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Synthesis, characterization and catalytic behaviour of entrapped transition metal complexes into the zeolite Y

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ABSTRACT

Zeolites encumbered with transition metal ions are promising heterogeneous catalysts. Knowledge about the location and structure of the metal centers is of paramount importance for the understanding of the catalytic potential of these materials. A series of entrapped transition metal complexes in the nanopores of zeolite-Y of the type [M(EVTCH)$_2$]-Y [where M = Mn(II), Co(II), Ni(II) and Cu(II); ethylvanillin thiophene-2-carboxylic hydrazone (EVTCH)] have been synthesized by Flexible Ligand Method (FLM). These materials have been characterized by various physico-chemical techniques such as ICP-OES, GC-MS, elemental analyses, (FT-IR, ^{1}H- and ^{13}C-NMR and electronic) spectral studies, BET, scanning electron micrographs (SEMs) as well as X-ray diffraction patterns (XRD). The catalytic significance of these materials has been carried out over the liquid-phase hydroxylation of phenol with 30 % H_2O_2 to give catechol as a major product and hydroquinone as a minor product. Copyright © 2012 VBRI Press.

Keywords: Zeolite-Y; flexible ligand method; catalytic hydroxylation of phenol.

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Introduction

Zeolites have a microporous system defining large cavities interconnected by smaller windows. These nano pores can accommodate large molecules whose size, however, can be too big to cross the windows. The most important examples of these tridimensional zeolites are faujasites X and Y **[1-3]**. The inclusion of large guests inside the cavities starts from smaller precursors such as transition metal ions that can diffuse through the zeolite pores via ion-exchange process and then react with Schiff base ligand inside the cavities to form the target guest. A system that has vast potential for application in catalysis as well as for nanotechnology is that in which a functional guest is enslaved within the zeolite nano cages exclusive of diffusing out of the particle **[4, 5]**. There are a number of reviews summarizing the use of zeolite encapsulated coordination complexes as oxidation catalysts **[6, 7]**. The use of these encapsulated complexes as nanocatalysts can enhance and increase the selectivity in the oxidation reaction. TS-1 and TS-2 showed the phenol hydroxylation with low concentration of H_2O_2 (30%) in the reaction **[8, 9]**.

In continuation of our earlier work [**10, 11**], this paper describes the preparation and characterization of entrapped transition metal complexes in the nanopores of zeolite-Y and their use in the hydroxylation of phenol as catalysts for the formation of catechol (CAT) and hydroquinone (HQ). These are very important organic intermediates and chemical materials which are utilized to synthesize the drugs, dye, polymerization inhibitors, perfumes, cocatalysts and so on. Up to now, hydroxylation of phenol with hydrogen peroxide as the oxidant has becomes the most general way to obtain diphenols; owing to its environmental acceptability. The potential benefits of this study are (1) to produce novel zeolite-Y encapsulated transition metal complexes with EVTCH Schiff base ligand by flexible ligand method (FLM), (2) to characterize these synthesized encapsulated complexes by various physico-chemical techniques and (3) to screen the encapsulated complexes for their catalytic aspects over liquid-phase hydroxylation of phenol.

Experimental

Instrumentation

The Si, Al, Na and transition metal ions in the encapsulated hybrid materials were determined by ICP-OES (Model: PerkinElmer optima 2000 DV). Carbon, hydrogen, and nitrogen were analyzed with a Perkin Elmer, USA 2400-II CHN analyzer. UV/Visible spectra were recorded on Spectrophotometer Make/model Varian Cary 500, Shimadzu. IR spectra of encapsulated hybrid materials were recorded on a Thermo Nicolet IR200 FT-IR spectrometer in KBr. The surface area of encapsulated hybrid materials was measured by multipoint BET method using ASAP 2010, micrometrics surface area analyzer. The structural crystallinity of compounds was ensured by XRD using a Bruker AXS D_8 Advance X-ray powder diffractometer with a Cu Kα target [**12**]. The GC-MS of Schiff base ligands were recorded on a model Shimadzu, QP-2010 equipped with a RTX-5 column. ^{1}H- & ^{13}C-NMR spectrum of Schiff base ligands were recorded on a model Advance 400 Bruker FT-NMR instrument and DMSO-d_6 used as a solvent. The scanning electron micrographs of encapsulated hybrid materials were recorded using a SEM instrument (Model: LEO 1430 VP). The compounds were coated with a thin film of gold before recording the SEM to protect surface material from thermal damage by the electron beam.

