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Functionalized mesoporous silica supported copper(II) and nickel(II) catalysts for liquid phase oxidation of olefins

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Highly ordered 2D-hexagonal mesoporous silica has been functionalized with 3-aminopropyltriethoxysilane (3-APTES). This is followed by its condensation with a dialdehyde, 4-methyl-2,6-diformylphenol to produce an immobilized Schiff-base ligand (I). This material is separately treated with methanolic solution of copper(II) chloride and nickel(II) chloride to obtain copper and nickel anchored mesoporous materials, designated as Cu-AMM and Ni-AMM, respectively. The materials have been characterized by Fourier transform infrared (FT-IR) and UV-vis diffuse reflectance (DRS) spectroscopy, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ adsorption–desorption studies and ¹³C CP MAS NMR spectroscopy. The metal-grafted mesoporous materials have been used as catalysts for the efficient and selective epoxidation of alkenes, *viz*. cyclohexene, *trans*-stilbene, styrene, α -methyl styrene, cyclooctene and norbornene to their corresponding epoxides in the presence of *tert*-butyl hydroperoxide (TBHP) as the oxidant under mild liquid phase conditions.

Introduction

Epoxidation of olefins is studied most intensively because epoxides are versatile building blocks for the synthesis of many bioactive molecules and organic fine chemicals.¹ Transition metal compounds have been used as catalysts for the epoxidation of olefins in the past few decades.² Schiff-base complexes of manganese(III), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) are reported in the literature where they have been employed as active catalysts for the oxidation of alkanes and alkenes; whereas polymer bound Schiff-base complexes of ruthenium, iron and molybdenum have shown better catalytic activity towards cyclooctene oxidation.³ Apart from their catalytic roles in epoxidation, inbound copper and nickel materials also have significant importance in other organic conversions. Copper complexes have been used as catalysts in various liquid-phase catalytic reactions⁴ e.g. catechol oxidation,⁵ alkane oxidation,6 sulfoxidation,7 epoxidation,8 etc.; and nickel compounds also play a crucial role in many catalytic conversions.⁹

The separation of products from the reaction mixture is the primary drawback associated with homogeneous catalysis, which makes use of soluble metal complexes. Whereas in heterogeneous catalysis, the use of insoluble solid catalysts provides the benefits of easy separation and catalyst recyclability, thereby minimizing the wastage of products arising during the catalyst separation and its disposal. Thus, now-a-days researchers are keener towards the development of effective heterogenized catalytic systems, which can be reused for several cycles thereby reducing the cost of production in chemical industries. Furthermore, such systems require minimum effort for the separation of catalysts from the substrate, product(s) and oxidant. The simplest approach to transform a successful homogeneous catalyst into a heterogeneous catalyst is by supporting the soluble catalyst on the surface of an insoluble solid.¹⁰ The highest level of development in the surface immobilization strategy is the covalent attachment of the organic compound or ligand to the solid surface and subsequent complexation with metal ions.

The use of mesoporous organosilica or related nanomaterials for the synthesis of effective catalysts through anchoring or grafting of organic groups within the nanochannels has been an active area of research. There are several reports where copper(II) has been anchored on to porous silica materials.¹¹ In such cases, the amine group containing organic moiety, generally 3aminopropyltriethoxysilane, has been first anchored on the surface of mesoporous silica via Si-O-Si bonds, taking advantage of the surface silanol groups. Then Schiff-base condensation between the amine group and a suitable aldehyde leads to the formation of a coordinating ligand in the mesoporous matrix which can bind covalently with copper(II) ions. A Cu(II)-Schiff base complex covalently grafted over 3-aminopropyl functionalized silica surface showed good catalytic activity in allylic oxidation of olefins in the presence of tert-butyl hydroperoxide.¹² Insoluble Nicompounds have also been employed as heterogeneous catalysts for olefin epoxidation.¹³ Previously we have reported the synthesis and characterization of Ni(II),14 Cu(II)15 and Mo(VI)16 complexes

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with N- and O-donor Schiff-base ligands and their applications as catalysts for epoxidation of olefins under heterogeneous conditions. The heterogenized catalysts were prepared by immobilizing the complexes onto 2D mesoporous silica.

