Zeolite-Y entrapped bivalent transition metal complexes as hybrid nanocatalysts: density functional theory investigation and catalytic aspects

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(Received 19 November 2013; final version received 15 July 2014)

The intriguing research toward the exploitation of zeolite-Y-based hybrid nanocatalysts for catalytic oxidation reactions has been growing significantly. In the present investigation, we describe the synthesis of zeolite-Y entrapped transition metal complexes of the general formulae [M(SFCH)\textsubscript{x}H\textsubscript{2}O]-Y (where, M = Mn, Fe, Co, Ni (x = 3) and Cu (x = 1)); H\textsubscript{2}SFCH = (E)-N\textsuperscript{′}-(2-hydroxybenzylidene)furan-2-carbohydrazide. These nanocatalysts have been characterized by various physicochemical techniques. Density functional theory calculations are performed to address the relaxed geometry, bond angle, bond length, dihedral angle, highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap, and electronic density of states of H\textsubscript{2}SFCH ligand and their neat transition metal complexes. The observed HOMO–LUMO gap and the Fermi energy is higher for Cu(II) complexes, which demonstrates the better catalytic activity of this nanocatalyst. The catalytic activity was performed in liquid-phase oxidation of cyclohexane using hydrogen peroxide as oxidant to give cyclohexanone (CyONE) and cyclohexanol (CyOL). Among them, [Cu(SFCH)H\textsubscript{2}O]-Y catalyst has the highest selectivity toward CyONE (84.5%).

Keywords: Zeolite-Y; hybrid nanocatalysts; cyclohexane oxidation; DFT

1. Introduction

The selective oxidation is an industrially momentous reaction for the synthesis of chemical intermediates in the manufacture of high tonnage commodities, high-value fine chemicals, and pharmaceutically important ingredients but still is an ineffective process. The heterogeneous catalysts offer great advantages such as effortless separation of product, catalyst revival, and make it suitable for continuous processing. As a result, heterogenization of homogeneous catalysts has become a significant approach for obtaining supported catalysts that sustain the active catalytic sites of the homogeneous analog (1, 2). The encapsulation of the transition metal complexes inside the nanopens of zeolite is one of the heterogenization methods and also is a theme of contemporary research (3–7). Heterogenization is accomplished either by entrapping the metal complex within the zeolite nanocavities or by anchoring and/or tethering them to inert supports (8). The structural design of zeolite-Y-based hybrid nanocatalysts via flexible ligand approach is convenient and ideal because the complex, once formed inside the cages of the zeolite is fitted suitably and not easily to diffuse out during the catalytic reaction (9, 10).

In particular, the selective oxidation of cyclohexane is an industrially important chemical reaction because of its oxidized products, such as cyclohexanol (CyOL) and cyclohexanone (CyONE), which are important intermediates in the production of adipic acid and caprolactam. Caprolactam is used in the manufacture of Naylon-6 and Nylon-66 polymers. In a recent industrial process, cyclohexane is oxidized at a temperature range of 150–170°C and pressure of 115–175 psi in the presence of homogeneous cobalt salt, where the conversion is very less (∼4%), and the process is environmentally hazardous (11, 12). With the emphasis on environmentally benign catalytic oxidation of cyclohexane, several research groups have been designing various catalytic systems (13–20).

The use of computational techniques in catalysis, homogeneous as well as heterogeneous, has become explored mainly because of the sophistication of...
several density functional theory software. Scientifically, many known catalytic materials are expected to gain better exploitations because of their new properties and possible high catalytic activities in the nanometer regime (density functional theory (DFT) approach) (21, 22). With these newer approaches and knowledge, our laboratory has been exploring the chemistry of this class of hybrid nanocatalysts (23, 24). Continuing our study, herein we report the synthesis, characterization, and catalytic activity of zeolite-Y entrapped bivalent transition metal complexes containing salicylaldehyde furoic-2-carboxylic hydrazone ligand (H₂SFCH) in combination with the DFT studies. Results of the DFT for Schiff base ligand (H₂SFCH), [Cu(H₂SFCH)·H₂O] and [Mn(H₂SFCH)·3H₂O] were used to explore the energetics of the metal–ligand interactions and the possibility for the compound to adopt different conformations.

