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Organic-Inorganic Hybrid Catalysts Containing New Schiff Base for Environment Friendly Cyclohexane Oxidation

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ABSTRACT

Organic and inorganic entities have been hybridized using 3-aminopropyltriethoxysilane (APTES) linker for the synthesis of three novel organic-inorganic hybrid catalysts (Cu(II), Co(II) and Ni(II). During the course of synthesis, the static inorganic moiety has been functionalized with versatile imine (C=N) groups. The prepared catalysts have been characterized by spectral techniques (EDS, FT-IR, DR UV-Vis., ^{29}Si CP MAS NMR, powder-XRD and ESR), thermal study (TG-DTG) and surface studies (SEM and AFM). The reported catalysts are significant due to their geometrical and dispersive surface properties. The synthesised catalysts were tested in the cyclohexane oxidation reactions using H_2O_2, to make the catalytic system as eco friendly one. Compared to the previously reported catalysts, the present catalysts have shown better cyclohexane conversion and selectivity, and they are also cost effective. Among the three catalysts studied, Cu(II) catalyst has exposed the maximum conversion efficiency (44%) with product selectivity of 29% cyclohexanol and 71% cyclohexanone. Owing to the combination of interesting structural properties, acceptable catalytic property with better selectivity and environment benign character in low cost, these hybrid catalysts would be the best bet to future catalysts for cyclohexane oxidation.

Keywords: Schiff base; organic-inorganic hybrid; heterogeneous catalysis; cyclohexane; AFM

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Introduction

Schiff bases formed by the reaction of primary amines with aldehydes/ketones display borderline character amid hard and soft Lewis bases, also exhibit stability under diverse conditions[1, 2]. In coordination chemistry, the role of Schiff bases as ligands is remarkable and widespread[3-5]. The fascinating fact is that the formation of Schiff base complexes with metal ions enlarges the applications of Schiff bases, predominantly as catalysts for many reactions such as oxidation, cyclo-propanation, polymerization, coupling, hydrogenation, etc[6-9]. Many Schiff base complexes are a typical class of homogeneous catalysts. But often homogenous catalysts are not environment friendly, owing to the troubles tied with them such as difficulties in catalyst recovery and product separation. Consequently, it is essential to find the new and effective route to eliminate these problems related with homogeneous catalysts. The best way to overcome aforementioned problems is by providing a solid support for the homogeneous complexes[10, 11]. Though many supports like alumina[12], synthetic and biopolymers[13, 14], zeolite and montmorillonite clay[15] have been attempted to make the immobilized Schiff base metal complexes, SiO_2 has been emerged as the preeminent and familiar solid support because of its high surface area, good accessibility, good mechanical and thermal stability; and flexible surface silanol groups[16]. SiO_2 containing Schiff base complexes are also termed as distinctive organic-inorganic hybrid catalysts where inorganic moiety is static and organic entity is flexible. Such hybrid catalysts are very exceptional due to their mixed properties of both homogeneous (mobile reactive centre) and heterogeneous catalysts (catalytic recovery and recyclability). 3-aminopropyltriethoxysilane (APTES) is the extensively employed chemical agent to embed the organic entity on to inorganic SiO_2 support *via* the functionalization of surface hydroxyl groups of SiO_2 gel. The entry of amino groups onto the surface of SiO_2 gel can offer opportunity to install range of functional groups, often imine groups, on SiO_2 gel's surface[17-19].

Oxidation of cyclohexane to cyclohexanol and cyclohexanone through inert C-H bond activation is the most desired organic transformation, since it's products are applied as intermediates for the synthesis of commercially essential products such as nylon-6 and nylon-6,6'. Cyclohexanol and cyclohexanone are also functioned as solvents for lacquers, shellacs and varnishes; stabilizers and homogenizers for soaps and emulsions; and starting materials for manufacturing insecticides, herbicides and pharmaceuticals[20-22]. In industries, the current cyclohexane oxidation process in the presence of homogeneous boric cobalt salts engages high temperature (150-170 °C) and pressure (115-175 psi) and ends up with only 4% conversion and poor product selectivity ratio (cyclohexanone/cyclohexanol). This industrial process is risky and environmentally hazardous reaction too[22-24]. These issues eventually drive different research groups to search the novel catalysts for the oxidation of cyclohexane under milder conditions. In quest of environment friendly oxidant, H_2O_2 and molecular O_2 seem to be the finest oxidants because they leave water as by-product. Conversely, high activation energies are required to break O-O double bond of molecular O_2 towards the addition with organic substrate and the spin mismatch between ground state of O_2 (triplet) and organic substrate (singlet) suppress the use of O_2 as oxidant and O_2 involving organic reactions may also cause explosions[25, 26]. Therefore H_2O_2 would be the better oxidant than molecular O_2.

In search of an improved catalytic system for cyclohexane oxidation in presence of H_2O_2, variety of heterogeneous catalysts has been investigated. A few cases are Co(II) and Cr(VI) on poly(4-vinylpyridine-co-divinylbenzene) (4.64% conversion)[27]; scorpionate Fe(III) complex on carbon materials (20.8% conversion)[28] and desilicated MOR zeolite (37.2% conversion)[29] in presence of co-catalyst and co-oxidant; Au nanoparticles on carbon materials (3.6% conversion)[30]; and chitosan supported Co(II) catalyst (26% conversion even after electron beam irradiation)[31]. Yet relatively superior cyclohexane conversion has been observed with SiO_2 supported catalysts. For instance, though Urus et al have achieved 99.9% cyclohexane conversion under microwave reaction conditions, the poor selectivity spoils the hope[32]. Alternatively the catalysts involving mesoporous SiO_2 supports such as MCM-41 (45.5% conversion with 51.9% cyclohexanol and 48.1% cyclohexanone selectivity)[33] and SBA-15 (71.1% conversion with 26% cyclohexanol and 74% cyclohexanone selectivity)[34] have shown sufficient cyclohexane conversion and better selectivity too. But tedious procedures, practising more chemicals and relatively high cost are necessitated in synthesis of mesoporous SiO_2 materials. These limitations may suppress the effective use of SiO_2 supported catalysts in cyclohexane oxidation. Thus, it seems very essential to synthesize simple, low cost and effectual SiO_2 supported catalysts for cyclohexane oxidation with enhanced selectivity. We have already reported a simple and low cost SiO_2 supported catalysts for adequate cyclohexane oxidation[35].

By considering the above facts and in the continuation of our work, we have attempted to establish a new catalytic system with adequate catalytic ability and selectivity under mild and environmentally tolerable conditions for cyclohexane oxidation. In this context, a novel SiO_2 supported Schiff base ligand and its Cu(II), Co(II) and Ni(II) complexes have been synthesized and their structural, thermal and morphological characterizations have also been studied. Very importantly, the reported complexes have been used as catalysts in cyclohexane oxidation using H_2O_2 as oxidant and the stability of catalysts has been assessed in the successive catalytic run.

Experimental methods

Materials

All the chemicals were of AnalaR grade and used without further purification. APTES and 1,2-diphenylethanedione (DPED) were obtained from Himedia. SiO_2 gel, cyclohexane, acetonitrile, toluene, H_2O_2 and metal salts were purchased from E-Merck, India.

Synthesis of SiO_2 supported APTES (Si-NH_2)

The synthesis protocol for installing APTES on to SiO_2 was adapted from the procedure reported earlier[32]. Typically, 50 g SiO_2 gel and 1:1 hydrochloric acid solution were mixed and refluxed for 6 h as the pre-treatment. This pre-treated SiO_2 gel was filtered off and rinsed with sufficient amount of deionized water till the pH of the filtrate reached 7. Then it was dried at 120 °C for 12 h under vacuum. In 100 ml toluene, a mixture of 20 g pre-treated SiO_2 gel and 20 ml APTES was mixed and refluxed for nearly 3 days. At last, ensuing suspension was filtered off, washed with excess amount of toluene, ethanol and diethyl ether and dried at 100 °C under vacuum.

