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Liquid-phase catalytic hydroxylation of phenol using Cu(II), Ni(II) and Zn(II) complexes of amidate ligand encapsulated in zeolite-Y as catalysts

Mannar R. Maurya[a,*], Salam J. J. Titinchi[a], and Shri Chand[b]

[a]*Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India*
[b]*Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247 667, India*

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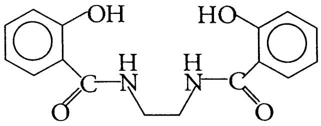
Copper(II), nickel(II) and zinc(II) complexes of amidate ligand 1,2-bis(2-hydroxybenzamido)ethane(H_2hybe) encapsulated in the super cages of zeolite-Y have been prepared and characterized by spectroscopic studies and thermal as well as X-ray diffraction (XRD) patterns. These complexes catalyze the liquid-phase hydroxylation of phenol with H_2O_2 to catechol as a major product and hydroquinone as a minor product. Considering the concentration of substrate and oxidant, amount of catalyst, temperature of the reaction and volume of solvent, a best-suited reaction condition has been optimized to get maximum hydroxylation. Under the optimized reaction conditions, [Cu(hybe)]-Y has shown the highest conversion of 40% after 6 h, which is followed by [Ni(hybe)]-Y with 37% conversion and [Zn(hybe)]-Y has shown the poorest performance with 33% conversion. All these catalysts are more selective towards catechol formation (~90%), irrespective of their catalytic performance.

KEY WORDS: [M^{H}(hybe)] complexes; zeolite-encapsulated metal complexes; hydroxylation of phenol; catechol and hydroquinone formation.

1. Introduction

Activity, selectivity, thermal stability and reusability are some important characteristics of catalysts for which fine and specialty chemical industries look for. Heterogenization of homogenous catalysts by encapsulating them in zeolite provides an ideal solution, as large size of the encapsulated metal complexes and their rigidity make them difficult to escape out of the zeolite cages. Zeolite-encapsulated metal complexes (ZEMCs) have provided the opportunity to develop catalytic process for the selective epoxidation/oxidation of olefins [1–3], cyclohexene [4–6], styrene [7], cyclohexane [8,9] cyclohexanol [10] and phenols [11–20] etc. The [Mn(salen)]-Y(H_2salen = *N,N′*-bis(salicylidene)ethane-1,2-diamine) has emerged as an industrially important catalyst for the oxidation of olefins [21,22].

Liquid-phase hydroxylation of phenol to catechol and hydroquinone using simple oxidants like O_2 and H_2O_2 is a reaction of industrial importance [23,24]. Different types of catalysts have been tested to enhance the hydroxylation of phenol [25–29]. Catalysts based on ZEMCs have played an important role in this regard [11–20]. Recently, we have optimized the conditions for the hydroxylation of phenol using vanadium complexes of H_2salen family encapsulated in zeolite-Y [20]. These complexes exhibit ~ 90% selectivity towards the formation of catechol. In continuation of our effort in this area, we have prepared copper(II), nickel(II) and zinc(II) complexes of 1,2-bis(2-hydroxybenzamido)ethane (H_2hybe, **I**) encapsulated in zeolite-Y and tested their catalytic activity for the selective liquid-phase hydroxylation of phenol. A suitable reaction condition has also been optimized to get maximum hydroxylation. These catalysts also exhibit ~ 90% selectivity towards the formation of catechol.



I: H_2hybe

2. Experimental

2.1. Materials

Methylsalicylate and 1,2-diaminoethane were obtained from E. Merck, India. Analytical reagent grade metal nitrates (nitrates of Cu(II), Ni(II) and Zn(II)), 30% aqueous H_2O_2 and phenol were obtained from Qualigens, India. Y-zeolite (Si/Al ~ 10) was obtained from Indian Oil Corporation (R&D), Faridabad, India. All other chemicals and solvents used were also of AR grade. 1,2-bis(2-hydroxybenzamido)ethane

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* To whom correspondence should be addressed.
E-mail: rkmanfcy@iitr.ernet.in

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(H_2hybe) was prepared as described by Dash and Mishra [30].

2.2. Preparations

1. Preparation of metal-exchanged zeolite, M-Y [M = Cu(II), Ni(II) and Zn(II)]

About 5.0 g of Na-Y zeolite was suspended in 300 mL distilled water, which contained 50 mol of metal nitrate [nitrates of Cu(II), Ni(II) or Zn(II)]. The reaction mixture was heated while stirring at ca. 90 °C for 24 h. The solid was filtered, washed with hot distilled water till the filtrate was free from any free metal ion on the surface of the zeolite and then dried for 15 h at 150 °C in air.

2. Preparation of [M(hybe)]-Y

The encapsulated complexes were prepared by general method. About 1.0 g M-Y [M = Cu(II, Ni(II) and Zn(II)] and 2.5 g H_2hybe were mixed in a 50 mL MeCN in a round-bottom flask and the reaction mixture was heated at reflux for ca. 15 h while stirring in an oil bath. After cooling, the slurry was Soxhlet, extracted with methanol (ca. 48 h) till the complex was free from unreacted ligand and any free metal complex on the surface of the zeolite. The uncomplexed metal ions present in the zeolite were removed by exchanging with aqueous 0.01 M solution of NaCl. Finally, the encapsulated complexes were filtered and washed with hot distilled water till no precipitation of AgCl was observed on treating filtrate with $AgNO_3$ solution. The colored (colorless in case of Zn(II)–solid) was dried at 150 °C for several hours till constant weight was achieved.