Synthesis and physicochemical data of schiff base ligand ethylvanillin thiphene-2-carboxylic hydrazone (EVTCH)

The Schiff base ligand EVTCH **(Fig. 1)** was synthesized by the condensation of ethylvanillin with thiphene-2-carboxylic acid hydrazide. An amount of 1.42 g of thiphene-2-carboxylic acid hydrazide (10.0 mmol) was dissolved in 25 ml of ethanol, and then transferred into a 250 ml three necked flask. Under reflux, 1.66 g (10.0 mmol) of ethylvanillin in 25 ml of ethanol was added drop-wise to the flask. The stirred mixture was kept reacting for 45 min under reflux, then cooled to room temperature. The solid mass was filtered, and the product, ethylvanillin thiphene-2-carboxylic hydrazone (EVTCH), was recrystallized from ethanol and vacuum-dried for 2 h. Yield, 76%; m.p. 202 °C. Found (%): C, 57.92; H, 4.86; N, 9.65; S, 11.04. $C_{14}H_{14}N_2O_3S$ requires (%): C, 57.92; H, 4.86; N, 9.65; S, 11.04. m/z: 290.0, 163.1, 135.1, 126.1, 111.0, 94.1. ^{1}H NMR (400MHz, DMSO-d_6): δ 1.37 (3H, s, $-OCH_2-\underline{CH_3}$), 4.11 (2H, s, $-O\underline{CH_2}-CH_3$), 7.09-7.15 (3H, m, Ar-H), 7.17-7.29 (3H, m, Thiophene-H), 7.40 (1H, s, -NH), 11.67 (1H, s, -OH), 9.48 (1H, s, -CH=N); ^{13}C-NMR (400MHz, DMSO-d_6): δ (ppm) = 15.1 (C_{19}), 64.9 (C_{20}), 111.6 (C_4), 116.0 (C_1), 122.0 (C_6), 129.1 (C_{14}), 129.7 (C_{15}), 131.9 (C_{13}), 130.7 (C_5), 138.9 (C_{11}), 146.1 (C_7), 148.6 (C_3), 149.7 (C_2), 161.5 (C_{10}).

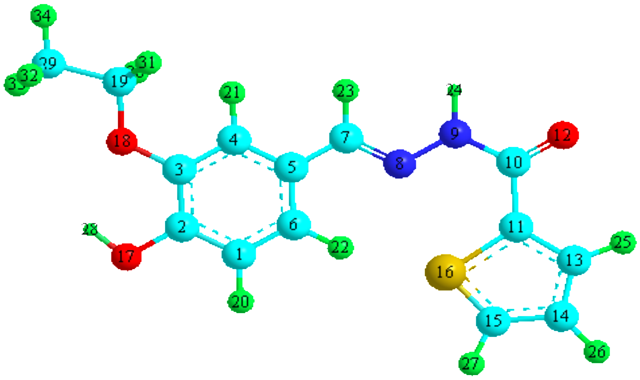


Fig. 1. The structure of Schiff base ligand ethylvanillin thiphene-2-carboxylic hydrazone (EVTCH).

Synthesis of zeolite-Y encapsulated [M(EVTCH)$_2$]-Y

A series of zeolite-Y encapsulated [M(EVTCH)$_2$]-Y have been prepared by Flexible Ligand Method (FLM) **[13]**. An amount of 5.0 g of Na-Y zeolite was suspended in 300 mL of deionized water containing 12 mmol metal salt ($Mn(CH_3COO)_2\cdot4H_2O$, $Co(CH_3COO)_2\cdot4H_2O$, $Ni(CH_3COO)_2\cdot4H_2O$ and $Cu(CH_3COO)_2\cdot H_2O$, respectively) heated at 90 °C with constant stirring (24 hr) 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 15 h at 150 °C in air.