To design and synthesize effective metal bound mesoporous silica materials for catalysis, the metal has to bind tightly with silica inside the cavity at the mesopore surface so that it does not percolate out into the reaction mixture during reactions. To obtain such materials the silica must be functionalized in such a way that sufficient donor sites are available for the metal cation to bind on its surface, and it can be used as an efficient catalyst. We have followed this approach in this present work. A heterogenized N, O donor Schiff-base ligand has been first immobilized on ordered mesoporous silica and then transition metal ions have been coordinated to this ligand. We have also applied this strategy to prepare Pd-catalysts, which has been successfully utilized for the synthesis of value added fine chemicals *via* C–C coupling reactions.¹⁷

We report here the synthesis and characterization of two heterogenized catalysts, Cu-AMM and Ni-AMM, comprised of Cu(II) and Ni(II) ions, respectively (Scheme 1). A heterogenized Schiffbase ligand, I, is produced when mesoporous silica functionalized with 3-aminopropyltriethoxysilane (3-APTES) reacts with 4-methyl-2,6-diformylphenol (DFP). Cu(II) and Ni(II) ions are allowed to react with this Schiff-base anchored ligand to produce Cu-AMM and Ni-AMM respectively. These materials have been used as catalysts for the epoxidation of cyclohexene, *trans* stilbene, styrene, α -methyl styrene, cyclooctene and norbornene in the presence of *tert*-butyl hydroperoxide as the oxidant under liquid phase conditions.

Experimental

Materials and physical methods

Cyclohexene, styrene, α -methyl styrene, *trans*-stilbene, cyclooctene, norbornene, 3-APTES and tetraethyl orthosilicate (TEOS) were purchased from Aldrich and used without purification. Other reagents were purchased from Loba Chemie and used without further purification. Solvents used for spectroscopic

studies were purified and dried by standard procedures before use.18 Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin-Elmer, USA. FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Characterization of the samples by powder X-Ray diffraction was performed by using a Bruker AXS D8 Advanced SWAX diffractometer, where the small and wide-angle goniometers are mounted. The X-ray source was Cu-K α radiation $(\alpha = 0.15406 \text{ nm})$ with an applied voltage and current of 40 kV and 20#x00A0;mA, respectively. Mesophases of different samples were analyzed using a JEOL, JEM 2010 transmission electron microscope at an accelerating voltage of 200 kV. N2 adsorption measurements were carried out using a Bel Japan Inc. Belsorp-HP surface area analyzer at 77 K. Pre-treatment of the samples was undertaken at 473 K for 3 h under high vacuum. A Shimadzu AA-6300 double beam atomic absorption spectrophotometer (AAS) was used for determining the percentage loading of Cu and Ni through wet chemical analysis. UV-visible diffuse reflectance spectra (DRS) were recorded on a Shimadzu 2401PC UVvisible spectrophotometer with an integrating sphere attachment using BaSO₄ as the background standard. Absorption spectra of dispersed samples were recorded on a Shimadzu UV 2100 spectrophotometer. Solid state ¹³C CP MAS NMR analyses were conducted on a CHEMAGNETICS 300 MHz CMX 300 spectrometer. Gas chromatography analysis was performed with an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary column ($30 \text{ m} \times 0.32 \text{ mm}$) and an FID detector. All experiments were carried out in air and room temperature unless reported otherwise. 4-Methyl-2,6-diformylphenol was synthesized following a published procedure.19

Syntheses of catalysts Cu-AMM and Ni-AMM

Mesoporous silica was synthesized following a published procedure.²⁰ It was functionalized by stirring 0.1 g of it with 0.180 g (0.81 mmol) of 3-APTES in chloroform following a published method.²¹ Heterogenized Schiff-base ligand, I, was synthesized by the reaction between 3-APTES functionalized mesoporous silica with 4-methyl-2,6-diformylphenol (0.082 g, 0.5 mmol) following a previously reported procedure.²⁰ For the synthesis of Cu-AMM,



Scheme 1 Preparation of Cu-AMM and Ni-AMM. Functionalization of mesoporous silica with (a) 3-aminopropyltriethoxysilane (3-APTES) and then with (b) 4-methyl-2,6-diformylphenol.

a methanolic solution of copper(II) chloride dihydrate (0.169 g, 1.0 mmol) was added to the above mention yellowish solid at room temperature and left overnight. After that it was filtered and washed with hot methanol several times until the filtrate became colorless and was finally dried under vacuum. Ni-AMM has been synthesized using nickel(II) chloride hexahydrate (0.236 g, 1.0 mmol) instead of copper(II) chloride following the same procedure as used for Cu-AMM.