2.3. Physical methods and analysis

The metal contents were measured using GBC Avanta Atomic Absorption Spectrometer. Thermogravimetric analyses of the catalysts were carried out using TG Stanton Redcroft STA 780. X-ray diffractograms of solid catalysts were recorded using Philips PW 1140/90 X-ray powder diffractometer with Cu K_α target at Institute Instrumentation Centre. IR spectra were recorded as KBr pellet on a Perkin-Elmer model 1600 FT-IR spectrometer. Electronic spectra were recorded in Nujol on a Shimadzu 1601 UV-visible spectrophotometer by layering the mull of the sample to the inside of one of the cuvette while keeping another one layered with Nujol as reference. All catalyzed reaction products were analyzed using Nucon 5700 gas chromatograph fitted with FID, a 2 m × 2 mm(i.d.) OV-17 (S.S.) column and ORACLE 2 computer software. Scanning Electron Micrographs (SEMs) of catalysts were recorded on a Leo instrument model 435 VP. The samples were dusted on alumina and coated with a thin film of gold to prevent surface changing and to protect the surface material from thermal damage by the electron beam. In all analyses, a uniform thickness of about 0.1 mm was maintained.

2.4. Catalytic activity studies

The catalytic activity study towards the hydroxylation of phenol was carried out in a 50-mL flask fitted with a water-cooled condenser. In a typical reaction, an aqueous solution of 30% H_2O_2 (5.67 g, 0.05 mol) and phenol (4.7 g, 0.05 mol) were mixed in 2 mL of MeCN, and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. An appropriate catalyst (0.025 g) was added to the reaction mixture, and with this the reaction was considered to begin. During the reaction, the products were analyzed using a gas chromatograph after specific interval of time by withdrawing small aliquot out. The effects of various parameters such as amounts of substrate, oxidant and catalyst as well as the temperature of the reaction were studied in order to see their effect on the reaction product pattern.

3. Results and discussion

3.1. Synthesis and characterization of catalysts

The synthesis of metal complexes encapsulated in the super cages of zeolite-Y was carried out by a general method, which consisted of mainly two steps (i) the preparation of metal-exchanged zeolite, M-Y [M = Cu(II), Ni(II) and Zn(II)] and (ii) refluxing the MeCN solution of ligand and suspension of metal-exchanged zeolite. The second step allowed the insertion of ligand owing to its flexibility in the cavity of the zeolite, followed by complexation with metal ions. Soxhlet extraction with methanol purified the crude mass and removed excess ligand as well as metal complex formed, if any, on the surface of the zeolite because of leaching. The remaining uncomplexed metal ions in the zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. Complexation of H_2hybe with Cu(II) Ni(II) ions were accompanied by the color change, while Zn(II) gave a colorless compound. The percentage of metal contents determined before and after encapsulation by Atomic Absorption Spectrometry (AAS) along with their expected formula and color is presented in table 1. As crude mass was extracted with methanol, the metal ion content found after encapsulation is only due to the presence of metal complexes in zeolite framework. The Scanning Electron Micrograph (SEM) of the metal-exchanged zeolite and their respective encapsulated complexes indicate the presence of well-defined zeolite crystals without any shadow of metal ions or complexes present on their external surface. The representative photographs of Cu-Y and [Cu(hybe)]-Y are reproduced in figure 1.

Table 1
Chemical composition, physical and analytical data

S. No.	Compound	Color	Metal content (Wt%)
1	Cu-Y	Pale blue-green	7.60
2	Ni-Y	Pale-green	6.82
3	Zn-Y	White	0.50
4	[Cu(hybe)]-Y	Pale brown	4.23
5	[Ni(hybe)]-Y	Creamy	2.58
6	[Zn(hybe)]-Y	White	0.10

3.2. Spectral studies

A partial list of IR spectral data of ligand and complexes is presented in table 2. The IR spectrum of ligand exhibits three sharp peaks at 1641, 1547 and 1252 cm^{-1} due to amide-I, II and III modes, respectively. Amide-I band arises because of v(C=O) mode, while amide-II and III arise because of v(C−N) and v(NH) (bending) modes. All three bands register low-frequency shift in the spectra of the encapsulated complexes, except Zn(II) complex, where amide-I and amide-III bands appear at nearly the same position, indicating the coordination of amide nitrogen to the metal ion. This is further supported by the lower-frequency shift of v(NH) peak, which appears at 3377 cm^{-1} in free ligand. The coordination of amide −NH group has been confirmed in several oxovanadium(IV) complexes [31]. A broadband appearing in the 2300–2600 cm^{-1} region owing to intramolecular hydrogen bonding between phenolic OH and amide C=O is also absent in the spectra of the complexes. This information supports the breaking of hydrogen bonding, deprotonation of phenolic oxygen and subsequent coordination of phenolic oxygen atom to the metal ion. Thus, IR spectra support ONNO donor dibasic tetradentate behavior of H_2hybe.

The electronic spectral data of the catalysts along with the ligand are also presented in table 2 and spectra of catalysts are presented in figure 3. The electronic spectrum of ligand exhibits two bands at 306.5 and 240 nm due to n–π^* and π–π^* transitions of the phenolic group, respectively. In catalysts, as shown in figure 2, these bands appear at nearly the same or little lower nanometer range, which suggest the association of ligand with metal ions. In addition, all these catalysts exhibit a band at 209.5–213.5 nm, which seems to be a ϕ–ϕ^* transition due to the presence of benzene ring. The band due to ligand to metal charge transfer (lmct) or d–d transitions could not be located in Nujol mull in any of the catalysts reported here.