In the next step, 1.0 g of M^{II}-Y was uniformly mixed with an excessive amount of EVTCH ligand (n_{ligand}/n_{metal} = 3) in ethanol, and sealed into a round bottom flask. The reaction mixture was refluxed (~24 h) in an oil bath with stirring. The resulting material was taken out, 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 zeolite. The extracted sample was ion-exchanged with 0.01 M NaCl aqueous solution for 24 h to remove uncoordinated M^{II} ions, followed by washing with deionized water until no Cl^- ion could be detected with $AgNO_3$ solution. The product [M(EVTCH)$_2$]-Y was collected and dried at 120 °C.

Results and discussion

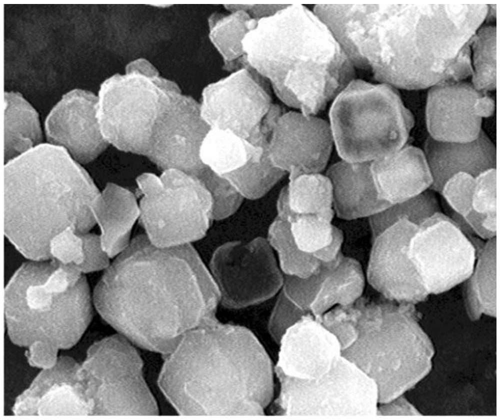
Morphological and textural properties of materials

The chemical analyses of the neat zeolite-Y and zeolite-Y encapsulated complexes reveal the presence of organic matter. Moreover, the Si/Al ratio is 2.60 for the neat zeolite-Y, indicating no dealumination during the encapsulation by FLM. The surface area and pore volume values estimated by nitrogen adsorption isotherms are given in **Table 1**. The results exhibited a great decrease of the surface area and pore volume of zeolite-Y on encapsulation of metal complexes, which show the presence of complexes inside the nanovoids of zeolite-Y **[14]**.

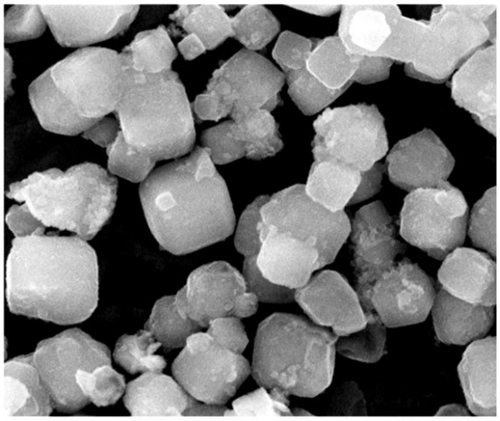
Table 1. Surface area and pore volume data of compounds

Compounds	Surface area (m^2/g)	Pore volume (cc/g)[a]
Na-Y	548	0.32
Mn^{II}-Y	538	0.29
[$Mn(EVTCH)_2$]-Y	290	0.20
Co^{II}-Y	530	0.30
[$Co(EVTCH)_2$]-Y	282	0.19
Ni^{II}-Y	527	0.30
[$Ni(EVTCH)_2$]-Y	279	0.18
Cu^{II}-Y	534	0.31
[$Cu(EVTCH)_2$]-Y	273	0.15

[a] Calculated by the BJH-method



(A) Before soxhlet extraction



(B) After soxhlet extraction

Fig. 2. SEM images of [$Mn(EVTCH)_2$]-Y (A) before and (B) after soxhlet extraction

Fig. 2 presents the scanning electron micrographs (SEMs) of [$Mn(EVTCH)_2$]-Y recorded before and after Soxhlet extraction. It is clear from the well defined crystals after Soxhlet extraction and the particle boundaries on the external surface of zeolite-Y are distinguishable. It reveals the efficiency of purification procedure to effect complete removal of extraneous complexes, leading to the presence of well-defined encapsulation in the cavity.

The powder X-ray diffraction patterns (XRD) of [$M(EVTCH)_2$]-Y were recorded at *2θ* degree between 10 and 70 are presented in **Fig. 3**. Essentially similar diffraction patterns were observed for all the encapsulated complexes, except little change in the relative peak intensities. This indicates that the crystallinity of the zeolitic matrix remained intact and not suffers any major structural modifications upon encapsulation of the metal complex. This is further supported by the SEMs analysis that all the [$M(EVTCH)_2$]-Y have retained the crystallinity of the zeolite-Y.