2. Results and discussion

Table 1 represents the chemical compositions which confirmed the purity and stoichiometry of the host zeolite-Y and zeolite-Y entrapped nanocatalysts. The chemical analyses of compounds reveal the presence of organic matter within the nanocavities of zeolite-Y. The mole ratio Si/Al obtained by chemical analysis for neat zeolite-Y and zeolite-Y entrapped nanocatalysts are shown in Table 1. The Si and Al contents in Na-Y and [Mn(SFCH)·3H₂O]-Y (where, M = Mn, Fe, Co, Ni (x = 3) and Cu (x = 1)) are almost in the same ratio, which indicates no dealumination during the metal ion exchange. The nitrogen adsorption–desorption isotherms for Na-Y, MnII-Y, and [Mn(SFCH)·3H₂O]-Y are analyzed and shown in Table 2. The results showed a decrease in the amount of N₂ adsorbed in case of Na-Y to zeolite-Y entrapped complexes, which indicates the filling of the nanocavities of zeolite-Y by complexes (25, 26).

The SEM images before and after Soxhlet extraction of [Ni(SFCH)·3H₂O]-Y are shown in Figure 1. The encapsulation of the complexes inside the zeolite-Y nanocavities can be confirmed by the absence of extraneous material by SEM image after Soxhlet extraction (Figure 1b).

Figure 2 shows the powder X-ray diffraction (XRD) patterns of zeolite-Y entrapped nanocatalysts. It is clear that the XRD pattern of [M(SFCH)·xH₂O]-Y (where, M = Mn, Fe, Co, Ni (x = 3) and Cu (x = 1)) was not rigorously affected by the introduction of the metal complex into the zeolitic structure. The entrapped complexes exhibit similar peaks to those of parent zeolite-Y and except for a slight change in the intensity of the peaks, no new crystalline pattern emerges. These facts confirmed that the framework and crystallinity of zeolite were not destroyed during

| Sr. No | Compound                  | Color       | %C  | %H  | %N  | %M  | %Si | %Al | %Na | Si/Al |
|-------|---------------------------|-------------|-----|-----|-----|-----|-----|-----|-----|-------|
| 1     | Na-Y                      | White       | –   | –   | –   | –   | 17.16| 6.60| 7.95| 2.60  |
| 2     | MnII-Y                    | Light pink  | –   | –   | –   | –   | 2.40 | 17.08| 6.56| 5.68  |
| 3     | [Mn(SFCH)·3H₂O]-Y         | Light yellow| 0.97| 0.85| 0.18| 2.18| 16.96| 6.52| 6.60| 2.60  |
| 4     | FeII-Y                    | Orange      | –   | –   | –   | 2.40| 17.08| 6.56| 5.68| 2.60  |
| 5     | [Fe(SFCH)·3H₂O]-Y         | Light orange| 1.30| 0.79| 0.14| 2.82| 16.85| 6.48| 6.25| 2.60  |
| 6     | CoII-Y                    | Pink        | –   | –   | –   | 3.53| 16.80| 6.46| 4.87| 2.60  |
| 7     | [Co(SFCH)·3H₂O]-Y         | Yellow      | 1.89| 0.68| 0.15| 1.78| 16.55| 6.36| 6.55| 2.60  |
| 8     | NiII-Y                    | Light green | –   | –   | –   | 3.62| 16.98| 6.53| 3.92| 2.60  |
| 9     | [Ni(SFCH)·3H₂O]-Y         | Light brown | 1.80| 0.73| 0.17| 2.66| 16.61| 6.39| 6.27| 2.60  |
| 10    | CuII-Y                    | Blue        | –   | –   | –   | 4.71| 16.90| 6.50| 7.01| 2.60  |
| 11    | [Cu(SFCH)·H₂O]-Y          | Dull green  | 1.94| 0.62| 0.12| 1.26| 16.37| 6.29| 5.87| 2.60  |

Table 1. Analytical and physical data of compounds.