3.3. Thermal studies

The TGA data of the encapsulated catalysts along with the percentage weight loss at different steps and their probable assignments are summarized in table 3. The thermal decomposition of these catalysts occurs in two major steps. The first endothermic loss of 16–22% occurs in the temperature range 150–270 °C owing to the presence of intra-zeolite water. Though all catalysts were dried at ca.150 °C for constant weight, it is expected that even at this temperature intra-zeolite water will remain present in these catalysts. In fact, the presence of at least four intra-zeolite water molecules have been reported for [Cu(salen)]-Y[10]. As shown in table 3, the exothermic loss of 10–12% starts immediately after the first step and is due to slow decomposition of the chelating ligand. A very small percent weight loss indicates the presence of only a small amount of metal complex insertion in the zeolite matrix. This is in agreement with the low-percent metal content estimated by atomic absorption.

3.4. X-ray powder diffraction study

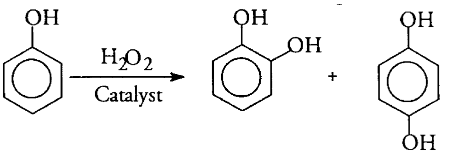
The X-ray powder diffraction (XRD) patterns of Na-Y, M-Y (M = Cu(II), Ni(II) and Zn(II)) and their complexes of H_2hybe encapsulated in zeolite-Y were recorded at 2θ values between 5 and 70°. These observations indicate that zeolite framework has not undergone any significant structural change during encapsulation of [M(hybe)] and thus crystallinity of zeolite-Y is preserved. The XRD pattern of Na-Y, Cu-Y and [Cu(hybe)]-Y are reproduced in figure 3. No new peaks in M-Y and [M(hybe)]-Y were detected in the XRD patterns, which is probably due to poor loading of the metal complexes during encapsulation.

3.5. Catalytic activity

The liquid-phase hydroxylation of phenol using three different catalysts and H_2O_2 as oxidant was studied as a function of time. As expected, only two products catechol and hydroquinone, as shown by equation 1, were detected with mass balance of >95%. Other products, if any, present as minor constituents could not be detected by the gas chromatograph under the conditions used herein and were neglected.

In order to achieve suitable reaction conditions for the maximum hydroxylation, the following parameters were studied in detail using [Cu(hybe)]-Y as a representative catalyst:

1. Effect of amount of catalyst per unit weight of phenol.



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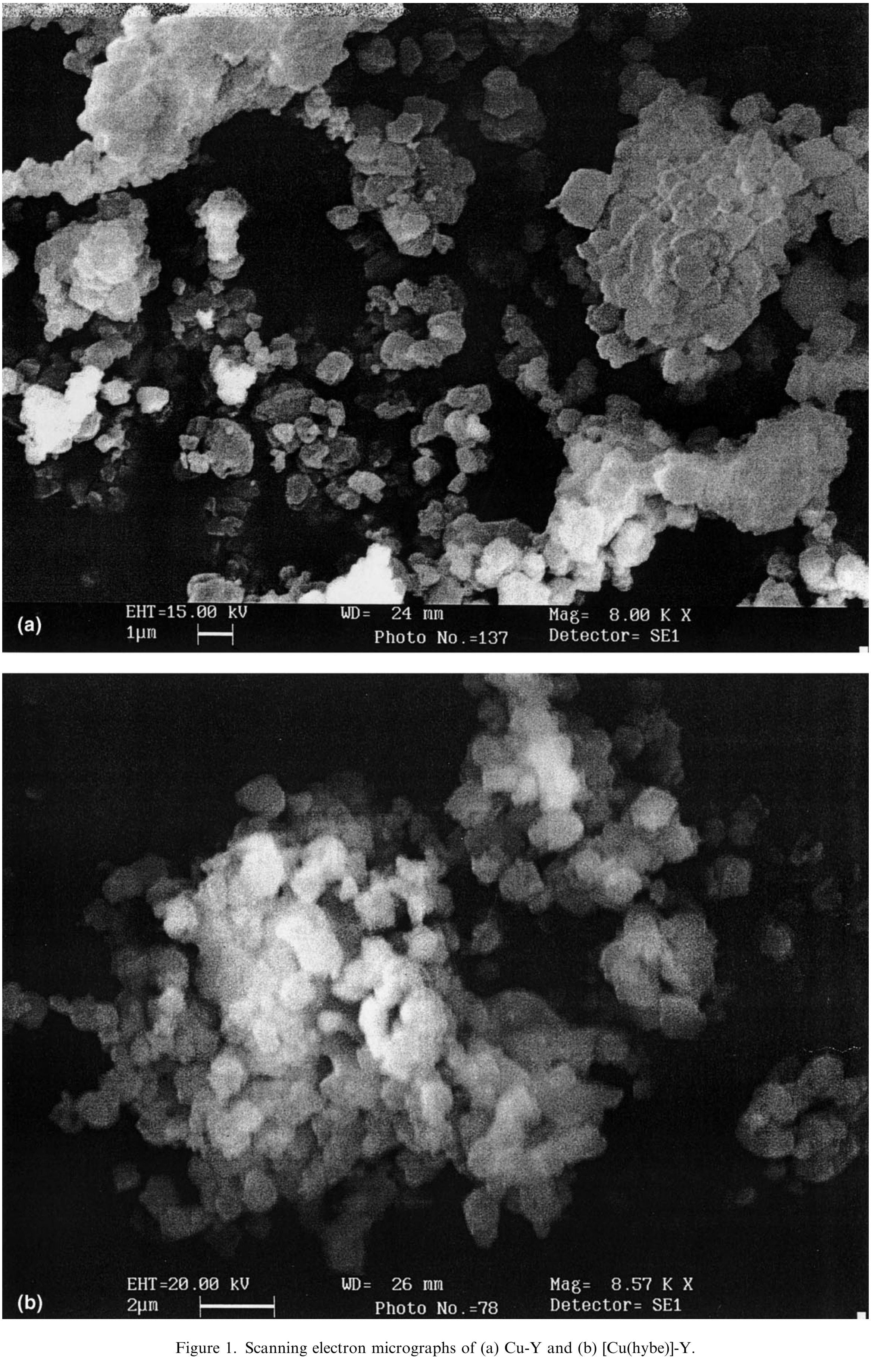