Synthesis of SiO_2 supported Schiff base (Si-NH_2-DPED)

A mixture of 5 g SiO_2-NH_2 and 5 mmol DPED was stirred in 100 ml water at 60 °C for 24 h. Subsequent solid product was filtered, washed with excess amount of water and dried at 100 °C.

Synthesis of organic-inorganic hybrids ([M(Si-NH_2-DPED)Cl_2])

2 g SiO_2-NH_2-DPED and 5 mmol metal chloride salt were mixed in 50 ml water. This mixture was then magnetically stirred at ambient temperature for 24 h. The final product was filtered, washed with excess amount of water and dried at 90 °C under vacuum.

Cyclohexane oxidation

Cyclohexane oxidation was carried out in a 25 ml flask equipped with magnetic stirrer using the following procedure. 0.05 g catalyst ([Cu(SiO_2-NH_2-DPED)Cl_2]/[Co(SiO_2-NH_2-DPED)Cl_2]/[Ni(SiO_2-NH_2-DPED)Cl_2]) was taken in 10 ml acetonitrile. Subsequently, 10 mmol of 30% H_2O_2 solution and 5 mmol of cyclohexane were added to the flask. This catalytic mixture was stirred at 70 °C under atmospheric pressure conditions for 12 h. Aliquots from the reaction mixture were taken at an interval of every 2 h up to 12 h for product analysis. By keeping the same reaction procedure, two separate blank catalytic experiments were also run, one without catalyst and another without oxidant. The product samples were assessed using Hewlett–Packard gas chromatograph (HP 6890) annexed with FID detector, a capillary column (HP-5), programmed oven with temperature range from 50 to 200 °C plying nitrogen as a carrier gas with 0.5 cm^3 min^{-1} flow rate.

Instruments

FT-IR spectra of the compounds were recorded on a Jasco FT-IR 4100 spectrophotometer in 4000-400 cm^{-1} wave number region with 2 cm^{-1} resolution using KBr disks having 1% sample. DR UV-Vis. spectra were computed within 200-800 nm wavelength range on a Shimadzu UV-2600 double beam spectrophotometer containing an integrating sphere attachment for solid samples. The solid-state ^{29}Si cross polarized magic angle spinning nuclear magnetic resonance (^{29}Si CP MAS NMR) spectral studies were performed for Si-NH$_2$-DPED and [Cu(Si-NH$_2$-DPED]Cl$_2$] by Mercury Plus 300 MHz NMR spectrometer (VARIAN, USA) annexed with a 5 mm dual broad band probe. Thermal properties of compounds were investigated up to 800 °C at a heating rate of 10 °C min^{-1} under dynamic nitrogen atmosphere using Mettler Toledo star system. Powder X-ray diffraction (powder XRD) measurements were accomplished with an X-ray diffractometer ((XPERT PRO PANalytical, Netherland)) for phase identification. The powder XRD patterns were obtained using CuKα radiation with a secondary monochromator (λ= 0.1540 nm) at 40 kV and 30 mA. X-band electron spin resonance (ESR) experiment of Cu(II) complex was performed on a JES-FA200 ESR spectrometer (JEOL, Japan) at 9.65 GHz micro wave frequency. Surface morphology of the compounds was assessed using a scanning electron microscope of JSM-SEM 6400 model at 15 kV accelerating voltage with 2 kX magnification range under liquid N$_2$ atmosphere. Atomic force microscopic (AFM) study of [Cu(SiO$_2$-NH$_2$-DPED)Cl$_2$] was performed on AFM XE 70, park systems to analyse the particle distribution.

Results and discussion

Characterization of hybrid catalysts

The presence of expected elements in each synthesized compound of this study has been identified and confirmed by their energy peaks. The EDS spectra of all the reported compounds are provided (see Supporting Information). The occurrence of metal ion peaks in respective EDS spectrum suggests the successful formation of organic-inorganic hybrid catalysts.

Vibrational spectroscopy is the best scientific tool to probe changes in SiO_2 during the chemical modifications. Figure 1 shows representative FT-IR spectra of SiO_2 gel, Si-NH_2, Si-NH_2-DPED and the catalysts. In FT-IR spectrum of pure SiO_2 gel (Figure 1(a)), the bands observed at 1094 and 798 cm^{-1} are attributed to the characteristic anti-symmetric and symmetric stretches of Si-O-Si bond, respectively. The band at 462 cm^{-1} could be due to the bending vibrations of O-Si-O units. A small shoulder at 978 cm^{-1} is allocated to Si-OH stretching mode. The significant stretch of surface silanol groups (Si-O-H) is found at 3548 cm^{-1} as a broad band[36]. All these characteristic bands are also present in the FT-IR spectra of all modified forms of SiO_2, which indicates that SiO_2 framework is not affected even after chemical modifications. In Figure 1(b), a new continuous band, attribute of –NH_2 stretch, has emerged in the region of 3290-3000 cm^{-1} confirming the aminopropylation of SiO_2. It is further supported by the occurrence of stretching and bending vibrations of aliphatic –CH_2 groups at 2938 and 1495 cm^{-1}, respectively. The –OH stretch of silanol has been shifted to lower wave number region which implies the grafting of APTES on to surface silanol groups[37]. In Figure 1(c), characteristic band of –NH_2 groups are found to be disappeared. It can be assigned to the reaction between Si-NH_2 and DPED. The new band at 1629 cm^{-1}, the distinctive stretch of –C=N group, further confirms the reaction between Si-NH_2 and DPED. It is also evidenced by significant aromatic -C=C- stretch which emerges at 1474 cm^{-1} as a medium band. Apart from these, an additional band is found at 1720 cm^{-1} and suggests that one of the –C=O groups of DPED could not undergo Schiff base reaction. FT-IR spectra of all complexes resemble with that of Si-NH_2-DPED but with few changes. Considerably, such changes are the shifts in stretching vibrations of –C=N and –C=O to lower wave number. This proves the coordination of –C=N and –C=O groups with metal ions[38-40]. But the significant M-O and M-N bonds have not perceived in FT-IR spectra of complexes because they may be hidden by bending vibrations of O-Si-O units.

The electronic absorption spectra of Si-NH_2-DPED and its complexes are depicted in Figure 2. The UV-Vis. spectra of SiO_2 gel and Si-NH_2 are also provided individually (Supporting Information). Unlike SiO_2, UV-Vis. pattern of Si-NH_2 shows a significant band below 400 nm which may be due to the characteristic n-π^* transition of non-bonded electrons of –NH_2 groups. The electronic spectrum of the Schiff base, formed by the reaction between SiO_2-NH_2 and DPED (Fig 2(a)), exhibits an additional band below 400 nm, which can be allotted to π-π^* transition of aromatic π-electrons. Emergence of this extra band apparently confirms the formation of the Schiff base, Si-NH_2-DPED. But the n-π* transition band is due to the existence of non-bonded electrons of C=N and C=O groups, and not of NH_2 groups. Further, UV-Vis. spectra of complexes display characteristic n-π^* and π-π^* transitions bands below 400 nm, but they slightly differ either in their position or intensity, which may be due to the coordination of metal with Si-NH_2-DPED. The charge transfer transition (metal to ligand π-back bonding) may also contribute to these absorption bands (below 450 nm) observed in the electronic spectra of metal complexes. Besides, a new band is appeared in the UV-Vis. spectra of all the complexes which can be the characteristic of d-d transition of the central metal ions. This band is very significant as it proclaims the information about geometry of metal complexes. In Figure 2(b), [Cu(Si-NH_2-DPED)Cl_2] shows its d-d transition band at around 600 nm which is a sign of $^2B_{1g}\rightarrow{}^2A_{1g}$ transition, characteristic of square planar geometry. In the UV-Vis. spectra of [Co(Si-NH_2-DPED)Cl_2] (Figure 2(c)) and [Ni(Si-NH_2-DPED)Cl_2] (Figure 2(d)), this band is observed at 600 and 460 nm, respectively due to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition which implies square planar geometry to the complexes[41-43].