Table 2. Surface area and pore volume data of compounds.*

| Compound                  | Surface area (m²/g) | Pore volume (cc/g) |
|---------------------------|---------------------|--------------------|
| Na-Y                      | 548                 | 0.32               |
| MnII-Y                    | 538                 | 0.29               |
| [Mn(SFCH)·3H₂O]-Y         | 388                 | 0.21               |
| FeII-Y                    | 530                 | 0.28               |
| [Fe(SFCH)·3H₂O]-Y         | 383                 | 0.20               |
| CoII-Y                    | 530                 | 0.30               |
| [Co(SFCH)·3H₂O]-Y         | 376                 | 0.22               |
| NiII-Y                    | 527                 | 0.30               |
| [Ni(SFCH)·3H₂O]-Y         | 380                 | 0.22               |
| CuII-Y                    | 534                 | 0.31               |
| [Cu(SFCH)·H₂O]-Y          | 395                 | 0.23               |

*Calculated by the Barrett–Joyner–Halenda (BJH) method.
the flexible ligand synthesis and that the complexes were well entrapped in the supercages of zeolite-Y.

The data obtained by vibrational spectroscopy can provide information on the integrity of the Schiff base ligand (H$_2$SFCH), zeolite-Y entrapped transition metal complexes, as well as the crystallinity of the host framework. The intensity of the bands of the entrapped complex is weak due to their low concentration in the zeolite matrix. The main Fourier transform-infrared spectroscopy (FT-IR) bands of the Schiff base ligand (H$_2$SFCH) and their entrapped transition metal complexes are tabulated in Table 3. Comparison between the spectra of H$_2$SFCH and their entrapped transition metal complexes provides evidence for the coordinating mode of Schiff base ligand in entrapped complexes. The spectra of H$_2$SFCH shows a sharp and strong band at 1603 cm$^{-1}$ due to $\nu$(C = N) of the azomethine group. This band undergoes hypsochromic effect in the spectra of entrapped complexes, indicating coordination of the azomethine nitrogen (27). The $\nu$(N–H) and $\nu$(C = O) modes of the lateral chain in the uncoordinated Schiff base appearing at 3216 and 1680 cm$^{-1}$, respectively (28). The reaction of the enolic ligand with M(II) ion is revealed by the presence of a new band in the spectra of 1275–1281 cm$^{-1}$ due to the $\nu$(C–O) (enolic) (29). In addition, the phenolic-OH vibration of the Schiff base ligand (3380 cm$^{-1}$) disappeared in the entrapped complexes. From these observations, it is concluded that the ligand reacts in enol form with prototropy, which incorporates into proton transfer through oxygen atoms of the ligand, forming two bonds with the metal ion. Furthermore, all zeolite-Y entrapped complexes exhibit bands around 1135, 1020, 790, and 720 cm$^{-1}$ due to host zeolite framework (30–32).

The electronic spectral bands of Schiff base ligand (H$_2$SFCH) and their entrapped metal complexes are discussed in Table 4. The H$_2$SFCH ligand exhibits three bands at 213, 339, and 382 nm due to $\phi$$\rightarrow$$\phi^*$, $\pi$$\rightarrow$$\pi^*$, and $n$$\rightarrow$$\pi^*$ transitions, respectively. The former band ($\phi$$\rightarrow$$\phi^*$) undergoes hypsochromic shift in Cu(II) and bathochromic shifts in Mn(II) and Co(II) entrapped complexes, resulting from chelation of the ligand with the transition metal. In the electronic

![Figure 1. SEM images of [Ni(SFCH)·3H$_2$O]-Y (a) before and (b) after Soxhlet extraction.](image1)

