hydroxylamine by amine/Cu catalyst resulting decrease in aniline selectivity.

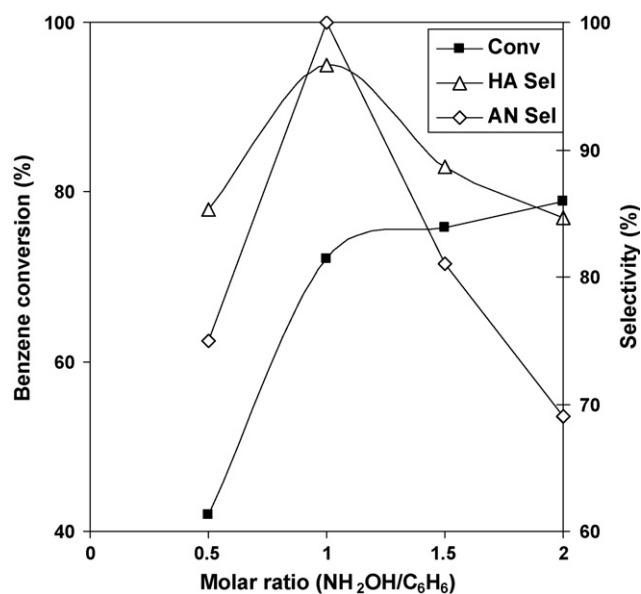


Fig. 12. Influence of $\text{NH}_2\text{OH}/\text{C}_6\text{H}_6$ ratio. Temperature = 70 °C, benzene = 11.25 mmol, catalyst amount = 0.05 g, acetic acid = 7.5 ml (70 vol%), NH_2OH = 11.25 mmol, time = 2 h.

3.2.5. Effect of catalyst amount

The effects of catalyst amount on amination of benzene were studied and the results are shown in Fig. 12. With the increase in catalyst amount from 0.01 g to 0.05 g, the benzene conversion, aniline and hydroxylamine selectivity increased from 23.5% to 72.7%, 90% to 100% and 43.3% to 95%, respectively. As the amount of catalyst further increases from 0.05 g to 0.1 g, the benzene conversion also increased from 72.2% to 83% but aniline and hydroxylamine selectivity decreased to 70% and 67.5% respectively. This may be due to the formation of more side products and unselective decomposition of hydroxylamine resulting decrease in formation of protonated amino ($\bullet\text{NH}_3^+$) radical.

3.3. Recyclability of the catalyst

Cu-amine-MCM-41 (20) is used for recycling study. In order to regenerate the catalyst after 2 h reaction, the catalyst was separated by filtration, washed with double distilled water several times, dried at 110 °C and used in the amination reaction with a fresh reaction mixture. In the regenerated sample after four cycles, the yield decreases by 3.22%.

4. Conclusion

Copper modified amine functionalized MCM-41 was prepared by co-condensation and impregnation method. The XRD pattern shows mesoporous nature of the material remains intact after amine and copper modification. Surface area, pore diameter and pore volume decrease with an increase in Cu content. FT-IR and DRS studies confirmed the presence of Cu and amino groups in the framework and frame wall position respectively. NMR shows the presence of T² and T³ functionalities confirmed the existence of the covalent linkage between the organic groups and the silica surface. Amine functionalized and Cu-amine modified MCM-41 show greater degree of condensation and higher hydrothermal stability than that of parent sample. The 20Cu-amine modified sample shows 39% of surface coverage of parent MCM-41. Sam-

ples prepared by co-condensation method shows higher amount of copper in framework compared to samples prepared by impregnation technique. Cu-amine-MCM-41 samples show good activity for single step liquid phase amination of benzene to aniline. The Cu-amine-MCM-41 (20) modified sample shows highest catalytic activity having 72.2% benzene conversion and 100% aniline selectivity. Samples prepared by co-condensation method shows better activity than samples prepared by impregnation technique.

References

- [1] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Frederickson, B.F. Chmelka, G.D. Stucky, *Science* 279 (1999) 548–552.
- [2] S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia, *Science* 269 (1995) 1242–1244.
- [3] R. Ryoo, J.M. Kim, C.H. Ko, C.H. Shin, *J. Phy. Chem.* 100 (1996) 17718–17721.
- [4] S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, K. Kuroda, *Bull. Chem. Soc. Jpn.* 69 (1996) 1449–1457.
- [5] L. Mercier, T.J. Pinnavaia, *Chem. Mater.* 12 (2000) 188–196.
- [6] Y. Mori, T.J. Pinnavaia, *Chem. Mater.* 13 (2001) 2173–2178.
- [7] A. Taguchi, F. Schuth, *Micropor. Mesopor. Mater.* 77 (2004) 1–45.
- [8] W.H. Zhang, X.-B. Lu, J.-H. Xiu, Z.-L. Hua, L.-X. Zhang, M. Robertson, J.-L. Shi, D.-S. Yan, J.D. Holmer, *Adv. Funct. Mater.* 14 (2004) 544–552.
- [9] A. Bhaumik, T. Tatsumi, *J. Catal.* 189 (2000) 31–39.
- [10] N. Igarashi, S. Kidani, R. Ahemaito, K. Hashimoto, T. Tatsumi, *Micropor. Mesopor. Mater.* 81 (2005) 97–105.
- [11] K. Hara, JP 6-293715 (21 October 1994).
- [12] J. Becker, W.F. Holderich, *Catal. Lett.* 54 (1998) 125–128.
- [13] H.E. Stitt, S.D. Jackson, PCT WO 0 009 473 (2000).
- [14] D. Poojary, R. Borade, A. Hagemeyer, C. Dube, Z.P. Zhou, U. Nothelis, R. Armbrust, *C. Rasp.* PCT WO 0 069 804 (2000).
- [15] K.M. Parida, S.S. Dash, S. Singha, *Appl. Catal. A: Gen.* 351 (2008) 59–67.
- [16] L.F. Zhu, B. Guo, D.Y. Tang, X.K. Hu, G.Y. Li, C.W. Hu, *J. Catal.* 245 (2007) 446–455.
- [17] M.A. Mantegazza, G. Leofanti, G. Petrini, M. Padovan, A. Zeccina, S. Bordiga, in: V.C. Corberan, S.V. Bellon (Eds.), *New Developments in Selective Oxidation*, Elsevier, New York, 1994, p. 51.
- [18] M. Selvaraj, P.K. Sinha, K. Lee, I. Ahn, A. Pandurangan, T.G. Le, *Micropor. Mesopor. Mater.* 78 (2005) 139–149.
- [19] T. Chen, Z.J. Fu, L.F. Zhu, C.W. Hu, A.M. Tian, *Acta Chim. Sinica (Huanxue Xuebao)* 61 (2003) 170.
- [20] H. Praliand, S. Mikhailenko, Z. Chajar, M. Primet, *Appl. Catal. B: Environ.* 16 (1998) 359–365.
- [21] A. Citterio, A. Gentile, F. Minisci, V. Navaovini, M. Sevravalle, S. Ventura, *J. Org. Chem.* 49 (1984) 4479–4482.
- [22] N.I. Kuznetsova, L.I. Kuznetsova, L.G. Dutesheva, V.A. Likholobov, G.P. Pez, H. Cheng, *J. Mol. Catal. A* 161 (2000) 1–9.