^{29}Si CP MAS NMR spectroscopy has been successfully employed in the characterization of SiO_2 based materials by studying silicon environment in the materials. Normally two characteristic peaks are expected for the unmodified SiO_2 gel at ~110 and ~105 ppm which are the evidences of $((SiO)_4Si)$ sites and $((SiO)_3SiOH)$ silanol sites, respectively. The abundance of $((SiO)_4Si)$ sites in SiO_2 gel would make the peak at 110 ppm predominant[44]. ^{29}Si NMR spectra of Si-NH_2-DPED and its Cu(II) complex are separately shown (Supporting Information). The two expected characteristic peaks of SiO_2 gel are observed in ^{29}Si NMR spectra of both Si-NH_2-DPED and its Cu(II) complex. But intensity of the peak at 105 ppm (characteristic of $(((SiO)_3SiOH))$ sites) seems to be very low which may support the successful modification of surface –OH groups with organic functional groups[45]. A new significant peak noted at ~65 ppm in the ^{29}Si NMR spectrum of Si-NH_2-DPED can be due to the formation of $((SiO)_3SiC)$ sites as the consequence of organic modification of surface –OH groups[46-48]. This peak is also found in ^{29}Si NMR spectrum of Cu(II) complex but with some changes in intensity and peak area. These changes may be ascribed to the coordination of Si-NH_2-DPED with Cu(II). Thus, the ^{29}Si NMR spectral data support the results obtained from FT-IR and UV-Vis. spectral studies.

Powder XRD patterns of all compounds were taken in wide angle region (between 10° and 80° 2θ region). The XRD patterns of SiO_2, Si-NH_2, Si-NH_2-DPED and complexes are presented in Figure 3. SiO_2 exhibits a broad band centered at $2\theta=22°$, characteristic of topological structure of SiO_2[49]. After modification with APTES and DPED, this peak is found to have lost its intensity and sharpness. This may be due to the slight disorder in topological structure of SiO_2 in its modified forms as the result of immobilization of DPED and entry of metal ions on to the porous wall of SiO_2 or reduction in X-ray scattering contrast between the channel wall of silicate frame work and ligand/complex[16, 50]. Few new intense peaks have also appeared in XRD pattern of Si-NH_2-DPED and significantly these new peaks seem to be analogous with characteristic peaks of DPED. This further supports the organo-functionalization of Si-NH_2 with DPED. Co(II) and Ni(II) complexes show similar XRD pattern like Si-NH_2-DPED while Cu(II) complex does not. It may be due to the higher crystallinity of Cu(II) complex compared to the other two.

ESR spectroscopy has been established as the most excellent technique to explore the geometry of metal complexes, especially Cu(II) complexes[51-53]. In this present study, ESR spectral study of Cu(II) complex was performed. The recorded ESR spectrum of Cu(II) complex is shown in Figure 4. It reveals two *g* factors such as $g_{\|}$ and $g_{\perp}$. The obtained spectrum shows evidence for the axial nature of Cu(II) complex. After comparison, the calculated *g* factors are found to have the order of $g_{\|}$ (2.223) > $g_{\perp}$ (2.094) > 2.0023 and it proposes the presence of unpaired electron in d_{x^2}-d_{y^2} orbital. From this scrutiny, the suggested geometry is square planar, agreeing with the result obtained from UV-Vis. spectroscopy[54]. The lesser value of $g_{\|}$ as compared to 2.3 is being the good support for covalent character of Cu-ligand interaction as recommended by Kivelson and Niemon[55].

The following expression can be employed to compute the exchange coupling factor (G):

$G = (g_{\|}-2) / (g_{\perp}-2)$

It has been already proved that parallely aligned or slightly misaligned local axes have G value greater than 4.0, whereas, the G value will be less than 4.0 for remarkably misaligned local axes with considerable exchange coupling. In this case, G value of Cu(II) complex is 4.9 and so the exchange coupling could be only negligible[56, 57].

The TG-DTG patterns of SiO_2, Si-NH_2, Si-NH_2-DPED and the complexes are illustrated in Figure 5 and in specific, TG-DTG curves of SiO_2 and Si-NH_2 are provided separately (see Supporting Information). TG-DTG pattern of SiO_2 gel exhibits two decomposition peaks corresponding to the loss of physically adsorbed water molecules (0-100 °C, 2.94%) and dehydroxylation of surface silanol groups (370-800 °C, 1.4%). Though Si-NH_2 shows two similar decomposition peaks, the second one is higher (345-645 °C, 5.67%), and this may be due to the decay of APTES entity. TG-DTG curves (Figure 6(a)) of Si-NH_2-DPED reveals different outline compared to that of both SiO_2 and Si-NH_2. There is no loss of physically adsorbed water molecules. However, two thermal decays are found. They are attributed to the loss of DPED moiety (100-355 °C, 22.90%) and loss of APTES and dehydroxylation of surface silanols (355-655 °C, 16.52%). The massive weight loss between 100-355 °C clearly mentions the loading of organic entity (DPED) onto Si-NH_2. TG-DTG models of all complexes are found to be akin to each other and disclose three mass loss steps. The initial step can be assigned to desorption of physically adsorbed water molecules, second step is due to loss of DPED and third step may collectively due to the removal of APTES and dehydroxylation of surface silanols. Apart from this similarity, Cu(II) complex alone shows weight gain above 580 °C which may be due to the oxidation reaction and this behaviour can be assigned to crystalline character of Cu(II) complex.

Changes in surface properties of SiO_2 gel upon series of chemical modifications have been examined by SEM analysis. SEM images of SiO_2 and Si-NH_2 are displayed in Supporting Information data file while that of Si-NH_2-DPED and its complexes are collectively portrayed in Figure 6. SEM photograph of SiO_2 gel exposes the lumpy shaped apparent surface. It is evident that the particle size of the modified forms is smaller than that of the unmodified SiO_2 gel. Hence it is apparent that the modification of SiO_2 with APTES, DPED and metal ions can provide more efficient catalysts. Further, chemical modifications of SiO_2 with functional groups generally assist and enhance the adsorption of metal ions[58, 59]. Due to the availability of functional groups, metal ions can be adsorbed on SiO_2's surface through coordination reaction. Such coordination of SiO_2's functional groups would enhance the life span of metal ions on the surface of SiO_2. Consequently, this may increase the stability of the complexes in the successive catalytic run. Surface of complexes is rougher than that of Si-NH_2-DPED as the consequence of metal ions' presence. All the complexes, explore well-dispersed metal ions which means that adsorbed particles are not agglomerated. This surface behaviour of organic-inorganic hybrids would help to achieve better catalytic ability.

2D and 3D AFM images of [Cu(Si-NH_2-DPED)Cl_2] are given in Figure 7 to ascertain the particles' dispersion and distribution. They signify that particles are beautifully arranged and dispersed. The particles look like cones. They are not agglomerated and support the surface information obtained from SEM images.