![Figure 2. XRD patterns of zeolite-Y entrapped nanocatalysts.](image2)
The spectrum of entrapped complex $[\text{Mn(SFCH)·3H}_2\text{O}]^-$, the characteristic bands appeared at 322 and 252 nm are assignable to $6A_{1g} \rightarrow 4A_{1g}$, $4E_g$ ($\nu_3$), and metal to ligand charge transfer (MLCT) transitions, respectively, due to distorted octahedral geometry around the metal ion. The electronic spectrum of $[\text{Fe(SFCH)·3H}_2\text{O}]^-$ exhibits band at 289 nm may be assignable to MLCT transition. Absence of d-d transitions in the spectra of entrapped Fe(II) complex may be due to the lower concentration inside the nanopores of zeolite-Y. $[\text{Co(SFCH)·3H}_2\text{O}]^-$ displays bands at 708, 319, and 257 nm are attributed to $4T_{1g}(F) \rightarrow 4A_{2g}(F)$, $4T_{1g}(F) \rightarrow 4T_{1g}(P)$, and MLCT transitions of an octahedral geometry around the metal ion, respectively. The absorption spectrum of $[\text{Ni(SFCH)·3H}_2\text{O}]^-$ exhibits two bands at 680 and 242 nm that may be attributed to $3A_{2g} \rightarrow 3T_{1g}(P)$ ($\nu_3$) and $3A_{2g} \rightarrow 3T_{1g}(F)$ ($\nu_2$) transitions, respectively. The electronic spectra of $[\text{Cu(SFCH)·H}_2\text{O}]^-$ consists of a band at 253 nm and a shoulder at 321 nm, which can be assigned to the $d_{x^2-y^2} \rightarrow d_{xy}$ and MLCT transitions, respectively, for tetrahedrally distorted (D$_{2h}$) mono-nuclear copper(II) complexes.

We have performed first-principles total energy calculations within the DFT using the plane-wave self-consistent field (PWSCF) implementation (35, 36). The wave functions describe only the valence and the conduction electrons, while the core electrons are taken into account for pseudo-potentials. For the exchange–correlation functional, we have employed the generalized-gradient approximation (GGA) functional developed by Perdew, Burke and Ernzerhof (PBE) (37) since it is known that GGA gives better results than the simpler local density approximation (LDA) when describing the structural properties of transition metal complexes. A set of convergence tests has been performed in order to choose correctly the mesh of $k$-points and the cut-off kinetic energy plane waves to start the ground-state and linear-response calculations. The kinetic energy cut-off for the plane wave basis is set to 40 Ryd for all structures. The electronic configurations of atoms are as follows: C \[\text{He}\]2s$^2$2p$^2$; N\[\text{He}\]2s$^2$2p$^3$; O\[\text{He}\]2s$^2$2p$^4$; Mn\[\text{Ar}\]3d$^5$4s$^2$; and Cu\[\text{Ar}\]3d$^{10}$4s$^1$. The self-consistent calculations were considered to be converged using the conjugate–gradient algorithm until the absolute value of the forces on unconstrained atoms was less than 0.03 eV/Å$^2$ and up to a precision of $10^{-4}$ eV in total energy difference. The Brillouin zone sampling was restricted to the gamma point (38). Marzari–Vanderbilt (39) Gaussian smearing with a width of 0.05 Ryd was used to accelerate the convergence of the total energy calculations. For density of states (DOS) calculations, we increased the sampling of the Brillouin zone. In our calculations, Broyden–Fletcher–Goldfarb–Shanno (BFGS) method is used to construct the geometry of the model structures for the ligand and their Mn(II) and Cu(II) neat transition metal complexes and then allowed to relax. The optimized structure of $[\text{Mn(SFCH)·3H}_2\text{O}]^-$ shows a distorted octahedral geometry, whereas in the case of $[\text{Cu(SFCH)·H}_2\text{O}]^-$ shows tetrahedrally distorted geometry along with one water molecule, two oxygen, and one azomethine nitrogen atoms of H$_2$SFCH, as shown in Table 5. However, the $[\text{Mn(SFCH)·3H}_2\text{O}]^-$ complex has shown some distortion in the relaxed structure (Figure 3), recognized by the dihedral angles O(8)-N(9)-O(17)-Mn and O(20)-O(19)-O(21)-O(8) with 30° and 105°, respectively. Further, dihedral angles of the Mn(II) complex O(8)-O(19)-O(17)-N(9) and C(11)-C(12)-O(17)-Mn are 56° and 29°, respectively, and confirm a distortion in geometry. In the
case of Cu(II) complex, the dihedral angle C(11)-C(10)-N(9)-Cu is 65° and reveals a very small distortion for azomethine nitrogen of the lateral chain. The bond lengths of Mn-N(9) and Mn-O(20) (∼2.0 Å) are consistent with the characteristic lengths in the octahedral coordinate Mn(II) complex. Similarly, the lengths of resultant bonds for the tetrahedral coordinate Cu(II) complexes are 1.6–1.7 Å [19]. The electronic DOS of Cu(II) and Mn(II) complexes and the Schiff base ligand (H$_2$SFCH) are shown in Figure 4. The most significant difference is observed at Fermi level where the density and shape of the spectra changes going from ligand to complex. An apparent gap just above the Fermi level where the density and shape of the spectra matches with that of the complexes. This might be due to structural changes in relaxation. Further, it is also seen that the higher Fermi energy (3.611 eV) in the case of [Cu(SFCH)·H$_2$O] may enhance the catalytic properties of the nanocatalysts and lower Fermi energy (2.828 eV) lower down the catalytic properties in the case of [Mn(SFCH)·3H$_2$O].

