

Hydroxylation of Phenol with H_2O_2 over Transition Metal Containing Nano-sized Hollow Core Mesoporous Shell Carbon Catalyst

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Abstract—The catalytic performance of transition metal (Fe^{2+} or Cu^{2+}) containing nano-sized hollow core mesoporous shell carbon (HCMSC) heterogeneous catalysts for the hydroxylation of phenol with hydrogen peroxide (H_2O_2) in water was investigated in a batch reactor. The metal-containing HCMSC catalyst showed higher activity than the same metal ion-exchanged zeolites. The nature of the metal and its content in the HCMSC had remarkable influence on the reaction results under the typical reaction conditions ($PhOH/H_2O_2=3$, reaction temperature=60 °C). Fe^{2+} containing HCMSC catalyst showed high catalytic activity with phenol conversion of 29%, selectivity to catechol (CAT) and hydroquinone (HQ) about 85%, H_2O_2 effective conversion about 70% and selectivity to benzoquinone (BQ) below 1% in the batch system.

Key words: Hydroxylation, Phenol, Hydrogen Peroxide, Catechol, Carbon Capsule

INTRODUCTION

Catechol and hydroquinone are two of the many high value phenolic derivatives. They are widely used as photography chemicals, antioxidants and polymerization inhibitors, and also in pesticides, flavoring agents, and medicine. There has also been interest in producing the dihydroxybenzenes directly by hydroxylation of phenol with the environmentally benign oxidant, H_2O_2 . Mineral acids [Bourdine et al., 1969; Varagnat, 1976], simple metal ions [Hamilton et al., 1966; Brook et al., 1982] and metal complexes [Chioccarelli et al., 1991] have been the traditional catalysts for this reaction, but these homogeneous catalysts are difficult to separate and recover from the reaction mixture for recycling. This problem therefore limits their practical use in industry. Therefore, heterogeneous catalysis involving various metal oxides and complexes has been of great interest for many researchers for a long time. In this context, pure metal oxides or supported ones [Goldstein et al., 1994], complex metal oxides [Yu et al., 1999; Sun et al., 2000], zeolite-encapsulated metal complexes [Maurya et al., 2002] and hydrotalcite-like compounds [Dubey et al., 2002] are worthy of note for the title reaction. However, most of these catalysts show either low catalytic activity or unsatisfied product selectivity, and some of them require very complicated synthesis routes. Although some transition metal framework-substituted zeolites have high activity, selectivity and stability in phenol hydroxylation, their somewhat complicated synthesis conditions, high cost and low reaction rate again limit their commercial applications. Some metal modified mesoporous materials, MCM-41 and MCM-48, have also been used as target catalysts with the aim of accelerating the reaction rate of phenol hydroxylation [Lee et al., 2001; Norena-Franco et al., 2002]. Some novel heterogeneous catalysts, such as copper hydroxylphosphate

[Xiao et al., 2001] and Group VIII metal heteropoly compounds [Kuznetsova et al., 2004] have also been investigated for this reaction recently. We have recently reported Fe^{2+} , Co^{2+} ion-exchanged Na β zeolite catalyst, as an active candidate for phenol hydroxylation with H_2O_2 at room temperature [Wang et al., 2003]. Cu^{2+} ion-exchanged zeolites such as NaY, HY, USHY, H β and HZSM-5 showed good performance in phenol hydroxylation with H_2O_2 at various reaction conditions [Wang et al., 2004]. Up to now, most of the previous works have been oriented towards studies within zeolites framework. But, in this work, we report the results of the catalytic activity of new Fe^{2+} and Cu^{2+} supported on heterogeneous framework, nano-sized HCMSC, and compare the same with zeolites for hydroxylation of phenol with H_2O_2 in aqueous solution at atmospheric pressure.