Catalytic study

Catalytic activities of reported catalysts ([Cu(Si-NH_2-DPED)Cl_2]/ [Co(Si-NH_2-DPED)Cl_2]/ [Ni(Si-NH_2-DPED)Cl_2]) were investigated by carrying out the model catalysis reaction where cyclohexane was oxidized into cyclohexanol and cyclohexanone in presence of H_2O_2. Such model reaction catalysed by organic-inorganic hybrid catalysts with H_2O_2 is promising and desirable owing to its industrial importance and environment friendly character. The product analysis was performed by gas chromatograph technique. During product analysis, there was no cyclohexane conversion identified either in the absence of catalyst or oxidant. This points the significance of catalyst and H_2O_2 in cyclohexane oxidation. Like catalyst, role of solvents in catalysis has been also found crucial because of their ability to convert different phases into uniform and thus upholding mass transportation. Significance of solvents also includes their ability to change the reaction mechanism by disturbing reaction intermediates and amend the surface properties of catalysts and reaction path-ways[60]. In literature, acetonitrile has been established as vastly used and effective solvent[31, 34, 61]. Hence, in our present study, all catalytic runs were executed in acetonitrile. In all experiments, the observed products were only cyclohexanone and cyclohexanol. No white precipitate was observed upon cooling the product mixture and the absence of acid in the product mixture was confirmed by titrating against NaOH. These results clearly demonstrated the absence of adipic acid in product mixture.

i) Influence of temperature on catalytic study

Initially, cyclohexane oxidation by H_2O_2 was tried at room temperature which resulted in very poor cyclohexane conversion. Perhaps this may be due to the inertness and strength of saturated C-H bonds available in cyclohexane. To overcome these barriers, temperature inside the catalytic system was increased by 10 °C up to 70 °C, to ascertain the optimum temperature for the reaction. The cyclohexane conversion increased steadily up to 60 °C, and a drastic increase was observed when the temperature was set at 70 °C. This temperature is closer to the boiling point of cyclohexane (80 °C), and hence further increase of temperature beyond 70 °C could not cause any effective change in cyclohexane conversion. Consequently, 70 °C was set as the optimum temperature to supply sufficient energy to overcome the energy barrier associated with cyclohexane conversion. This examination was attempted with all catalysts and obtained results are illustrated in Figure 8.

ii) Influence of time on cyclohexane conversion

Catalytic efficacy of all the organic-inorganic hybrid catalysts was monitored independently for 12 h at 70 °C. The impact of reaction time on catalytic activity of catalysts was studied by analyzing the aliquots taken from the catalytic reaction mixture at the time interval of every 2 h. The results of this time-dependant catalytic study are given in Table (see Supporting Information). From the table, it is very clear that cyclohexane conversion rapidly increased up to 8 h. However, after 8 h, the rate of increase in the cyclohexane conversion was slower, and no further increase was noticed after 12 h. The selectivity of products at every 2 h was calculated. Initially, cyclohexanol was found to be the major product. But cyclohexanone % was found to increase with the increase of time. The percentage of cyclohexanol and cyclohexanone obtained at various time intervals are portrayed in Figure 9. It is evidently seen that cyclohexane was oxidized first into cyclohexanol and is subsequently oxidized into cyclohexanone. Hence, if cyclohexanol is the desired product, then the reaction can be stopped by 6 h, and if cyclohexanone formation is preferred, the time of the reaction may be extended up to 12 h.

Among the three catalysts, [Cu(Si-NH_2-DPED)Cl_2] was found to show higher catalytic efficacy compared to the other two. The cyclohexane conversion efficiencies of [Cu(Si-NH_2-DPED)Cl_2], [Co(Si-NH_2-DPED)Cl_2] and [Ni(Si-NH2-DPED)Cl_2] were 44, 38 and 35%, respectively at 70 °C for 12 h (see Table S1 in Supporting Information). From Figure 9, we can conclude that [Cu(Si-NH_2-DPED)Cl_2] would be the better choice for the formation of cyclohexanol and [Ni(Si-NH_2-DPED)Cl_2] can be preferred for cyclohexanone. This study shows that better cyclohexanol selectivity by [Cu(Si-NH_2-DPED)Cl_2] can be achieved only below 6 h of reaction. This problem can be possibly eliminated by removing cyclohexanol concurrently from catalytic reaction mixture. The variation in product selectivity may depend on the surface morphology of the catalysts.

iii) Catalytic recyclability

One of the main interesting characters of SiO_2 based organic-inorganic hybrid catalysts is their reusability in successive catalytic experiments. [Cu(Si-NH_2-DPED)Cl_2] was opted as model hybrid catalyst for investigating catalytic reusability since it exhibited higher activity than other two catalysts. Before carrying out the next catalytic run, the opted catalyst was separated from the reaction mixture and washed with ethanol and ether. The stability of [Cu(Si-NH_2-DPED)Cl_2] was studied by performing five consecutive catalytic experiments without changing other reaction conditions. As revealed in Figure 10, the catalytic efficiency of [Cu(Si-NH_2-DPED)Cl_2] remains nearly the same. In detail, [Cu(Si-NH_2-DPED)Cl_2] exposed 44% cyclohexane conversion in first catalytic run and 40% conversion in fifth catalytic run. Only 4% of its cyclohexane conversion efficiency was dropped. It clearly signifies the advantage of the reported heterogeneous organic-inorganic hybrid catalysts. This catalytic reusability study further suggests that Cu(II) ions are not leached out from [Cu(Si-NH_2-DPED)Cl_2]. FT-IR spectrum of used catalyst was also recorded and compared with fresh catalyst. They were well comparable and no notable differences were observed.

We have already reported the similar kind of catalysts for cyclohexane oxidation but there support was chitosan, not SiO_2. Our current study suggests that the SiO_2 based organic-inorganic hybrid catalysts are more effective than the chitosan based catalysts for the oxidation of cyclohexane[62]. The reason may be the well dispersive character of SiO_2 based catalysts than their chitosan supported analogues. These SiO_2 supported catalysts were also appeared as good reusable catalysts than corresponding chitosan supported catalysts.

Like the blank catalytic experiments without oxidant and catalyst, two other experiments were accomplished with the motive to check the catalytic activity of SiO_2 gel and Si-NH_2-DPED under identical conditions and no cyclohexane conversion was detected. It proves the inability of SiO_2 and Si-NH_2-DPED to oxidize cyclohexane. To study the mechanism of cyclohexane oxidation, UV-Vis. spectroscopy has been involved. For this mechanistic study, the mixture of H_2O_2, nitric acid and catalyst in acetonitrile has been prepared and its electronic spectrum has been recorded. A shoulder peak has been identified between 410-420 nm in the UV-Vis. spectra of all the complexes. This can be the attribute of metal-peroxo species[63] and it further suggests that here cyclohexane oxidation has followed the peroxidative mechanism as given in the supplementary data.

Conclusions

Three organic-inorganic hybrid catalysts (Cu(II), Co(II) and Ni(II) complexes) were synthesized by embedding imine (C=N) functional groups on to SiO_2 gel surface with the help of APTES linker. The studied hybrid catalysts were characterized by spectral, thermal and surface analytical techniques. The catalytic activities of catalysts were studied in generic, facile and mild cyclohexane oxidation with H_2O_2 oxidant in an eco-friendly approach. The salient features of the study have been that all the catalysts exposed adequate catalytic activity as well as good selectivity in the reasonable temperature and atmospheric pressure. Importantly, except cyclohexanone and cyclohexanol (KA oil), no other products were obtained at the end of the cyclohexane oxidation. Upon increasing the reaction time, cyclohexanone % was found to be increased while the cyclohexanol % was decreased. It is found that the cyclohexane is first oxidised to cyclohexanol which is subsequently to cyclohexanone. Therefore by lengthening reaction time, our present catalytic system would become more selective. Cu(II) hybrid catalyst exhibited superior catalytic efficiency than the Co(II) and Ni(II) catalysts. The reusability study confirmed the stability of organic-inorganic hybrid catalysts inside the catalytic reactions and thereby our catalysts can be used in repeated catalytic run without any major drop in their catalytic efficacy. With the merits of H_2O_2 oxidant, better product selectivity, dispersive nature and reusability of catalysts, the present hybrid catalysts for cyclohexane oxidation would be effective and prominent for future catalysis. Currently, the electron beam impact on structural and catalytic properties of these organic-inorganic hybrid catalysts is under way in our laboratory.

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Figure Captions

Figure 1. FT-IR spectra of (a) SiO_2 gel, (b) Si-NH_2, (c) Si-NH_2-DPED, (d) [Cu(Si-NH_2-DPED)Cl_2], (e) [Co(Si-NH_2-DPED)Cl_2] and (f) [Ni(Si-NH_2-DPED)Cl_2].

Figure 2. DR UV-Vis. spectra (a) Si-NH_2-DPED, (b) [Cu(Si-NH_2-DPED)Cl_2], (c) [Co(Si-NH_2-DPED)Cl_2] and (d) [Ni(Si-NH_2-DPED)Cl_2].