Figure 1. Scanning electron micrographs of (a) Cu-Y and (b) [Cu(hybe)]-Y.

Table 2
IR and electronic spectral data

Compound	IR frequency(cm^{-1})					λ_{max}(nm)
	v(NH)	Amide-I	Amide-II	Amide-III	v(M-N) / (M-O)	
H_2 hybe[a]	3377	1641	1547	1252	—	306.5, 240
[Cu(hybe)]-Y	3250	1635	1330	1247	428, 454, 468	209.5, 240, 306
[Ni(hybe)]-Y	3250	1636	1400	1248	406, 426, 462	213.5, 248, 304
[Zn(hybe)]-Y	3225	1641	1377	1251	416, 451, 468, 496	209.5, 240.5, 302.5

[a] Electronic spectrum recorded in methanol.

2. Effect of H_2O_2 concentration (moles of H_2O_2 per mole of phenol).
3. Effect of phenol concentration (moles of phenol per mole of H_2O_2).
4. Effect of temperature and volume of solvent.

The results of all these effects along with their possible explanations are summarized below:

(i) *Effect of amount of catalyst*

The effect of the amount of catalyst on the oxidation of phenol is presented in figure 4. Four different amounts *viz*. 5, 10, 25 and 40 mg were taken for the fixed amounts of phenol (4.7 g) and H_2O_2 (5.67 g) in 2 mL of MeCN at 80 °C. It was observed that increasing the amount of catalyst from 5 to 10 mg increases the rate of oxidation. Approximately 2 h is required to achieve ca. 32% conversion with 5 mg catalyst, while such conversion was achieved in 1 h using 10 mg catalyst. However, the total conversion was almost the same (36%) after 6 h reaction time. Increasing the amount of catalyst to 25 mg causes further increase in oxidation to ca. 40%, but no further improvement in the oxidation was achieved on increasing the amount of catalyst above 25 mg. This has been interpreted in terms of thermodynamic- and mass-transfer limitations at higher reaction rate.

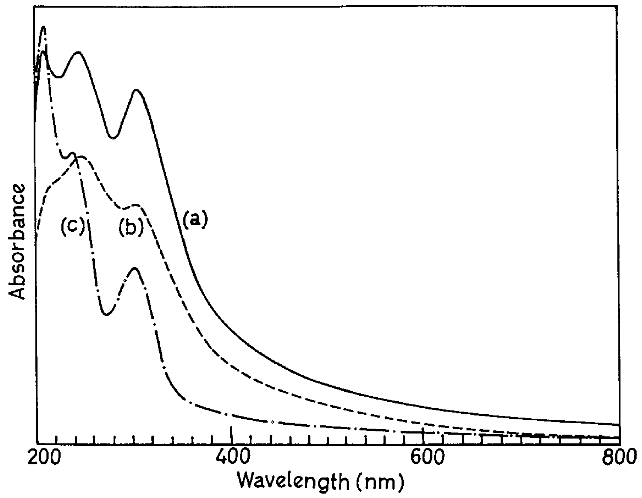

Figure 2. Electronic spectra of catalysts (a) [Cu(hybe)]-Y, (b) [Ni(hybe)]-Y, and (c) [Zn(hybe)]-Y.

(ii) *Effect of H_2O_2 concentration*

The different molar ratios of H_2O_2/phenol *viz*. 0.5 : 1, 1 : 1 and 2 : 1 were considered while keeping the fixed amounts of phenol (4.7 g, 0.05 mol) and catalyst (25 mg) in 2 mL of MeCN. The percent phenol conversion after 6 h reaction time has been compared in figure 5. It is evident from the figure that 1 : 1 and 2 : 1 molar ratios gave maximum percentage conversion of about 40 and 42%, respectively, in 6 h reaction time. However, the percentage H_2O_2 efficiency with 1 : 1 molar ratio is much better (~40%) than 2 : 1 molar ratio (~21%). These results suggest that 1 : 1 molar ratio is the minimum required condition for the effective oxidation of phenol along with better percentage H_2O_2 efficiency.

(iii) *Effect of phenol concentration*

In order to study the effect of phenol concentration, three different weights (molar ratios of phenol to H_2O_2): 2.35 g (0.5 : 1), 4.7 g (1 : 1) and 9.4 g (2 : 1) were considered while keeping other concentrations fixed (5.67 g H_2O_2, 0.025 g catalyst in 2 mL MeCN) at 80 °C. Figure 6 presents the results. It is clear from the results that molar ratio 1 : 2 gave slightly better phenol conversion (42%) than 1 : 1 ratio (40%). However, the percentage of H_2O_2 efficiency is just reverse and decreases considerably from 40% for 1 : 1 ratio to 21% for 1 : 2. In case of 9.4 g of phenol (i.e. 2 : 1 molar ratio), only 28% conversion with 56% H_2O_2 efficiency was recorded. The results thus reveal that the molar ratio of phenol to H_2O_2 must be kept at 1 : 1 to get maximum phenol conversion along with better selectivity of H_2O_2 conversion. The percentage hydroxylation is also higher with 1 : 1 ratio as it reaches about 33% within 60 min and a steady state in 6 h with 40% hydroxylation.