EXPERIMENTAL

1. Preparation of Catalyst

HCMSC was prepared by adopting a procedure reported in the literature [Yoon et al., 2002]. It was treated with an aqueous solution of $Fe(SO_4)_2 \cdot 7H_2O$ (Aldrich, G. R. purity) with the liquid/solid weight ratio of 0.5, 1.5 and 2.5 by stirring the mixture at 70 °C for 5 h. The suspension was filtered, washed with water, and dried at 120 °C for 8 h. Cu^{2+} containing HCMSC was prepared by the similar method using $Cu(NO_3)_2 \cdot 3H_2O$ (Aldrich, G. R. purity). The metal content in the solid powders was analyzed by an inductively coupled plasma emission (ICPE) spectrometer (J. Y. Ultima C, Jobin Yvon) according to the literature [Evmerides and Dwyer, 1982].

2. Catalytic Tests

The catalytic studies of the metal containing HCMSC for phenol hydroxylation with H_2O_2 were carried out in a 1 L four-necked round bottom flask, a batch reactor, equipped with a magnetic stirrer, a reflux condenser and a temperature controlled heating mantle. 100 g of Phenol (Kumho P&B Chem., Inc.) was dissolved in 500 mL distilled water, and 2 g of the catalyst was added to it. After the desired

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temperature was reached, 25 g of aqueous H_2O_2 solution (50 wt%, DC Chem. Co., Ltd.) was added dropwise into the reaction mixture by using a syringe pump for 30 min. The product was sampled periodically at the end of every 60 min, and both the reactants and products were analyzed by high-performance liquid chromatography (HPLC, Shimadzu, LC-10ADVP, equipped with a RP, C18 column) using 4-fluorophenol as the external standard, and UV/Vis as the detector (ICI, LC1200). Besides the target products, CAT, HQ, 1,4-benzoquinone (BQ) and by-Products (BPs), such as maleic acid, acrylic acid and acetic acid, oligomerization products were also detected.

RESULTS AND DISCUSSION

The results of the characterization of the catalysts used in this study are summarized in Table 1. ICP-AES analysis shows a similar copper or iron content in the HCMSC as used in the experiment. Hence, the HCMSC is capable of entrapping and holding the whole metal from aqueous solution in its porous framework. Typical physical properties of nano-sized HCMSC are as follows: outer diameter of 500 nm, shell thickness of 90 nm, surface area of 1,230 m^2/g , pore volume of 1.27 cm^3/g and average pore diameter of 4 nm [Lee et al., 2005; Yoon et al., 2002]. In this work, the surface areas of HCMSC and metal containing HCMS are in the range of

Table 1. Metal content and surface area of catalysts

Sample	Cu or Fe content (wt%)	BET surface area (m^2/g)	Av. pore volume (cm^3/g)
HCMSC	-	1,270	1.27
Cu(1.5)-HCMSC	1.51	1,210	1.21
Fe(0.5)-HCMSC	0.49	1,250	1.21
Fe(1.5)-HCMSC	1.50	1,200	1.20
Fe(2.5)-HCMSC	2.52	1,180	1.18

1,180–1,270 m^2/g , and their pore volume is in the range of 1.18–1.27 cm^3/g . This indicates that the basic properties of metal containing HCMSC are almost identical to those of the parent HCMSC, and therefore metals are finely dispersed over the hollow core mesoporous shell carbon.

Table 2 compares the catalytic performance of the catalysts at different conditions. HCMSC as such is incapable of exhibiting catalytic activity. There is a striking difference between the activity of Cu-HCMSC and Cu-NaY with the former more active than the latter; the phenol conversion is 23% vs. 17%, but the $\text{H}_2\text{O}_{2\text{eff}}$ is nearly the same over Cu-NaY and Cu-HCMSC, around 60%, under typical reaction conditions. An important observation is that the metal containing HCMSC shows reduced selectivity to BQ, below 1%. Fe-HCMSC gives higher conversion, 28%, than Cu-HCMSC, which