Figure 3. Powder XRD patterns of (a) SiO_2 gel, (b) Si-NH_2, (c) Si-NH_2-DPED, (d) [Cu(Si-NH_2-DPED)Cl_2], (e) [Co(Si-NH_2-DPED)Cl_2] and (f) [Ni(Si-NH_2-DPED)Cl_2].

Figure 4. X-band ESR spectrum [Cu(Si-NH_2-DPED)Cl_2].

Figure 5. TG-DTG patterns of (a) Si-NH_2-DPED, (b) [Cu(Si-NH_2-DPED)Cl_2], (c) [Co(Si-NH_2-DPED)Cl_2] and (d) [Ni(Si-NH_2-DPED)Cl_2].

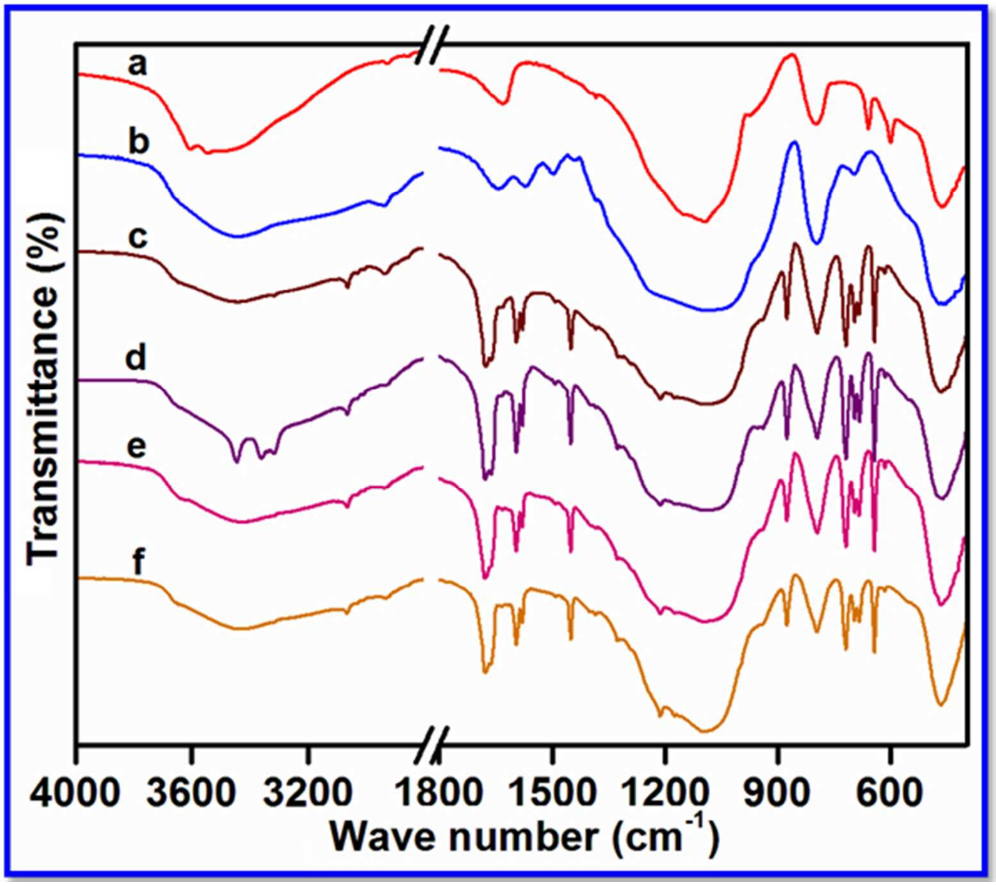
Figure 6. SEM images (a) Si-NH_2-DPED, (b) [Cu(Si-NH_2-DPED)Cl_2], (c) [Co(Si-NH_2-DPED)Cl_2] and (d) [Ni(Si-NH_2-DPED)Cl_2].

Figure 7. 2D (a) and 3D (b) AFM images (10X10 μm); 2D (c) and 3D (d) AFM images (2.5X2.5 μm) of [Cu(Si-NH_2-DPED)Cl_2].

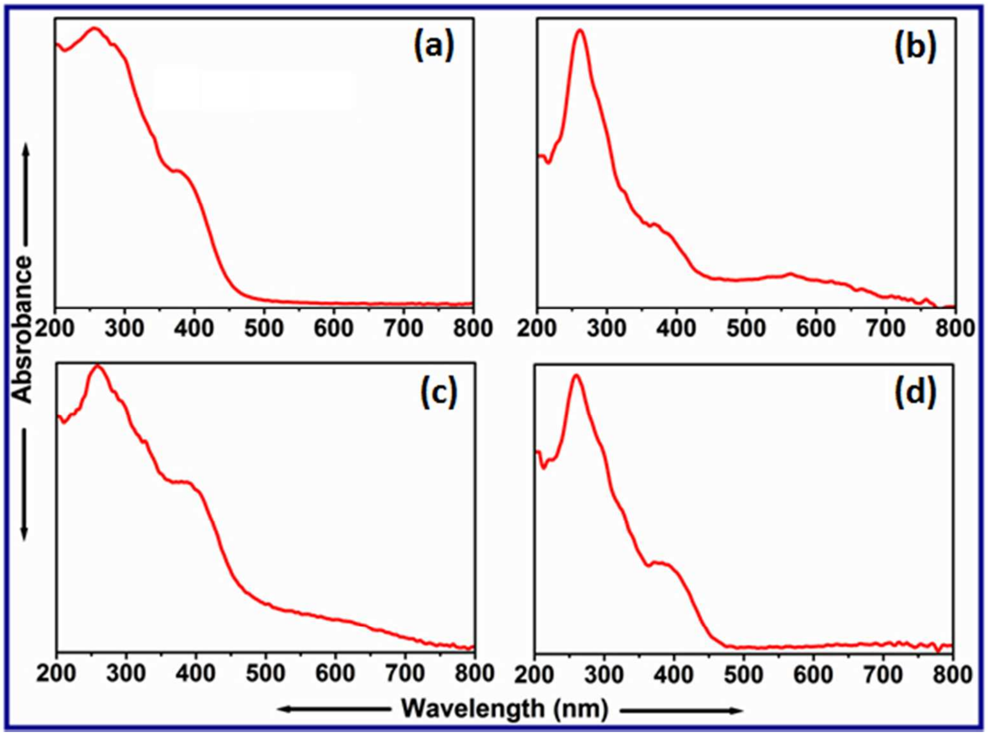
Figure 8. Effect of temperature on cyclohexane oxidation catalysed by Cu(II), Co(II) and Ni(II) hybrid catalysts.

Figure 9. Effect of time on selectivity of products obtained from cyclohexane oxidation catalysed by Cu(II), Co(II) and Ni(II) hybrid catalysts.