In a typical reaction of cyclohexane oxidation, 30% H$_2$O$_2$ (20 mmol), cyclohexane (10 mmol), and catalyst (45 mg) were mixed in 2 mL acetonitrile in an oil bath at 80°C with continuous stirring for 2 h. The progress of the reaction was checked as a function of time by withdrawing portions of the sample at fixed time intervals and analyzing them by gas chromatography. The host–guest catalyzed oxidation of cyclohexane gives mainly CyOL and CyONE as given in Table 7. The catalyst was filtered, thoroughly washed with different solvents like acetone, methanol, water, and dried under similar conditions.

The catalytic conversion of cyclohexane by various zeolite-Y entrapped nanocatalysts is illustrated in Figure 5. This shows the hydrocarbon yield 15.2, 22.0, 26.4, 39.1, and 45.1% conversion corresponding to [Mn(SFCH)·3H$_2$O]-Y, [Ni(SFCH)·3H$_2$O]-Y, [Fe(SFCH)·3H$_2$O]-Y, [Co(SFCH)·3H$_2$O]-Y and [Cu(SFCH)·H$_2$O]-Y, respectively, at the same reaction condition. The effect of reaction time at 80°C, with various zeolite-Y entrapped nanocatalysts over the oxidation of cyclohexane was investigated and summarized in Table 6. It was found that the conversion of cyclohexane gradually increases and reaches a maximum of 45.1% after 2 h.

The effect of amount of zeolite-Y entrapped nanocatalysts for the cyclohexane oxidation using

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| Bond length (Å) | [Mn(SFCH)·3H$_2$O] | [Cu(SFCH)·H$_2$O] |
|----------------|------------------|------------------|
| Mn-O(19) | 1.75 | Cu-O(18) | 1.74 |
| Mn-N(9) | 2.01 | Cu-N(9) | 1.45 |
| Mn-O(21) | 1.31 | Cu-O(16) | 2.43 |
| Mn-O(8) | 1.47 | Cu-O(8) | 1.65 |
| Mn-O(20) | 2.15 | Cu-O(18) | 1.74 |
| Mn-O(17) | 2.40 | Cu-O(18) | 1.74 |