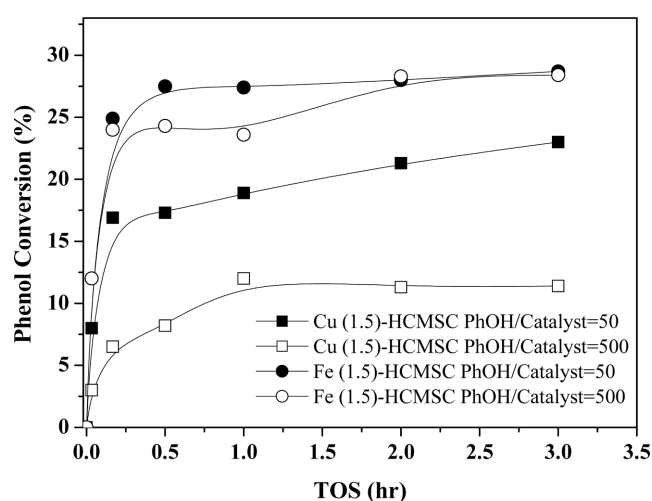


Fig. 1. Effect of time on-stream on phenol conversion over Cu (1.5)-HCMSC and Fe (1.5)-HCMSC (Reaction conditions: reaction temperature=60 °C, solvent=water, Phenol/ H_2O_2 molar ratio=3).

Table 2. Catalytic activities of Cu-HCMSC, Fe-HCMSC and 5CuNaY in the hydroxylation of phenol with H_2O_2 ^a

Catalyst	X_{phenol}^b (%)	S_{hydrox}^c (%)	Selectivity (%)				CAT/HQ ^d	$\text{H}_2\text{O}_{2\text{eff}}^*$ (%)
			HQ	BQ	CAT	BPs		
HCMSC	0	-	-	-	-	-	-	-
Cu(1.5)-HCMSC	23.0	84.9	36.7	0.8	47.4	15.1	1.3	59.0
Fe(0.5)-HCMSC	24.4	84.3	34.2	0.4	49.7	15.7	1.5	62.0
Fe(1.5)-HCMSC	28.7	87.2	32.4	1.0	53.8	12.8	1.7	76.1
Fe(2.5)-HCMSC	27.3	85.9	33.5	0.3	52.2	14.1	1.6	70.6
5CuNaY**	17.4	90.1	17.2	25.2	47.7	9.9	2.8	60.2

^aReaction conditions: reaction temperature=60 °C, solvent=water, Phenol/ H_2O_2 molar ratio=3, Phenol/Catalyst weight ratio=50, reaction time=3h.

^b $X_{\text{phenol}} (\%) = 100 \times ([\text{phenol}]_i - [\text{phenol}]_f) / [\text{phenol}]_i$, where X_{phenol} is the phenol conversion, $[\text{phenol}]_i$ is the molar concentration of phenol before reaction, and $[\text{phenol}]_f$ is the molar concentration of phenol after sampling.

^c $S_{\text{hydrox}} (\%) = 100 \times ([\text{CAT}]_f + [\text{HQ}]_f + [\text{BQ}]_f) / ([\text{phenol}]_i - [\text{phenol}]_f)$, where S_{hydrox} is the selectivity of hydroxylation, and $[\text{CAT}]_f$, $[\text{HQ}]_f$ and $[\text{BQ}]_f$ are the molar concentrations of catechol, hydroquinone and 1,4-benzoquinone, respectively.

^d $\text{CAT}/\text{HQ} = [\text{CAT}]_f / [\text{HQ}]_f$.

* $\text{H}_2\text{O}_{2\text{eff}} (\%) = 100 \times ([\text{CAT}]_f + [\text{HQ}]_f + 2[\text{BQ}]_f) / [\text{H}_2\text{O}_2]_{\text{add}}$, where $\text{H}_2\text{O}_{2\text{eff}}$ is the effective conversion of H_2O_2 , and $[\text{H}_2\text{O}_2]_{\text{add}}$ is the molar concentration of the total H_2O_2 added to the reactants mixture.

5CuNaY [from reference, Wang, J. et al., *Energy & Fuels*, **18, 474, table 5 (2004)], Cu wt%=2.39.