(iv) *Effect of temperature*

Figure 7 illustrates the hydroxylation of phenol at three different temperatures 50, 65 and 80 °C as a function of time while keeping the optimized conditions of 4.7 g phenol, 5.67 g H_2O_2 and 0.025 g catalyst in 2 mL MeCN as concluded above. It is evident from the figure

Table 3
Thermogravimetric analysis data of catalysts

Catalyst	Temperature range (°C)	Loss (Wt%)	Group lost[a]	Type of loss
[Cu(hybe)]-Y	150–270	16.0	n H_2O	Endothermic
	270–520	10.0	L	Exothermic
[Ni(hybe)]-Y	150–240	18.0	n H_2O	Endothermic
	240–575	12.0	L	Exothermic
[Zn(hybe)]-Y	150–215	22.0	n H_2O	Endothermic
	215–585	10.0	L	Exothermic

[a] L stands for hybe^{2-}.

that the performance of [Cu(hybe)]-Y catalyst is poor at 50 °C (33%) and improves partially at 65 °C (36%). At 80 °C, however, the performance is much better with 40% hydroxylation and reaches a steady state in about 6 h. Thus, conducting catalytic reaction at ca. 80 °C is the most suitable one to maximize the transformation of phenol.

The volume of solvent also influences the rate of the reaction. Increasing the volume of solvent or with no added solvent, the catalytic reaction always led to the poor performance.

3.6. Catalytic activity of other catalysts

After acquiring the optimized reaction conditions for [Cu(hybe)]-Y, other catalysts *viz.* [Ni(hybe)]-Y and [Zn(hybe)]-Y were also tested under these reaction conditions (i.e. 4.7 g phenol, 5.67 g H_2O_2 and 0.025 g catalyst and 2 mL MeCN at 80 °C) for the hydroxylation of phenol. The results of the performance are shown in figure 8. Under the optimized reaction conditions, [Ni(hybe)]-Y and [Zn(hybe)]-Y both have shown poor performance in the beginning. As time elapses, the former catalyst improves the conversion to 37% in 6 h, while the latter gives only 33% in the above stipulated time. Induction period in the plot for [Ni(hybe)]-Y and [Zn(hybe)]-Y indicates either slow formation of peroxo species or longer time taken to transfer oxygen to the substrate. The performance of [Cu(hybe)]-Y, on the other hand, is much better in comparison to the above two catalysts giving more than 33% conversion of phenol within 1 h of reaction time and reaching the

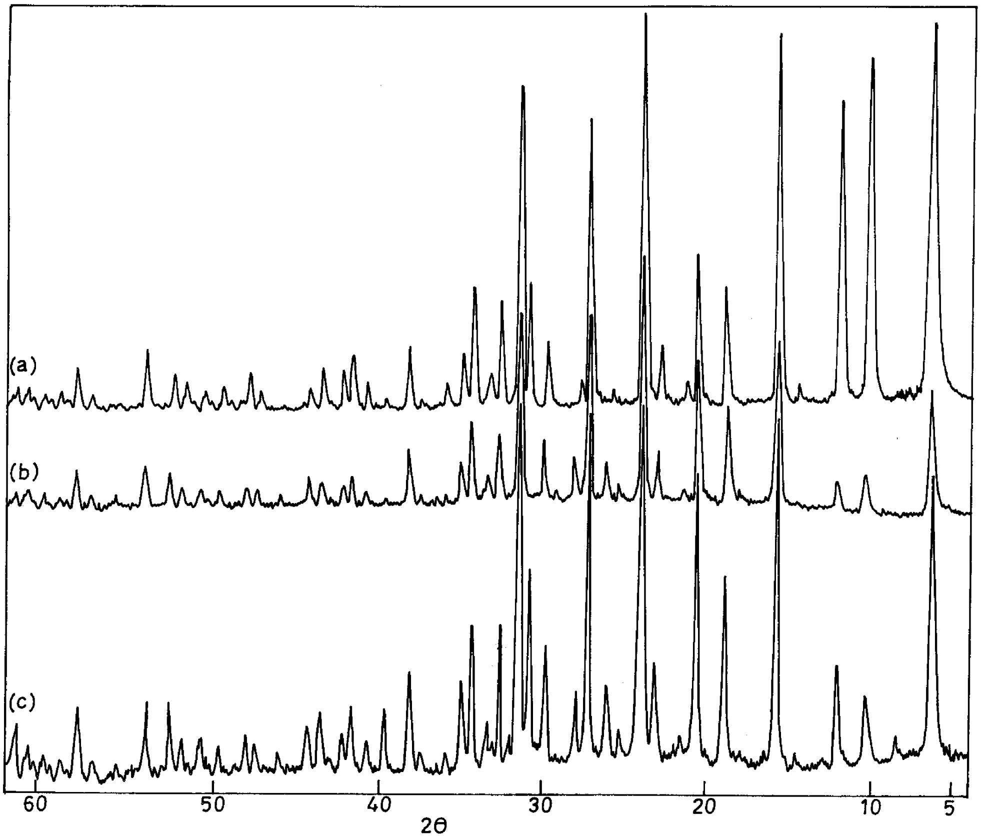

Figure 3. XRD patterns of (a) Na-Y, (b) Cu-Y and (c) [Cu(hybe)]-Y.