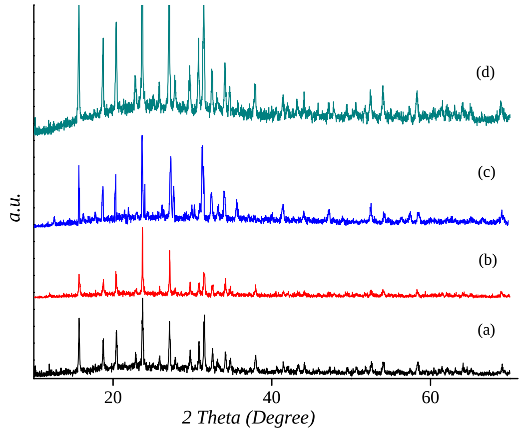


Fig. 3. XRD of (a) [$Mn(EVTCH)_2$]-Y (b) [$Co(EVTCH)_2$]-Y, (c) [$Ni(EVTCH)_2$]-Y and [$Cu(EVTCH)_2$]-Y.

Spectroscopic characterization

FT-IR spectral data of Schiff base (EVTCH) containing ν(N-H) and ν(C=O) **[15]** mode of the lateral chain appeared at 3189 and 1695 cm^{-1}, respectively indicates that the ligand exist in keto form in the solid state **[16]**. However, these bands are absent in the spectra of zeolite-Y encapsulated complexes and a new band observed at 1310-1323 cm^{-1} due to ν(C-O) **[17, 18]**. From these observations, it is concluded that the ligand reacts in enol form with prototropy, via proton transfer through oxygen atom forming bond with the metal ion. The sharp and strong band is observed at 1633 cm^{-1} due to ν(C=N) of azomethine group of the lateral chain. This band is appeared at ~1622-1636 cm^{-1} in the spectra of encapsulated complexes that suggests the coordination of azomethine nitrogen **[19]**. The framework vibration bands of zeolite-Y show the spectra below 1200 cm^{-1} in the regions 569-578, 713-788 and 1019-1127 cm^{-1}, which are attributed to double ring, symmetric stretching and asymmetric stretching vibrations, respectively **[20]**. No shift is observed upon introduction of metal ions and inclusion of metal complexes, further substantiating that the zeolite-Y framework remains unchanged.

The electronic spectral bands of Schiff base ligand EVTCH and there encapsulated complexes are discussed. In the exploited wavelength domain from 200 to 800 nm, the electronic spectra of Schiff base showed a highly intense band at ~324 nm due to intra-ligand charge transfer transitions ($\pi \rightarrow \pi^*$). However, this band has undergone bathochromic shifts in Mn(II) and hypsochromic shifts in Co(II) and Ni(II) encapsulated complexes resulting from the chelation of the ligand with the transition metal ions. As expected for Mn(II) encapsulated complex, *d-d* transition bands are not observed in dilute solution because of their being doubly forbidden. The spectra of Co(II) encapsulated complex show two additional absorption bands at ~267 nm attributed to the MLCT transition, concordant with square-planar structure **[21]**. Square-planar d^8 metal complexes are characterized by three spin allowed *d-d* bands, $d_{xy}(b_{1g})\rightarrow d_{x^2-y^2}(b_{1g})$, $d_{z^2}(a_{1g})\rightarrow d_{x^2-y^2}(b_{1g})$ and $d_{xz,yz}(e_g)\rightarrow d_{x^2-y^2}(e_g)$ corresponding to $^1A_{1g}\rightarrow{}^1A_{2g}$ (ν_1), $^1A_{1g}\rightarrow{}^1B_{1g}$ (ν_2) and $^1A_{1g}\rightarrow{}^1E_g$ (ν_3) transitions **[22]**. Of the three expected low energy ligand field (*d-d*) bands, corresponding to transitions from the three lower d-levels to the empty $d_{x^2-y^2}$ orbitals, only one is observed in the visible spectra of [Ni(EVTCH)$_2$]-Y near 644 nm. This may be assigned to $^1A_{1g}\rightarrow{}^1A_{2g}$ (ν_1) transition of Ni(II) in square-planar structure. The weak band observed near 401 nm for Cu(II) encapsulated complex assigned to $^2B_{1g}\rightarrow{}^2E_g$ transition of square-planar geometry **[23]**.