Epoxidation reactions

Catalytic reactions were carried out over the Cu- and Ni-grafted materials in a similar manner. The heterogeneous oxidation reactions were performed in a magnetically stirred two necked round-bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. Typically, 1.0 g of the substrate was added to 5 mL of acetonitrile (solvent), followed by the addition of 0.1 g of the catalyst and the mixture was then preheated to 333 K. The reaction was initiated with the addition of *tert*-butyl hydroperoxide (equimolar with respect to the substrate). Aliquots from reaction mixtures were collected at regular intervals. After cooling, nitrobenzene was added as the internal standard. The substrate and product(s) from the reaction mixture were analyzed by gas chromatography. They were identified by comparison with known standards.

One blank reaction has been carried out without adding any catalyst keeping other experimental conditions unchanged. Another blank reaction has been performed in the presence of **I** under similar conditions.

Results and discussion

Syntheses and elemental analyses

The immobilized Schiff-base ligand has been synthesized via condensation between the dialdehyde, 4-methyl-2,6-diformylphenol and the heterogenized amine. We attempted to synthesize efficient heterogeneous catalysts by immobilization of metal ions over a silica host via coordination with electron donor sites. For this purpose, we first synthesized a heterogeneous ligand and then metal ions were allowed to coordinate with it. Mesoporous silica was functionalized in such a way that the amine group was appended with the silica. Then diformyl compound was allowed to condense with it to form the Schiff-base. Metal ions were then allowed to bind with this heterogenized ligand. Atomic absorption spectroscopy has been used to determine the concentrations of metal ion and chloride. The results show that Cu-AMM and Ni-AMM contain 0.34% copper and 0.42% nickel respectively. It has been further revealed from AAS results that the molar ratio of metal and chloride is 2:2.93 for Cu-AMM and 2:2.85 for Ni-AMM. These results have been supported by the elemental analyses of the materials. Elemental analyses show that the molar ratios for nitrogen: metal in Cu-AMM and Ni-AMM are ca. 1.05:1 and 1.10:1 respectively. The molar ratios for carbon: metal in Cu-AMM and Ni-AMM are ca. 6.92: 1 and 6.95: 1 respectively. All these data support the possible structure of the catalysts as shown in Scheme 1. A similar structure in the heterogenized donor system has been proposed for Zn²⁺ supported functionalized mesoporous sensor.²⁰ There are reports of μ_2 -Cl bridged

copper(II) and nickel(II) complexes with similar N_2O donor ligands and coordination environment MN_2OCl_3 (M=Cu or Ni).²²

FT-IR spectroscopy

FT-IR spectra of mesoporous silica (MS), heterogenized Schiffbase ligand (I), Cu-AMM and Ni-AMM are presented in Fig. 1. The FT-IR spectrum of I shows a band in the region of 3000-2800 cm⁻¹ and 1655–1500 cm⁻¹. The spectrum suggests the presence of various N-H and C-H vibration bands in the material. These bands are generated after functionalization of 3-APTES over MS and were absent in the mesoporous silica. The FT-IR band at 1655 cm⁻¹ for compound I could be attributed to the C=N stretching frequency and the band at 1530 cm⁻¹ is probably due to the C=C stretching, which comes from the phenyl ring. In the FT-IR spectrum of 4-methyl-2,6-diformylphenol, the band at 1681 cm⁻¹ appears due to the presence of aldehyde group,²⁰ but in the spectrum of I, no peak at around 1681 cm⁻¹ is observed which indicates that both the aldehyde groups are converted to imine. Cu-AMM and Ni-AMM showed FT-IR bands at 1630 and 1632 cm⁻¹ which indicate the retention of C=N moiety in both the materials. These bands in Cu-AMM and Ni-AMM are shifted towards lower wave number regions indicating coordination of the imine-N with the metal ions.23



Fig. 1 FT-IR spectra of mesoporous silica MS (a), heterogenized Schiff-base ligand I (b), Cu-AMM (c) and Ni-AMM (d).