Table 3. Activity of Cu (1.5)-HCMSC and Fe (1.5)-HCMSC catalysts

(A) Cu (1.5)-HCMSC

Phenol/Catalyst (wt/wt)	X_{phenol} (%)	S_{hydrox} (%)	Selectivity (%)				CAT/HQ	H_2O_{2eff} (%)
			HQ	BQ	CAT	BPs		
25	23.5	88.7	37.5	1.3	49.9	11.3	1.3	63.5
50	23.0	84.9	36.7	0.8	47.4	15.1	1.3	59.0
500	11.4	87.2	38.1	3.3	45.8	12.8	1.2	30.9

(B) Fe (1.5)-HCMSC

Phenol/Catalyst (wt/wt)	X_{phenol} (%)	S_{hydrox} (%)	Selectivity (%)				CAT/HQ	H_2O_{2eff} (%)
			HQ	BQ	CAT	BPs		
50	28.7	87.2	32.4	1.0	53.8	12.8	1.7	76.1
500	28.4	85.0	32.0	0.4	52.7	15.0	1.7	72.7
800	18.1	84.5	26.3	3.6	54.7	15.5	2.1	47.8

Reaction conditions: reaction temperature=60 °C, solvent=water, Phenol/H₂O₂ molar ratio=3, reaction time=3 h.

gives 23% for the same metal concentration. The H_2O_{2eff} level is found higher over Fe-HCMSC (76% vs. 59%) than Cu-HCMSC. Also observed is an increase of phenol conversion with increase in the Fe content in the HCMSC. The phenol conversion and selectivity to hydroxylated products attain a maximum of 28.7 and 87.2%, respectively, over Fe (1.5)-HCMSC. In Cu-HCMSC and Fe-HCMSC, the high phenol conversion is attributed to large BET area of support and fine dispersion of metal.

Fig. 1 shows the effect of reaction time on the hydroxylation of phenol over Fe and Cu-HCMSC for different metal contents. The overall percentage of the phenol conversion rapidly increases with the increase in reaction time in the first 30 min, and then approaches a constant value after 2 hr. The phenol conversion over Fe (1.5)-HCMSC is nearly independent of Phenol/Catalyst ratio, since the conversion is the same at the end of 3 hr of time on-stream for both Phenol/Catalyst ratios of 50 and 500. But, Cu (1.5)-HCMSC shows different levels of conversion for Phenol/Catalyst ratios of 50 and 500; the former gives higher conversion than the latter. A total reaction time of 3 hr is therefore sufficient for the completion of the hydroxylation reaction.

Table 3 compares the phenol conversion over Cu (1.5)-HCMSC and Fe (1.5)-HCMSC at different phenol/catalyst (wt/wt) ratios. It is found that Cu (1.5)-HCMSC is very active in the phenol/catalyst (wt/wt) range of 25-50, but Fe (1.5)-HCMSC, at the same optimum range is very active only between the range 50-500. Under such optimum weight ratios, higher H_2O_{2eff} level is obtained over Fe-HCMSC than Cu-HCMSC. As expected, Fe²⁺ gives higher activity than Cu²⁺ in the case of HCMSC framework as well. But in both cases, in spite of a high level of S_{hydrox} (over 85%), the selectivity to BQ is extremely low (below 1%) in the optimum range.

CONCLUSIONS

Based on the results discussed above, it is concluded that the Fe²⁺ containing HCMSC is very active and selective to dihydroxybenzenes in the phenol hydroxylation with H₂O₂ in aqueous medium. Transition metal sites (Fe²⁺ or Cu²⁺) of HCMSC cages act as active sites for the reaction. HCMSC is supposed to take the role of oxi-

dation regulator by concentrating the active ingredients near the active sites located in its hydrophobic pores. The results described herein are expected to open a new avenue for industrial production of dihydroxybenzenes. Further studies on the reaction mechanism and roles of HCMSC are under progress.

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