Catalytic activity studies

The catalytic hydroxylation of phenol was undertaken in a two-necked 50 mL round bottomed flask. In a typical reaction, 30 mmol of the substrate was taken in 2 mL of acetonitrile, add 60 mg of the catalyst to it and equilibrated at 80 °C in an oil-bath. 45 mmol of 30% H_2O_2 solution was added to this with continuous stirring for 6 h and their results are given in **Table 2**. Blank experiments were performed without catalyst or with Na-Y zeolite show a lesser amount of % conversion. The products were collected at different time intervals and were identified and quantified by GC.

Table 2. Hydroxylation of phenol to catechol and hydroquinone with 30% H_2O_2 catalyzed by zeolite-Y encapsulated complexes.

Sr. No.	Compounds	Conversion (%)	Selectivity (%)	
			Catechol	Hydroquinone
1.	[Mn(EVTCH)$_2$]-Y	14.2	55.1	44.9
2.	[Co(EVTCH)$_2$]-Y	29.8	72.4	27.6
3.	[Ni(EVTCH)$_2$]-Y	20.6	59.8	40.2
4.	[Cu(EVTCH)$_2$]-Y	40.3	79.5	20.5
5.	[Cu(EVTCH)$_2$]-Y^a	38.9	77.4	22.6
6.	[Cu(EVTCH)$_2$]-Y^b	36.6	75.1	24.9
7.	Na-Y	3.1	44.3	55.7

^{a}First reused catalyst ^{b}Second reused catalyst

Fig. 4 summarizes the percentage conversion of phenol along with catechol and hydroquinone formations. It is clear from the results that the selectivity of catechol formation found to be varied (55-80%) from catalyst to catalyst. The conversion (%) of phenol increases in the order: [Cu(EVTCH)$_2$]-Y > [Co(EVTCH)$_2$]-Y > [Ni(EVTCH)$_2$]-Y > [Mn(EVTCH)$_2$]-Y towards the formation of catechol selectively. In order to achieve suitable reaction conditions for the maximum hydroxylation, the parameters such as (I) Effect of amount of catalyst and (II) Effect of temperature were studied using [Cu(EVTCH)$_2$]-Y as a representative catalyst. The results of these effects along with their possible explanations are summarized below:

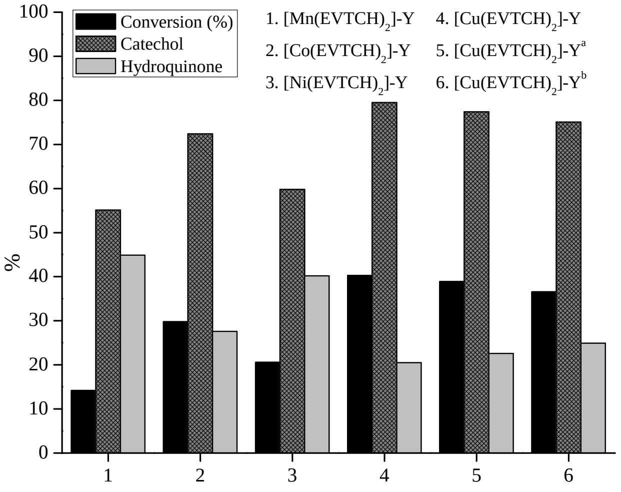


Fig. 4. Catalytic % conversion of phenol to catechol and hydroquinone.

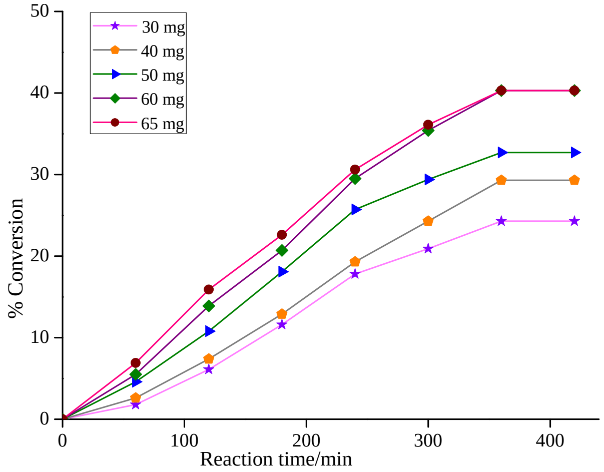


Fig. 5. Effect of amount of catalyst on phenol hydroxylation.