UV-vis spectroscopy

UV-vis diffuse reflectance spectra of Cu-AMM and Ni-AMM are shown in Fig. 2 (UP). Both the materials showed broad bands in the region of 210–290 nm. These bands could be attributed to $\pi \rightarrow \pi^*$ transitions of the ligand. Cu-AMM showed a broad absorption band ranging from 360–470 nm, with a maximum at *ca.* 385 nm. This band could appear due to ligand to metal charge transfer (LMCT). The weak broad band in the range of 670–740 nm could arise due to d–d transition in metal center (shown in the inset of Fig. 2 (UP)). Cu(II) complexes immobilized onto mesoporous silica with a similar coordination environment showed an identical spectral behavior.¹⁵ Ni-AMM showed a ligand to metal charge transfer band in the region of 430–480 nm.²² In addition to that, it showed a broad band due to d–d transition



Fig. 2 UP: UV-vis diffuse reflectance spectra of Cu-AMM (a) and Ni-AMM (b). Inset: UV-vis diffuse reflectance spectra of Cu-AMM (a') and Ni-AMM (b') from 600–800 nm. Down: Solution phase UV-vis spectra of Cu-DFP/3-APTES (a) and Ni-DFP/3-APTES Schiff-base (b) taken in methanol.

in the region of 700–770 nm. This implies that copper(II) and nickel(II) ions have been successfully coordinated to the donor atoms of the heterogenized Schiff-base ligands. In Fig. 2 (down) we have shown the solution phase UV-visible spectra of Cu and Ni complexes of DFP/3-APTES Schiff-bases in methanol. Cu-DFP/3-APTES Schiff-base showed bands at 264 and 388 nm due to $\pi \rightarrow \pi^*$ and LMCT transitions, respectively.²⁴ Whereas the d–d transition band of copper(II) appeared in the range of 640–750 nm. Ni-DFP/3-APTES Schiff-base, on the other hand, showed bands at 276 and 448 nm due to $\pi \rightarrow \pi^*$ and LMCT transitions and a broad band in the region 675–775 nm due to a d–d transition.²⁵ These spectral data support the fact that heterogenized metal catalysts also retain their LMCT and d–d transition bands and thus the presence of metal grafted Schiff-base ligand (I) in the anchored mesoporous materials.

Powder X-ray diffraction

The powder X-ray diffraction patterns for the mesoporous silica, Schiff-base ligand I and metal-anchored functionalized mesoporous materials, Cu-AMM and Ni-AMM, are shown in



Fig. 3 Small angle XRD patterns of mesoporous silica MS (a), heterogenized Schiff-base ligand I (b), Cu-AMM (c) and Ni-AMM (d).

Fig. 3. The mesoporous silica (Fig. 3a) shows three strong diffractions for (100), (110) and (200) planes and a weak one for the (210) plane of 2D-hexagonal mesophase,²⁶ indicating the formation of a highly ordered mesophase. The Schiff-base ligand I shows a similar diffraction pattern (Fig. 3b), which indicates that the 2D hexagonal ordering is retained after grafting with 3-APTES and functionalization with 4-methyl-2,6-diformylphenol. An overall decrease in intensity is observed, which could be attributed to the lowering of local order, such as variations in the wall thickness or reduction of scattering contrast between the channel wall of the silicate framework and the Schiff-base ligand present in I.²⁷ The same pattern is restored for Cu-AMM and Ni-AMM (Fig. 3c and d) but the intensity of the peaks are further reduced indicating a further decrease in the ordering. There is a small but gradual decrease in d-spacing from mesoporous silica to the catalysts. The d_{100} values calculated from the corresponding 2θ values in the XRD patterns for mesoporous silica, Schiff-base ligand I, Cu-AMM and Ni-AMM are 3.56, 3.53, 3.49 and 3.50 nm respectively. This gradual decrease of d-spacing could be attributed to the contraction of unit cells upon surface functionalization and further coordination of the Schiff-base and metal ions within the pores of I.