| Angle (°) | [Mn(SFCH)·3H$_2$O] | [Cu(SFCH)·H$_2$O] |
|-----------|------------------|------------------|
| O(20)-Mn-N(9) | 76 | O(16)-Cu-O(18) | 123 |
| O(20)-Mn-O(19) | 89 | O(16)-Cu-N(9) | 80 |
| O(19)-Mn-O(21) | 59 | O(18)-Cu-O(8) | 109 |
| O(21)-Mn-N(9) | 105 | N(9)-Cu-O(8) | 101 |
| O(19)-Mn-N(9) | 165 | N(9)-Cu-O(8) | 101 |
| O(20)-Mn-O(21) | 89 | N(9)-Cu-O(8) | 101 |
| O(17)-Mn-O(8) | 114 | N(9)-Cu-O(8) | 101 |

| Dihedral angle (°) | [Mn(SFCH)·3H$_2$O] | [Cu(SFCH)·H$_2$O] |
|-------------------|------------------|------------------|
| O(20)-O(19)-(O(21)-O(8)) | 105 | O(16)-O(18)-(O(8)-N(9)) | 53 |
| O(8)-O(19)-(O(17)-N(9)) | 56 | C(11)-C(12)-(O(16)-Cu) | 10 |
| C(11)-C(12)-(O(17)-Mn) | 29 | N(7)-C(6)-(O(8)-Cu) | 4 |
| N(7)-C(6)-(O(8)-Mn) | 5 | C(11)-C(10)-(N(9)-Cu) | 65 |
| O(20)-O(19)-O(8)-Mn | 1 | C(6)-N(7)-(N(9)-Cu) | 57 |
| O(8)-N(9)-(O17)-Mn | 30 | N(9)-Cu-O(8) | 101 |
[Cu(SFCH)·H₂O]-Y as a representative catalyst was investigated at four different amounts namely, 35, 40, 45, and 50 mg, keeping with all other reaction parameters fixed. The results are shown in Figure 7, indicating 22.1, 31.8, 45.1, and 45.2% conversion corresponding to 35, 40, 45, and 50 mg catalyst, respectively. The maximum percentage conversion was observed with 45 mg catalyst, but there was no remarkable difference in the progress of reaction when 45 or 50 mg of catalyst was employed. Therefore, 45 mg amount of catalyst was taken to be optimal.

The test for recyclability using [Cu(SFCH)·H₂O]-Y as a representative catalyst has been carried out. This nanocatalyst was recycled for the oxidation of cyclohexane with 30% H₂O₂ with a view to finding the effect of encapsulation on stability. It was observed that the conversion was nearly the same as for the first cycle, and there was only a minor loss in catalytic activity for the second cycle may be due to some blocking of zeolite channels during the first cycle. The initial run showed a conversion of 45.1%; this is marginally reduced to 43.6% on first reuse and 42.3% on second reuse of the catalyst, respectively.

Figure 3. Representative structures for H₂SFCH ligand (a), neat distorted octahedral [Mn(SFCH)·3H₂O] (b), tetrahedrally distorted [Cu(SFCH)·H₂O] (c), zeolite-Y nanocavity (d), encapsulated [Mn(SFCH)·3H₂O]-Y (e) and [Cu(SFCH)·H₂O]-Y (f).
This revealed that \([\text{Cu(SFCH)·H}_2\text{O}]\)-Y catalyst is almost stable to be recycled for cyclohexane oxidation. Thus, the zeolite-Y entrapped complexes are found to increase the life of the catalyst by a reduction of leaching due to the host zeolite framework.

### 3. Conclusions

The results obtained in this study allow the following conclusions:

- A series of \([\text{M(SFCH)·xH}_2\text{O}]\)-Y complexes (where, \(\text{M} = \text{Mn, Fe, Co, Ni (x = 3) and Cu (x = 1)}\}) have been successfully synthesized by flexible ligand method as evidenced by inductively coupled plasma/optical emission spectrometry (ICP-OES), elemental analyses, (FT-IR and electronic) spectral studies, BET, SEMs, and X-ray diffraction pattern results.