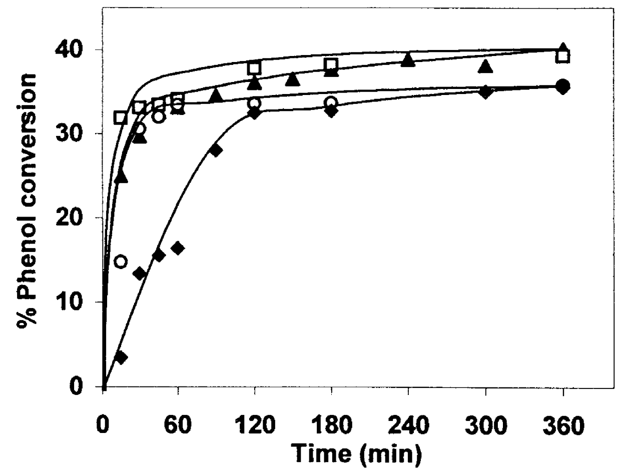

Figure 4. Effect of catalyst weight on phenol oxidation (-◆-) 5 mg, (-○-) 10 mg, (-▲-) 25 mg, (-■-) 40 mg.

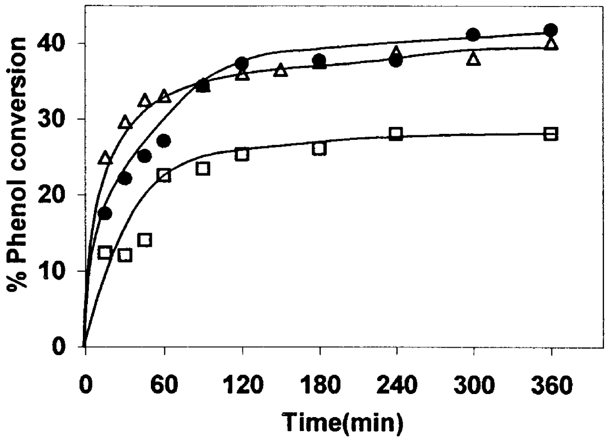

Figure 6. Effect of phenol concentration (phenol: H_2O_2 ratio) on phenol oxidation (-●-) 0.025 mol (0.5 : 1), (-△-) 0.05 mol (1 : 1), (-□-) 0.1 mol (2 : 1).

steady state in 6 h with a conversion of 40%. Thus, for the three catalysts the order of performance is as [Cu(hybe)]-Y > [Ni(hybe)]-Y > [Zn(hybe)]-Y. The reported range of percent phenol hydroxylation using various encapsulated zeolite catalysts is 5–35% [11–20]. The role of ligand is also an important factor as copper (II)-exchanged zeolite, Cu-Y, gives only a maximum of 15% hydroxylation in the presence of catalyst, while just 1% hydroxylation when reaction was carried out without using catalyst [32].

Though percent phenol hydroxylation with the catalysts reported here are at the upper side of the reported range, a further increment of hydroxylation appears to be influenced by clogging the pore system of zeolite with reaction products [33]. As the color of the reaction mixture in the experiment carried out here is light brown, the formation of a small amount of polymeric material seems to be likely. The poisoning of the catalyst by such polymeric products may also arise, as these materials would create partial hindrance for the substrate in approaching the catalyst sitting in the cavity of zeolite [34]. Interestingly, recycled catalysts after regeneration exhibit almost similar catalytic activity and this observation support above factors for limiting the conversion of phenol during catalytic hydroxylation.

The metal complexes encapsulated in zeolite-Y have been reported to yield catechol in much higher proportion in comparison to hydroquinone. The product selectivity of such molecular sieve–based catalysts is based on the shape and size of the product molecule. In terms of the formation of catechol and hydroquinone, all these catalysts reported here are also highly selective towards the formation of catechol and least selective for hydroquinone after 6 h of reaction time. Table 4 summarizes these results along with the Turnover Frequency (TOF) for phenol conversion after 6 h of reaction time and figure 9 presents all these results as a bar diagram. It is clear from the table that the selectivity

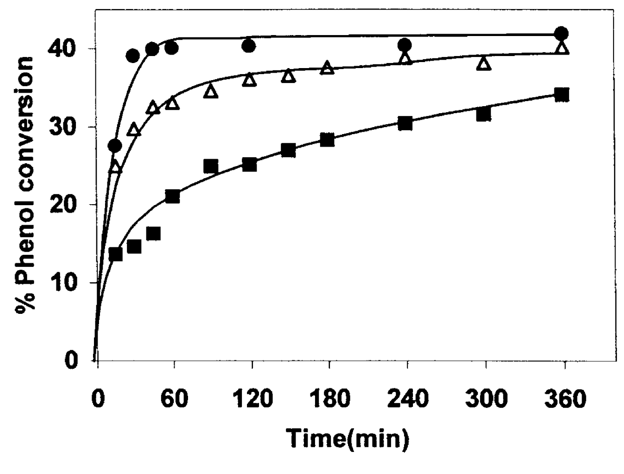

Figure 5. Effect of H_2O_2 concentration (phenol: H_2O_2 ratio) on phenol oxidation (-■-) 0.025 mol (1 : 0.5), (-△-) 0.05 mol (1 : 1), (-●-) 0.1 mol (1 : 2).