High resolution TEM

The high resolution transmission electron microscopy images of **MS**, heterogenized Schiff-base ligand **I**, Cu-AMM and Ni-AMM are shown in Fig. 4. It can be clearly seen that all the materials have a 2D-hexagonal arrangement of pores (different contrast than that of the pore walls). The hexagonal ordering of the pores are restored even after grafting the silica framework with 3-APTES and functionalization with 4-methyl-2,6-diformylphenol as well as for metal-bound complexes Cu-AMM and Ni-AMM. The selected-area electron diffraction pattern (SAED) shown in the inset of Fig. 4a, further confirms the hexagonal ordering of the mesopores in **MS**.

Nitrogen adsorption-desorption

Fig. 5 shows the N_2 adsorption–desorption isotherms of the mesoporous materials (MS), Schiff-base ligand I, Cu-AMM and Ni-AMM. These isotherms could be classified as type IV characteristic of mesoporous materials.^{26–28} The mesopores in MS,



Fig. 4 HRTEM images of mesoporous silica (MS) (a), heterogenized Schiff-base ligand I (b); Cu-AMM (c) and Ni-AMM (d). Selected area electron diffraction (SAED) pattern of MS is shown in the inset of (a).



Fig. 5 Nitrogen adsorption–desorption isotherms of mesoporous silica **MS** (a), heterogenized Schiff-base ligand **I** (b), Cu-AMM (c) and Ni-AMM (d). The values of the *Y*-axis for (b) and (c) are offset by +100 and +50 cc g^{-1} , respectively, for clarity.

Schiff base ligand I, Cu-AMM and Ni-AMM are uniform in size, which is indicated by the sharp increase in N_2 uptake for adsorption, observed at P/P_0 ca. 0.27–0.46. Pore size distributions (PSD) of these samples have been estimated by employing BJH (Barrett-Joyner-Halenda) method (Fig. 6). The PSD patterns suggest the peak pore diameter for mesoporous silica, I, Cu-AMM and Ni-AMM to be 3.15, 2.48, 1.98 and 1.95 nm respectively. These results are in good agreement with the pore diameter estimated from the respective TEM image analyses (Fig. 4). The BET (Brunauer-Emmett-Teller) surface area and pore volume of MS, I, Cu-AMM and Ni-AMM are 941 m² g⁻¹ and 0.62 cc g⁻¹; 274 $m^2 g^{-1}$ and 0.16 cc g^{-1} ; 169 $m^2 g^{-1}$ and 0.09 cc g^{-1} ; and 160 $m^2 g^{-1}$ and $0.08 \text{ cc } \text{g}^{-1}$, respectively. It is pertinent to mention here that a comparatively lower amount of 4-methyl-2,6-diformylphenol has been allowed to react with 3-APTES functionalized silica than diimine functionalized PMO material.²⁹ So it is expected that



Fig. 6 Pore size distribution of mesoporous silica **MS** (a), heterogenized Schiff-base ligand **I** (b), Cu-AMM (c) and Ni-AMM (d) determined by employing BJH method. The values of *Y*-axis of (a), (b) and (c) are offset by +0.024, +0.012 and +0.006 cc Å⁻¹ g⁻¹, respectively, for clarity.

less 4-methyl-2,6-diformylphenol will be incorporated into the material. However, unlike PMO most of the Schiff base sites are located at the surface, which can bind with active metal centers. From the above results it is clearly seen that surface area and pore volume gradually decrease with subsequent functionalization with 4-methyl-2,6-diformylphenol and complexation with metal ions. Such a drastic decrease in these parameters could be attributed to the loading of an organic moiety and metal binding, which might occupy the void space inside the mesopores. Thus we can conclude that the dialdehyde as well as the metal ions are grafted inside the mesopore cavity.