- The geometries of neat Mn(II) and Cu(II) complexes with the Schiff base ligand (H\(_2\)SFCH) are characterized by a quantum mechanical method based on the DFT. From the DFT calculations, it was observed that the complexes are suitable in size for the zeolite channels, which confined the complex and restricted it from coming out of the nanocavity of zeolite-Y.
- The HOMO–LUMO gap and the Fermi energy is higher in the case of Cu(II) complexes, which demonstrates the better catalytic activity of this nanocatalyst.
- The catalytic behavior of these zeolite-Y entrapped nanocatalysts was performed over the oxidation of cyclohexane affording CyOL and CyONE, with good CyONE selectivity.
- Among them, \([\text{Cu(SFCH)·H}_2\text{O}]\)-Y catalyst has the highest percentage of selectivity toward CyONE (84.5%).
- To summarize, zeolite-Y entrapped transition metal complexes have interesting catalytic potential particularly with respect to the activity for the oxidation of cyclohexane selectively and offer an open field to design efficient catalyst systems.

### 4. Experimental

#### 4.1. Materials and methods

Furoic-2-carboxylic acid was obtained from Spectrochem (India). Salicylaldehyde was purchased from Loba Chemie (India). Thirty percent H\(_2\)O\(_2\) was purchased from Rankem (India). Sodium form of zeolite-Y (Si/Al = 2.60) was procured from Hi-media, India. The carbon, hydrogen, and nitrogen were analyzed with a Perkin Elmer, USA 2400-II CHN analyzer. The Si, Al, Na, and transition metal ions were determined by ICP-OES (Model: Perkin Elmer optima 2000 DV). UV-vis spectra were recorded on Spectrophotometer Make/model Varian Cary 500, Shimadzu. FT-IR spectra of compounds were recorded on a Thermo Nicolet IR 200 FT-IR spectrometer. The crystallinity of compounds was ensured by XRD using a Bruker AXS D\(_8\) Advance X-ray powder diffractometer with a Cu K\(_\alpha\) target. The surface area of entrapped nanocatalysts was measured by multipoint BET method, using Micromeritics, ASAP 2010 surface area analyzer. The scanning electron micrographs of entrapped nanocatalysts were recorded using a SEM instrument (Model: LEO 1430 VP).

### Table 6. Relaxed parameters and HOMO and LUMO energy difference of H\(_2\)SFCH and their neat Mn(II) and Cu(II) complexes.

| Compound                   | Total energy (eV) | Fermi energy (eV) | One electron contribution (eV) | Ewald contribution (eV) | HOMO–LUMO (eV) |
|----------------------------|-------------------|-------------------|-------------------------------|-------------------------|----------------|
| H\(_2\)SFCH                | −3852.589         | 2.002             | −2369.700                     | −2012.344               | −1.992         |
| \([\text{Cu(SFCH)·H}_2\text{O}]\) | −5934.494         | 3.611             | −3480.972                     | −3126.732               | −3.617         |
| \([\text{Mn(SFCH)·3H}_2\text{O}]\) | −8072.563         | 2.828             | −7018.031                     | −3410.458               | −2.924         |

*Harris–Foulkes estimate.*
4.2. Synthesis of salicylaldehyde furoic-2-carboxylic hydrazone (H$_2$SFCH)

Salicylaldehyde furoic-2-carboxylic hydrazone (H$_2$SFCH) was prepared by following the procedure reported earlier (24).

4.3. Synthesis of zeolite-Y entrapped transition metal complexes

An amount of 5.0 g of Na-Y zeolite was suspended in 300 mL of deionized water containing 12 mmol metal salts (Mn(CH$_3$COO)$_2$·4H$_2$O, FeSO$_4$·7H$_2$O, Co (CH$_3$COO)$_2$·4H$_2$O, Ni(CH$_3$COO)$_2$·4H$_2$O, and Cu (CH$_3$COO)$_2$·H$_2$O, respectively) and heated at 90°C with constant stirring (24 h) for the synthesis of metal exchanged zeolite-Y. Then the solid was filtered, washed with hot deionized water until the filtrate was free from any metal ion content, and dried for 12 h at 120°C. In the next step, 1.0 g of MII-Y was uniformly mixed with an excessive amount of H$_2$SFCH ligand ($n_{\text{ligand}}/n_{\text{metal}} = 3$) in ethanol and sealed into a round-bottom flask. The reaction mixture was refluxed (~24 h) in an oil bath with stirring followed by Soxhlet extraction with ethanol, acetone, and finally with acetonitrile (6 h) to remove uncomplexed ligand and the complex adsorbed on the exterior surface of the zeolite-Y. The extracted sample was ion-exchanged with 0.01 M NaCl aqueous solution for 24 h, followed by washing with deionized water until the filtrate was free from any metal ion content, and dried for 12 h at 120°C.