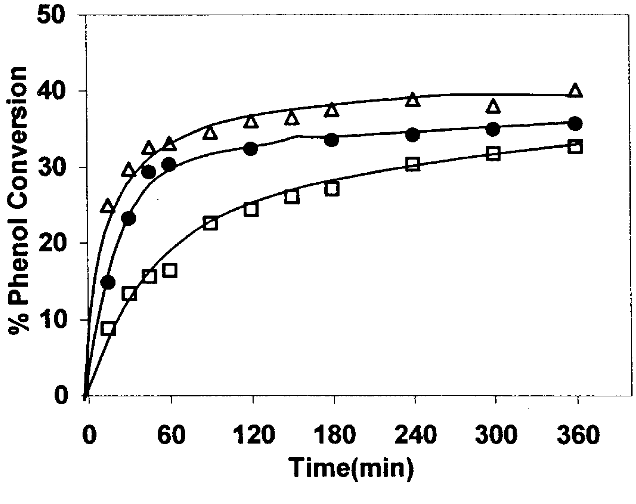

Figure 7. Effect of temperature on phenol oxidation (-□-) 50 °C, (-●-) 65 °C, (-△-) 80 °C.

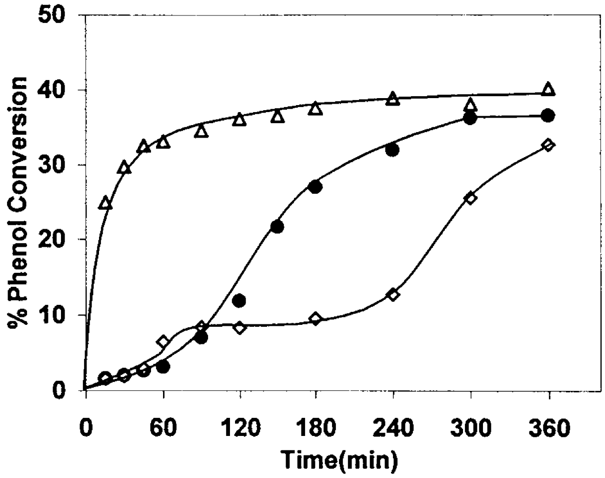

Figure 8. Kinetic plots of percentage phenol conversion (-△-) [Cu(hybe)]-Y, (-●-) [Ni(hybe)]-Y, (-◇-) [Zn(hybe)]-Y.

Table 4
Percent selectivity of catechol and hydroquinone formation and percent conversion of phenol after 6 h of reaction time

Catalyst	% Conversion	TOF h^{-1} [a]	% Selectivity	
			Catechol	Hydroquinone
[Cu(hybe)]-Y	40.14	201.5	90.9	9.1
[Ni(hybe)]-Y	36.5	279.1	90.4	9.6
[Zn(hybe)]-Y	32.66	513.5	89.0	11.0

[a] TOF h^{-1} (Turnover frequency) moles of substrate converted per mole of metal (in the solid-state catalyst) per hour.

of catechol formation is comparable (89–91%) in all cases, though the transformation of phenol varied from catalyst to catalyst. Interestingly, this high selectivity of catechol formation is maintained even after 24 h of reaction time.

As *m*-dihydroxybenzene is not detected in the product mixture, the involvement of hydroxyl radical as direct oxidizing agent is unlikely. The hydroxylation of phenol may involve the coordination of oxygen atoms at the vacant sites of the metal atom in the complex to form peroxo complex [35]. This intermediate transfers the coordinated oxygen atoms to the substrates to obtain the product. All these catalysts reported here can extend the vacant sites easily. Thus, the catalytic performance of the encapsulated complexes could be attributed to the formation of facile and reversible intermediate species. The hydroxylation of phenol may also proceed by an eletrophilic substitution mechanism that is common for the hydroxylation of phenol catalyzed by strong acids or organic peracids [15]. Masri and Hronec have suggested the formation of an intermediate ionic species $[M(Pc)(HOOH)^+]$ in case of phthalocyanine [36]. The activated hydrogen peroxide or peroxo metal complexes undergo heterolysis at the O–O bond and produce the ionic OH^+ attacking species, which in turn hydroxylate phenol via an electrophilic substitution mechanism at the *ortho* and *para* positions. The difference in the reactivity of the catalysts reported here is, thus, related to their ability to form intermediate acidic species.

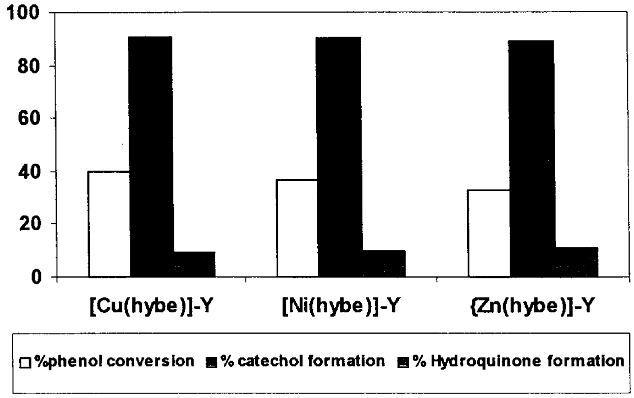

Figure 9. Bar diagram showing phenol conversion and catechol and hydroquinone formation for various catalysts.