Solid state ¹³C MAS NMR studies

¹³C CP MAS NMR study provides useful information regarding the presence of organic moiety and its chemical environment (interaction of metal ions with the donor sites) in the hybrid frameworks. In Fig. 7 the ¹³C CP MAS NMR spectra for I, Cu-AMM and Ni-AMM are shown. The spectrum for the metal-free heterogeneous Schiff-base ligand containing mesoporous material I exhibits strong signals at 8.7, 19.2, 21.8, 28.8, 52.7, 117.3, 127.4 and 168.8 ppm, corresponding to different aliphatic and aromatic



Fig. 7 ¹³C CP MAS NMR of 2D-hexagonal mesoporous silica containing Schiff-base ligand I (a), Cu-AMM (b) and Ni-AMM (c).

carbon atoms present in I.29 This result indicates that the Schiffbase ligand is grafted in I. On the other hand, for Cu-AMM and Ni-AMM although all these ¹³C signals are present, little shifts in the signals are observed. Specially the signal at 168.8 is shifted downfield to 163.8 and the intensity for the signal at ca. 52.9 has been largely enhanced. These could be attributed to the covalent interaction of metal atoms (Cu and Ni) with the lone pair of electrons on the imine-N (corresponding signals coming from carbon atoms adjacent to these N atoms) present in the Schiff base ligand. Solution state ¹³C NMR chemical shifts of the DFP/3-APTES Schiff-base precursor used for the synthesis of diimine containing periodic mesoporous organosilica have been reported previously by our group.29 Comparison of the 13C NMR spectra of I in solid state with that reported data in solution shows that both of these materials have similar ¹³C chemical shifts. Only three small intensity peaks of the solution state ¹³C signals at 8.0, 133.3 and 159.5 ppm could not be resolved in these solid state MAS NMR for Cu-AMM and Ni-AMM due to weak signal intensity. Nevertheless, this result suggested that both have same carbon skeleton. Compound I as well as Cu-AMM and Ni-AMM are insoluble in common organic solvents, which makes it difficult to carry out ¹³C NMR in solution.

Catalytic reactions

The epoxidation reactions of cyclohexene, trans-stilbene, styrene, α -methyl styrene, cyclooctene and norbornene have been carried out heterogeneously with Cu-AMM and Ni-AMM as catalysts in the presence of tert-butyl hydroperoxide as the oxidant at 333 K. In all the cases, it has been found that the respective epoxide is the major product. The results of the catalytic activities of Cu-AMM and Ni-AMM are shown in Table 1. All the liquid phase oxidation reactions of the olefins have been performed using acetonitrile as the solvent. As seen in Table 1, the selectivity for the epoxides for all the substrates is quite high after a 24 h reaction time. It is quite usual in the case of liquid phase partial oxidation reaction of olefins that the epoxide formed undergoes hydrolysis in the presence of water, formed as a by-product from the oxidant in the reaction mixture, which facilitates the epoxide ring opening. Thus, after a few hours when the conversions reach their respective maxima, epoxide selectivity goes down gradually with increase in selectivity for the respective diols.³⁰ Among the substrates studied herein, cyclohexene shows the highest conversion of 93.4% with 90% selectivity towards the formation of its corresponding epoxide (cyclohexene oxide) in the presence of Cu-AMM. 2-Cyclohexen-1-ol and 2-cyclohexen-1-one are the other by-products formed during the reaction. For all the substrates, Cu-AMM behaves as a better catalyst compared to nickel bound catalyst, Ni-AMM (Table 1). Among all the catalytic transformations, Ni-AMM shows its lowest activity when trans-stilbene is used as the substrate. In the presence of Cu-AMM and Ni-AMM, transstilbene is converted to 89.5 and 75.2% respectively with high selectivity for epoxide. Epoxidation of styrene to styrene oxide is of particular interest from both scientific as well as commercial point of view. For epoxidation of styrene, the conversions are found to be 86.3 and 78.2% with excellent selectivity for epoxide formation in the presence of both Cu-AMM and Ni-AMM, respectively. Apart from epoxide, benzaldehyde has been detected as the minor product for these reactions. Our results for styrene epoxidation are