Table 7. Catalyzed oxidation of cyclohexane to CyOL and CyONE by zeolite-Y entrapped nanocatalysts (temperature, 80°C; H$_2$O$_2$/cyclohexane molar ratio, 2:1; time, 2 h; amount of catalyst, 45 mg).

| Sr. no. | Compound               | Conversion (%) | TOF (h$^{-1}$) per 2 h | CyOL (%) | CyONE (%) |
|---------|------------------------|----------------|------------------------|----------|-----------|
| 1       | Na-Y                   | 2.1            | –                      | 48.6     | 51.4      |
| 2       | Mn(II)-Y               | 6.5            | 1.64                   | 47.6     | 52.4      |
| 3       | Fe(II)-Y               | 7.9            | 0.91                   | 46.9     | 53.1      |
| 4       | Cu(II)-Y               | 9.3            | 1.40                   | 44.2     | 55.8      |
| 5       | Co(II)-Y               | 8.2            | 1.48                   | 45.8     | 54.2      |
| 6       | [Mn(SFCH)·3H$_2$O]·Y   | 15.2           | 4.25                   | 27.6     | 72.4      |
| 7       | [Fe(SFCH)·3H$_2$O]·Y   | 26.4           | 5.52                   | 31.3     | 68.7      |
| 8       | [Co(SFCH)·3H$_2$O]·Y   | 39.1           | 14.4                   | 42.9     | 57.1      |
| 9       | [Ni(SFCH)·3H$_2$O]·Y   | 19.5           | 4.80                   | 22.6     | 77.4      |
| 10      | [Cu(SFCH)·H$_2$O]·Y    | 45.1           | 25.28                  | 15.5     | 84.5      |
| 11      | [Cu(SFCH)·H$_2$O]·Y$^a$| 43.6           | 24.43                  | 17.1     | 82.9      |
| 12      | [Cu(SFCH)·H$_2$O]·Y$^b$| 42.3           | 23.71                  | 17.8     | 81.2      |

Note: CyOL is a cyclohexanol product; CyONE is a cyclohexanone product.

$^a$First reused catalyst; $^b$Second reused catalyst; TOF (h$^{-1}$) (turnover frequency): mol of substrate converted per mol of metal (in the solid catalyst).

Figure 5. Percentage conversion of cyclohexane oxidation.

Figure 6. Effect of time on the cyclohexane oxidation.
water until no Cl\(^-\) ion could be detected with AgNO\(_3\) solution. The product \([\text{M(SFCH)·xH\(_2\)O}]\cdot\text{Y}\) (where, M = Mn, Fe, Co, Ni (\(x = 3\)) and Cu (\(x = 1\))) was collected and dried in air.

**Acknowledgments**

We express our gratitude to the Head, Department of Chemistry, M. K. Bhavnagar University, Bhavnagar, India, for providing the necessary laboratory facilities. Mr. Parthiv M. Trivedi would like to acknowledge UGC, Delhi, for providing meritorious fellowship. One of us (SKG) is indebted to the Ministry of New and Renewable Energy (MNRE) for awarding the post-doc fellowship. An analytical facility provided by CSMCRI, Bhavnagar and Computations were carried out on the computer cluster PAWAN at the Department of Physics, M.K. Bhavnagar University, Bhavnagar, financed by the Department of Science and Technology, Govt. of India are highly acknowledged.

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