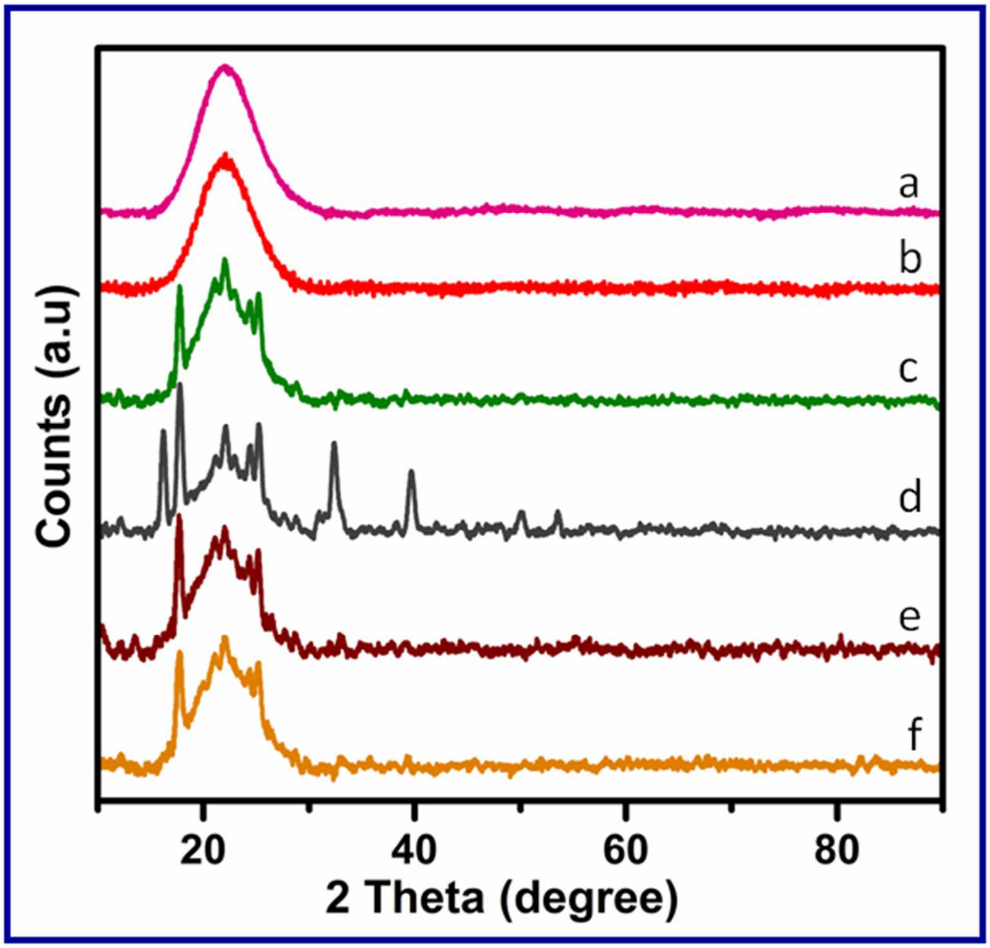
Figure 10. Catalytic Reusability of [Cu(Si-NH_2-DPED)Cl_2]. Reaction conditions: cyclohexane 5 mmol, 10 mmol 30% H_2O_2, 0.05 g catalyst, 10 ml CH_3CN, 70 °C and 12 h



FT-IR spectra of (a) SiO2 gel, (b) Si-NH2, (c) Si-NH2-DPED, (d) [Cu(Si-NH2-DPED)Cl2], (e) [Co(Si-NH2-DPED)Cl2] and (f) [Ni(Si-NH2-DPED)Cl2]
158x140mm (96 x 96 DPI)



DR UV-Vis. spectra (a) Si-NH2-DPED, (b) [Cu(Si-NH2-DPED)Cl2], (c) [Co(Si-NH2-DPED)Cl2] and (d) [Ni(Si-NH2-DPED)Cl2]
164x121mm (96 x 96 DPI)



Powder XRD patterns of (a) SiO2 gel, (b) Si-NH2, (c) Si-NH2-DPED, (d) [Cu(Si-NH2-DPED)Cl2], (e) [Co(Si-NH2-DPED)Cl2] and (f) [Ni(Si-NH2-DPED)Cl2]
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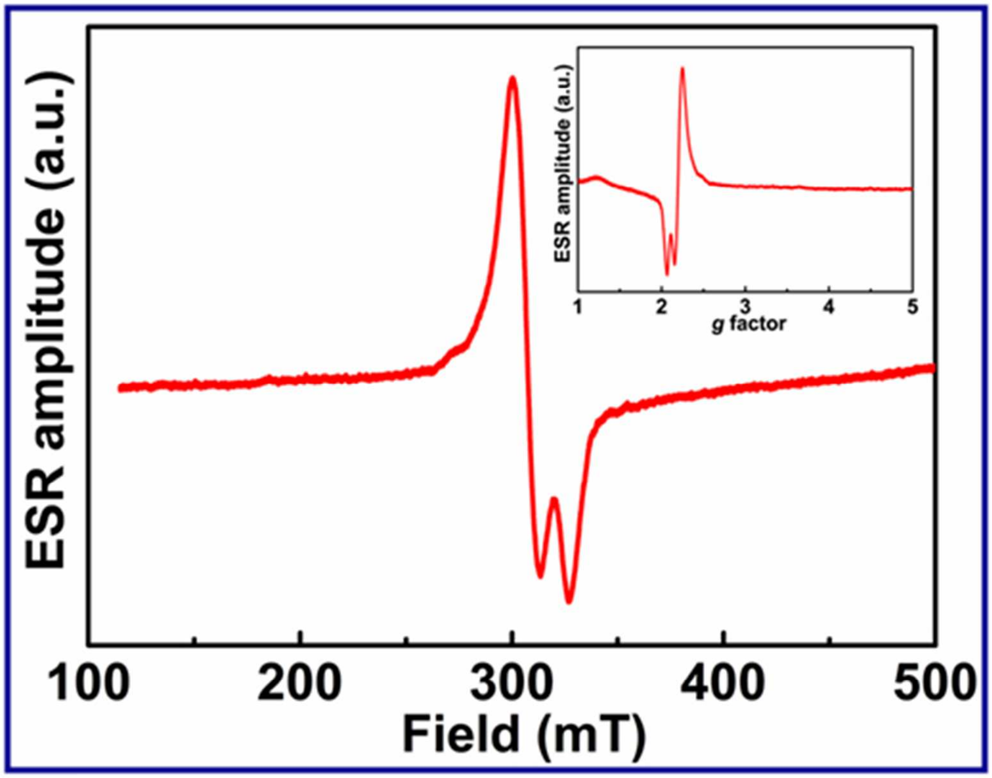
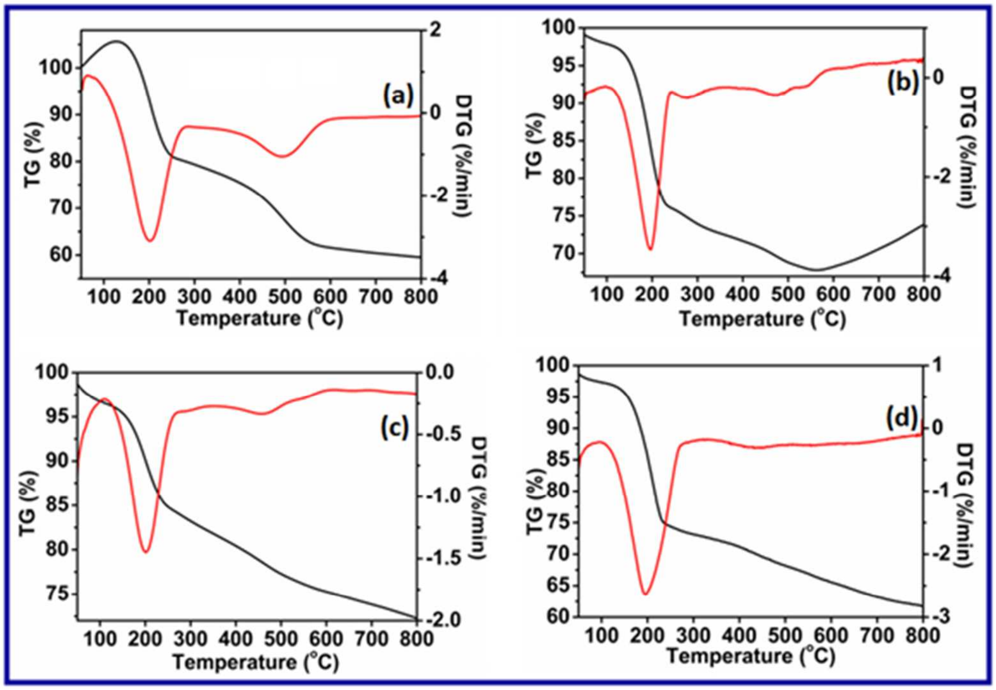
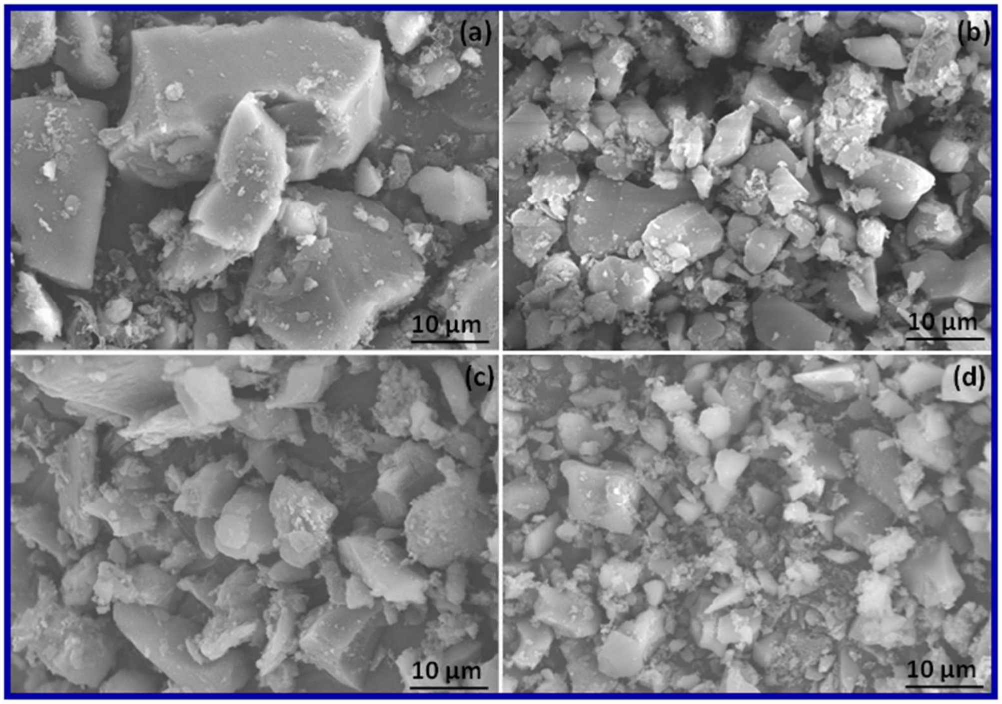