Table 1 Epoxidation of olefins over Cu-AMM and Ni-AMM^a

	Cu-AMM			Ni-AMM		
Alkenes	Conversion ^b	Selectivity	TOF	Conversion ^b	Selectivity	TOF
\bigcirc	93.4	90.0	88.0	84.2	89.5	60.0
	89.5	91.0	38.4	75.2	88.0	24.1
	86.3	95.0	64.2	78.2	90.0	44.1
	84.0	92.1	55.0	80.1	86.4	39.2
	92.2	93.1	65.4	83.8	92.0	44.8
	90.3	94.0	74.1	82.5	93.1	51.7

^{*a*} Solvent: CH₃CN; temperature: 333 K; oxidant: *tert*-butyl hydroperoxide peroxide; catalyst: Cu-AMM and Ni-AMM. ^{*b*} conversions were measured after 24 h of the reaction, average of at least three measurements (each reaction done at least three times under identical conditions). ^{*c*} TOF: turnover number = moles of substrate converted per mole of metal center per hour.

better or comparable to the earlier reports.^{10,31} For the epoxidation of α -methyl styrene, the conversions are *ca*. 84.0 and 80.1% with high selectivity for epoxide formation in the presence of Cu-AMM and Ni-AMM, respectively.

These catalysts can also effectively epoxidize relatively bulky cycloalkenes *viz*. cyclooctene and norbornene. *Exo*epoxynorbornane is the major product in the case of norbornene epoxidation. Norbornene is converted to 90.3 and 82.5% in the presence of Cu-AMM and Ni-AMM, respectively, with high selectivity. The conversion and selectivity over Cu- and Nigrafted functionalized mesoporous materials are better than the previously reported results on their respective metal oxides.³² Further, in our study, high turnover frequencies (TOFs) have been observed for all the substrates. This could be attributed to the higher surface area of our Cu-AMM and Ni-AMM catalysts. Thus we can conclude that our Cu(II) and Ni(II) Schiff-base complexes Downloaded by Western Kentucky University on 06/05/2013 20:19:38. Published on 11 October 2011 on http://pubs.rsc.org | doi:10.1039/C1DT10157A

Recycling test

We have studied the recycling efficiency of the catalysts *i.e.* whether the catalysts can be reused further for several cycles. To test the catalytic efficiency for further cycles and also to ensure whether any metal percolates out from the catalyst, one control experiment has been performed over the catalysts using cyclohexene as the substrate. Cyclohexene has been chosen as a representative case for recycling experiments since maximum conversion takes place for cyclohexene epoxidation when either Cu-AMM or Ni-AMM is used as the catalyst. After each reaction cycle the catalysts were recovered by filtration, washed thoroughly with acetonitrile and then treated with 0.1 M HCl solution in ethanol at 338 K for 8 h for regeneration and finally dried at 373 K for 2 h. The catalytic reactions have been carried out following the same experimental procedure as that with the original catalysts. The catalytic activities in five consecutive cycles for the epoxidation of cyclohexene in the presence of Cu-AMM and Ni-AMM have been plotted in Fig. 8. As seen from the Figure, the catalytic activity decreases marginally in the successive catalytic cycles. However, epoxide selectivity remains almost unaltered in these repetitive reactions, suggesting a high reusability of these Cu/Nigrafted functionalized mesoporous materials in liquid phase partial oxidation catalysis.



Fig. 8 Activity of Cu-AMM and Ni-AMM in the repeating cycles. Error bars are shown for each conversion.

Effect of different oxidants

Epoxidation reactions have been carried out using different oxidants like hydrogen peroxide,³⁴ *tert*-butyl hydroperoxide,³⁵ molecular oxygen,³⁶ sodium hypochlorite,³⁷ iodosylbenzene,³⁸ *etc.* The ability to oxidize styrene in the presence of different oxidants such as hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP) and sodium hypochlorite has been examined using Cu-AMM as the catalyst under identical reaction conditions. The results show 43%, 86% and 37% conversion of styrene using hydrogen peroxide, TBHP and sodium hypochlorite as the oxidants, respectively. The yield of the reactions has been measured after 24 h. It is clear from the results that TBHP serves as the best oxidant, where as other oxidants show distinctly low activity. Although hydrogen peroxide would have been the most desired oxidant from an environmental

point of view, TBHP has been chosen as the oxidant because of its better reactivity.