Effect of amount of catalyst

The amount of catalyst has a significant effect on the hydroxylation of phenol. Five different amounts of [Cu(EVTCH)$_2$]-Y catalyst viz., 30, 40, 50, 60 and 65 mg were used, keeping with all other reaction parameters fixed: namely temperature (80 °C), phenol (30 mmol), 30% H_2O_2 (45 mmol) in acetonitrile (2 mL) and reaction time (6 h). The results are shown in **Fig. 5** indicating 24.3, 29.3, 32.7, 40.3 and 40.3% conversion corresponding to 30, 40, 50, 60 and 65 mg catalyst, respectively. Lower conversion of phenol with 60 and 65 mg catalyst may be due to fewer catalytic sites. The greater conversion percentage was observed with 60 mg catalyst but there was no remarkable difference in the progress of reaction when 65 mg of catalyst was employed. Therefore, 60 mg amount of catalyst was taken to be optimal.

Effect of temperature

Similarly, for four different temperatures viz. 60, 70, 75 and 80 °C, the effect of temperature on the hydroxylation of phenol **(Fig. 6.)** was examined at under the above reaction conditions, phenol (30 mmol), 30% H_2O_2 (45 mmol), catalyst (60 mg) in acetonitrile (2 mL) for 6 h. The result reveals that on increasing the temperature from 60 to 80 °C, the improvements was observed and further no change in percentage conversion of hydroxylation of phenol for more than 80 °C. Consequently at 80 °C for 6 h time is considered to be the optimum.

Test for recyclability

[Cu(EVTCH)$_2$]-Y was recycled for the catalytic hydroxylation of phenol as a representative catalyst to found the effect of encapsulation on stability. The initial run demonstrates a conversion of 40.3% and it slightly abridged to 38.9 and 36.6% after first and second recycling the catalyst, respectively. These results confirm that [Cu(EVTCH)$_2$]-Y catalyst is almost stable to be recycled for the hydroxylation of phenol without much loss in activity. Accordingly, the encapsulation of metal complexes inside the nanocavity of zeolite-Y is found to boost the life of catalyst by reducing dimerization due to restriction of internal framework structure.

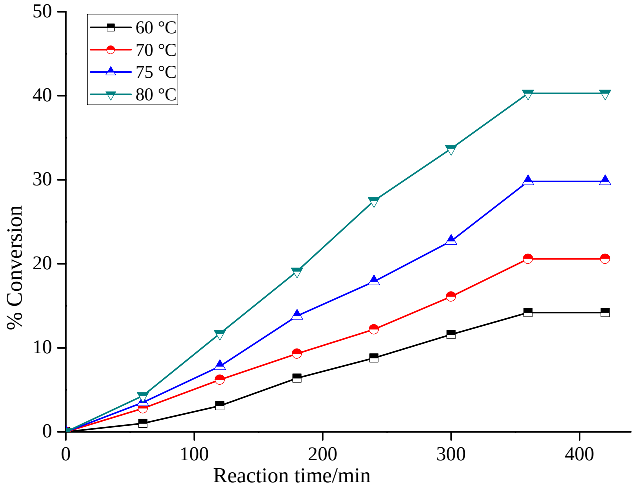


Fig. 6. Effect of temperature on phenol hydroxylation.

Conclusion

The results obtained in this study allow the following conclusions:

A series of [M(EVTCH)$_2$]-Y complexes [where, M = Mn(II), Co(II), Ni(II) and Cu(II)] have been successfully synthesized by flexible ligand method, as evidenced by ICP-OES, elemental analyses, (FT-IR and electronic) spectral studies, BET, SEMs and X-ray diffraction patterns results.

The catalytic behaviour of entrapped transition metal complexes were performed over the hydroxylation of phenol affording catechol and hydroquinone, with good catechol selectivity in the order: [Cu(EVTCH)$_2$]-Y > [Co(EVTCH)$_2$]-Y > [Ni(EVTCH)$_2$]-Y > [Mn(EVTCH)$_2$]-Y. This shows that [Cu(EVTCH)$_2$]-Y catalyst has the highest % of selectivity towards catechol (79.5%).

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