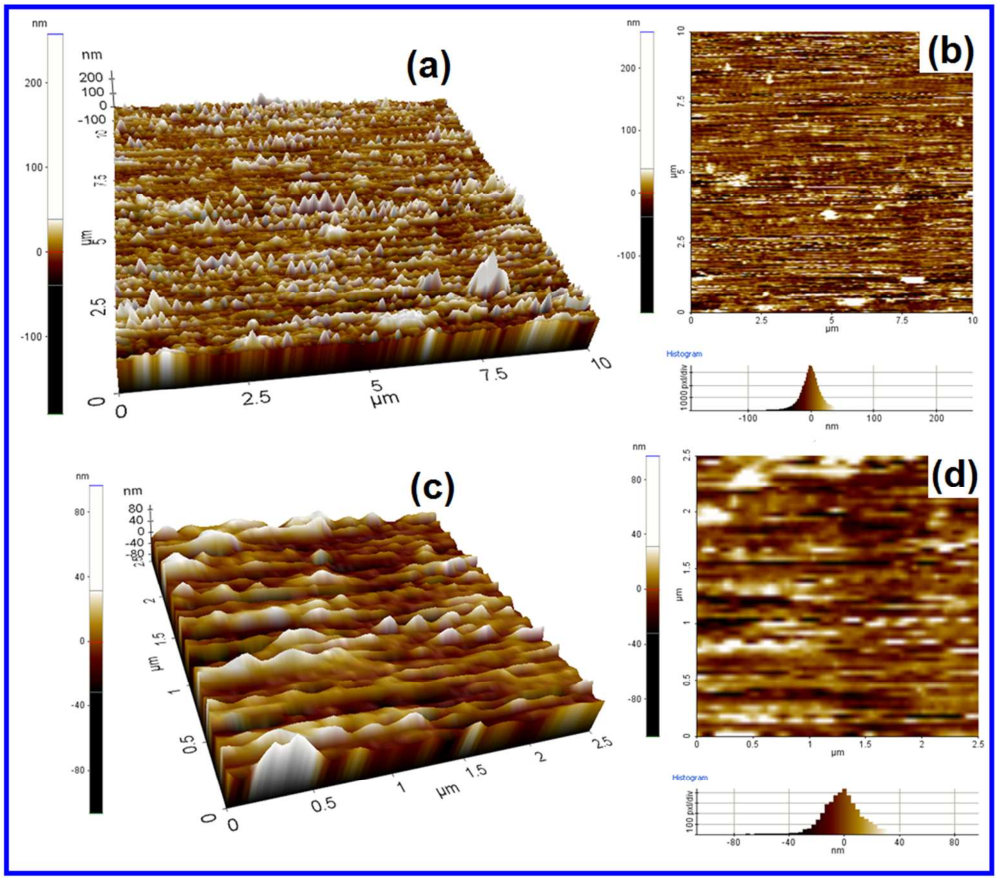
X-band ESR spectrum [Cu(Si-NH2-DPED)Cl2]
138x109mm (96 x 96 DPI)



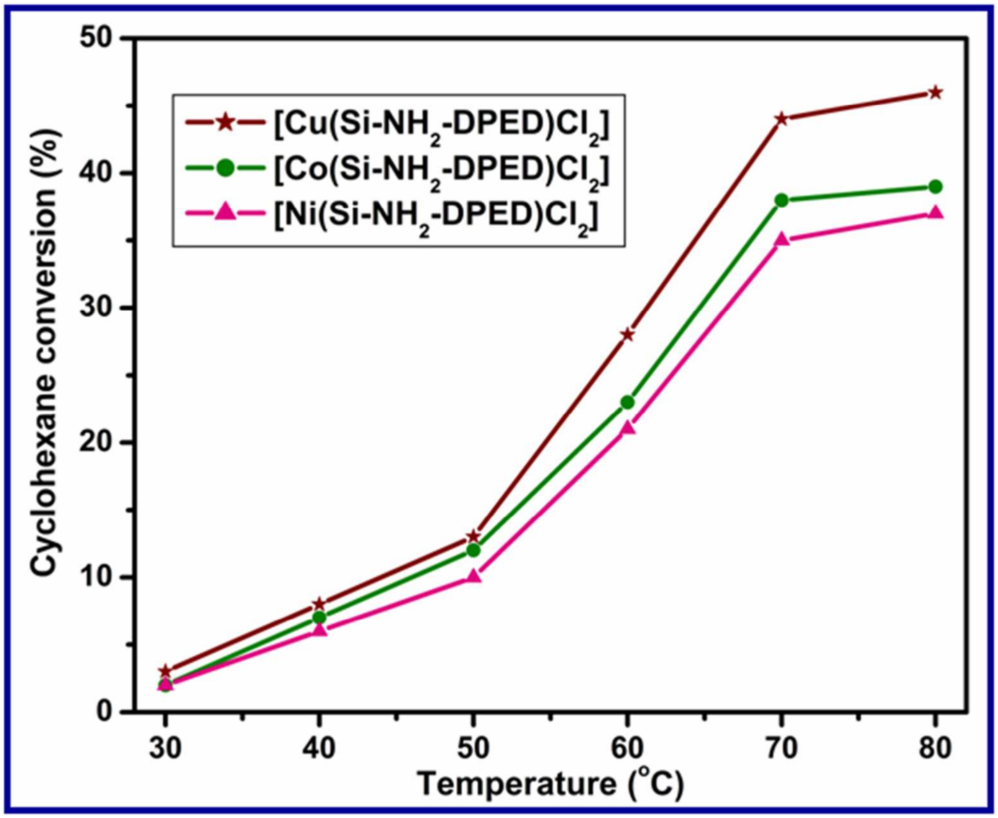
TG-DTG patterns of (a) Si-NH2-DPED, (b) [Cu(Si-NH2-DPED)Cl2], (c) [Co(Si-NH2-DPED)Cl2] and (d) [Ni(Si-NH2-DPED)Cl2]
154x107mm (96 x 96 DPI)