Leaching test

Any Cu or Ni species present in solution phase in the reaction mixture can also catalyze the epoxidation reaction of olefins. Thus it becomes very important to determine whether the catalyst actually functions in a heterogeneous manner or not. In order to determine that hot-filtration tests were performed in the epoxidation of cyclohexene over both the catalysts Cu-AMM and Ni-AMM. During the catalytic epoxidation reactions, the solid catalysts were separated from the reaction mixture under hot conditions through filtration after 4 h. The conversion of cyclohexene after 4 h is ca. 25%. Then the reaction was continued with the filtrate for another 4 h. However, the reaction mixture did not show any further improvement in the conversion of cyclohexene. On the other hand, the uninterrupted reactions in the presence of the catalysts proceeded as usual with further conversion of cyclohexene to its epoxide. Further, atomic absorption spectroscopy has been employed to detect/determine the amount of metal that leached out into the reaction mixture. It has been found that there is no detectable Cu/Ni in the reaction mixtures. This further suggested almost no leaching of metal ions takes place during the course of the reaction from these catalysts and the catalysts are heterogeneous in nature.

A blank reaction (control reaction) with cyclohexene, in the absence of any catalyst under similar experimental conditions has also been performed. A very poor conversion of cyclohexene (31%) together with epoxide selectivity *ca.* 29% was observed after 24 h of reaction. Apart from this, another blank reaction was performed in the presence of the Schiff base ligand I as the catalyst under identical conditions where the conversion of cyclohexene was *ca.* 35%. These results suggested the catalytic role played by Cu/Ni-grafted functionalized mesoporous materials in the epoxidation reactions of alkenes. The reactivity of these catalysts can be compared with the previous results obtained using other catalysts, which contain transition metals heterogenized over silica frameworks. The catalytic systems discussed in this article are more or less comparable with that of Mn-,³⁹ Mo-,⁴⁰ Ru-,⁴¹ and V-complexes.⁴²

Probable reaction pathways

Porous titanium silicates have been widely used as catalysts for the epoxidation of olefins using hydrogen peroxide as the oxidant. During the catalytic reactions, titanium hydroperoxo species is formed as the active intermediate.³⁰ Copper complexes have been used as catalysts for the epoxidation of olefins using TBHP or hydrogen peroxide in homogeneous media and in all the cases copper–hydroperoxo species have been detected in the reaction media.^{15,33} A similar pathway is expected to be functioning also in this case and accordingly a probable mechanism has been proposed in Scheme 2. The reaction may proceed *via* formation of a copper–peroxo species together with the formation of *tert*butanol, which is detected during the course of the reactions for all the reactants. When Ni-complexes are used as catalysts in the epoxidation reactions, the Ni–hydroperoxo species is the active intermediate in the presence of TBHP.¹⁴ Hence, a similar pathway



Scheme 2 Probable mechanism for the catalytic conversion using copper bound material (representative case).

is expected to be followed for the nickel grafted Ni-AMM sample in the liquid phase partial oxidation reactions.

Conclusions

We have synthesized two new catalytic systems Cu-AMM and Ni-AMM, based on functionalized mesoporous silica. The mesoporous silica surface is at first functionalized with 3-APTES. and then allowed to undergo a Schiff base condensation reaction with the dialdehyde, 4-methyl-2,6-diformylphenol. Active copper or nickel centers are immobilized through the reaction of the heterogenized ligand supported mesoporous silica with the salts of Cu(II) or Ni(II). The materials have been thoroughly characterized by FT-IR and UV-vis diffuse reflectance spectroscopy, XRD, TEM and N₂ adsorption-desorption studies and ¹³C CP MAS NMR spectroscopy. Catalytic reactions carried out with Cu-AMM and Ni-AMM suggest that these materials are highly active catalysts towards the selective epoxidation of olefins like cyclohexene, transstilbene, styrene, α -methyl styrene, cyclooctene and norbornene in the presence of tert-butyl hydroperoxide oxidant under mild liquid phase reaction conditions.

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