4. Conclusion

Copper(II), nickel(II) and zinc(II) complexes of H_2hybe have been encapsulated in the super cages (α-cages) of zeolite-Y. Chemical analysis, spectroscopic studies and XRD as well as thermogravimetric pattern present clear evidence for the encapsulation. Among these catalysts, [Cu(hybe)]-Y catalyses the hydroxylation of phenol with very good yield of catechol, which is followed by [Ni(hybe)]-Y which in turn is better than [Zn(hybe)]-Y. The catalytic activities of these catalysts are only due to encapsulated complexes as no leaching of metal ions or metal complexes were detected in solution when blank reaction was carried out using 5.7 g H_2O_2, 0.025 g catalyst in 2 mL of MeCN at 80 °C for several hours. Under the best-suited reaction conditions, the selectivity of catechol formation is about 90% with all these catalysts. Such high selectivity has only been noticed with oxovanadium(IV) complexes with H_2salen family [20]. Other metal complexes with H_2salen family always gave mixtures of catechol and hydroquinone in nearly equal proportions. All these catalysts have been used twice again after recovering from reaction mixture, washing with acetonitrile and drying at 150 °C. The results reflect the reusability of the catalysts as not much loss in their catalytic activity was noticed.

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References

[1] C. Bowers and P.K. Dutta, J. Catal. 122 (1990) 271.
[2] P.-P. Knops-Gerrits, D.D. Vos, F. Thibaut-Starzk and P.A. Jacobs, Nature 369 (1994) 543.
[3] D.D. Agrawal, R.P. Bhatnagar, R. Jain and S. Srivastava, J. Chem. Soc., Perkin. Trans. 2 (1990) 989.
[4] K.J. Balkus Jr., A.K. Khanmamedova, K.N. Dixonnd and F. Bedioui, Appl. Catal., A: Gen. 143 (1996) 159.
[5] T. Joseph, S.B. Halligudi, C. Satyanarayan, D.P. Sawant and S. Gopinathan, J. Mol. Catal. A: Chem. 168 (2001) 87.
[6] T. Joseph, D.P. Sawant, C.S. Gopinath and S.B. Halligudi, J. Mol. Catal. A: Chem. 184 (2002) 289.
[7] S.P. Varkey and C.R. Jacob, Indian J. Chem. 37A (1998) 407.
[8] K.J. Balkus Jr., M. Eissa and R. Levado, J. Am. Chem. Soc. 117 (1995) 10753.
[9] R. Raja and P. Ratnasamy, Catal. Lett. 48 (1997) 1.
[10] C. Ratnasamy, A. Murugkar, S. Padhye and S.A. Pardhy, Indian J. Chem. 35A (1996) 1.
[11] K.J. Balkus Jr. and A.G. Gabrielov, J. Inclusion Phenom. Mol. Recognit. Chem. 21 (1989) 159.
[12] R. Raja and P. Ratnasamy, Stud. Surf. Sci. Catal. 101 (1996) 181.
[13] R. Raja and P. Ratnasamy, Appl. Catal. A: Gen. 143 (1996) 145.
[14] C.R. Jacob, S.P. Varkey and P. Ratnasamy, Appl. Catal. A: Gen. 168 (1998) 353.
[15] C.R. Jacob, S.P. Varkey and P. Ratnasamy, Microporous Mesoporous Mater. 22 (1998) 465.
[16] T. Joseph, C.S. Sajanikumari, S.S. Deshpade and S. Gopinathan, Indian J. Chem. 38A (1999) 792.
[17] S. Deshpande, D. Srinivas and P. Ratnasamy, J. Catal. 188 (1999) 261.
[18] S. Chavan, D. Srinivas and P. Ratnasamy, J. Catal. 192 (2000) 286.
[19] S. Seelan, A.K. Sinha, D. Srinivas and S. Sivasanker, Bull. Catal. Soc. India 1 (2002) 29.
[20] M.R. Maurya, M. Kumar, S.J.J. Titinchi, H.S. Abbo and S. Chand, Catal. Lett. 86 (2003) 97.
[21] W. Zhang, J.L. Loebach, S.R. Wilson and E.N. Jacobson, J. Am. Chem. Soc. 112 (1990) 2801.
[22] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[23] R.A. Sheldon and R.A. Vansanten, *Catalytic Oxidation: Principles and Applications* (World Scientific, Singapore, 1995).
[24] Industrial organic chemicals: starting materials and intermediates, *An Ullamann's Encyclopaedia* Vol. 6 (Wiley-VCH, New York, 1999).
[25] A. Thangaraj, R. Kumar and P. Ratnasamy, J. Catal. 131 (1991) 294.
[26] V. Rives, A. Dube and S. Kannan, Phys. Chem. Chem. Phys. 3 (2001) 4826.
[27] H. Zhang, X. Zhang, Y. Ding, L. Yan, T. Ren and J. Suo, New J. Chem. 26 (2002) 376.
[28] R.J. Mahalingam, S. Bodamali and P. Selvam, Chem. Lett. 11 (1999) 1141.
[29] K. Takai, Y. Shimashaki, T. Shishido and K. Takehira, Bull. Chem. Soc. Jpn. 75 (2002) 311.
[30] A.C. Dash and A. Mishra, Indian J. Chem. 37A (1998) 961.
[31] M.R. Maurya, Coord. Chem. Rev. 237 (2003) 163.
[32] M.R. Maurya, S.J.J. Titinchi and S. Chand, Appl. Catal. A: Gen. 228 (2002) 177.
[33] F. Bedioui, Coord. Chem. Rev. 144 (1995) 39.
[34] J. Sun, X. Meng, Y. Shi, R. Wang, S. Feng, D. Jiang, R. Xu and F.-S. Xiao, J. Catal. 193 (2000) 199.
[35] R.A. Sheldon and J.K. Kochi, *Metal-Catalysed Oxidations of Organic Compounds* (Academic Press, New York, 1981).
[36] Y. Masri and M. Hronec, Stud. Surf. Sci. Catal. 66 (1991) 455.