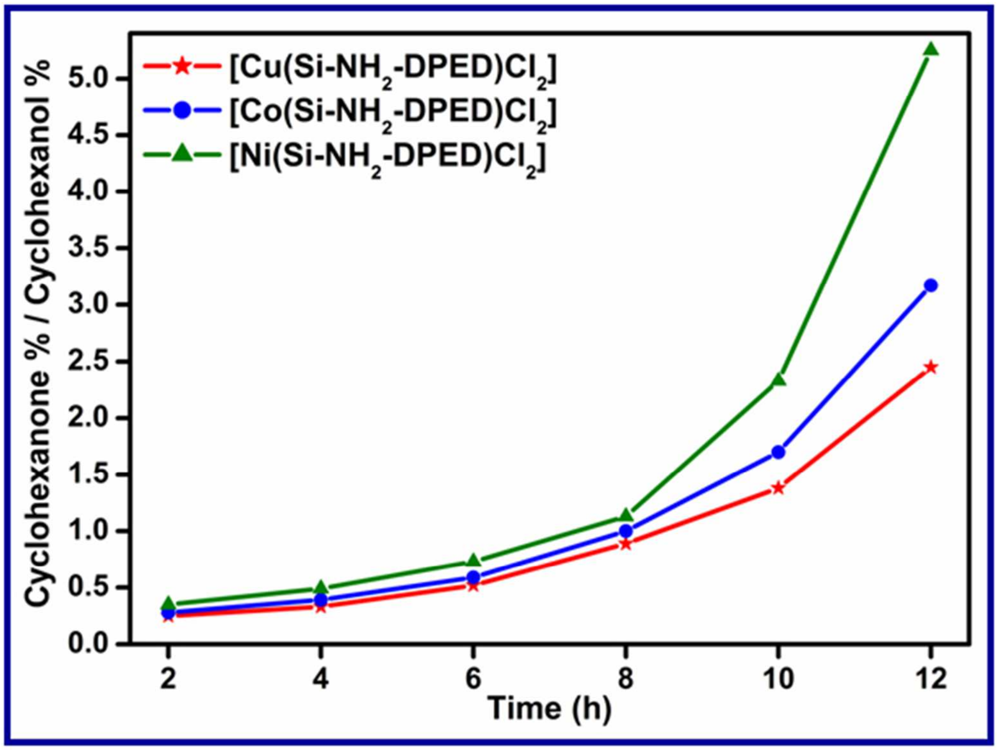
SEM images (a) Si-NH2-DPED, (b) [Cu(Si-NH2-DPED)Cl2], (c) [Co(Si-NH2-DPED)Cl2] and (d) [Ni(Si-NH2-DPED)Cl2]
204x144mm (96 x 96 DPI)



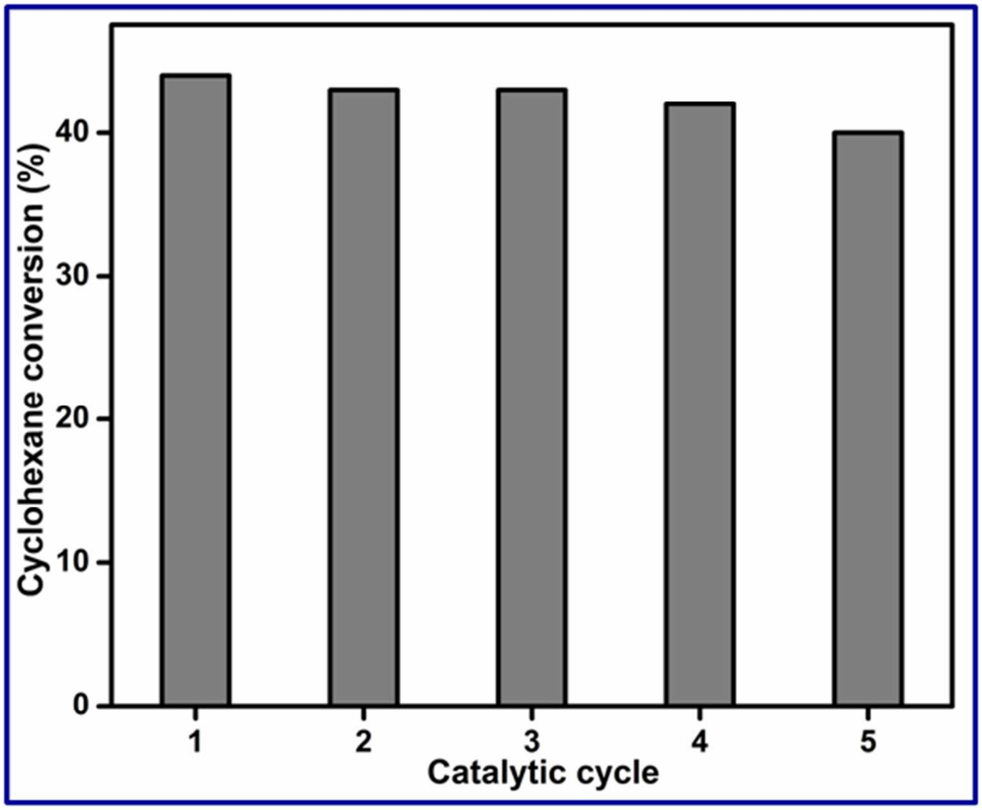
2D (a) and 3D (b) AFM images (10X10 µm); 2D (c) and 3D (d) AFM images (2.5X2.5 µm) of [Cu(Si-NH2-DPED)Cl2]
276x243mm (96 x 96 DPI)



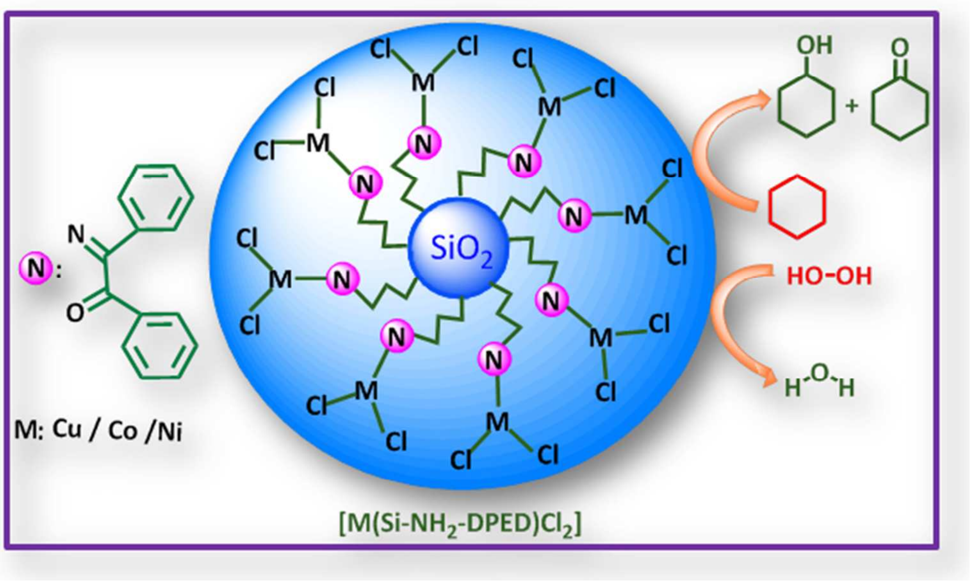
Effect of temperature on cyclohexane oxidation catalysed by Cu(II), Co(II) and Ni(II) hybrid catalysts
163x134mm (96 x 96 DPI)



Effect of time on selectivity of products obtained from cyclohexane oxidation catalysed by Cu(II), Co(II) and Ni(II) hybrid catalysts
163x123mm (96 x 96 DPI)



Catalytic Reusability of [Cu(Si-NH2-DPED)Cl2]. Reaction conditions: cyclohexane 5 mmol, 10 mmol 30% H2O2, 0.05 g catalyst, 10 ml CH3CN, 70 °C and 12 h
163x132mm (96 x 96 DPI)



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