

# Cu- and Fe-ZSM-5 as catalysts for phenol hydroxylation

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## Abstract

Cu- and Fe-ZSM-5 catalysts were hydrothermally synthesized and characterized by XRD, BET, FT-IR and UV–vis. The catalytic activity of several samples was tested for the aqueous hydroxylation of phenol with hydrogen peroxide. Two different mineralizing agents were used to prepare Cu-ZSM-5 catalysts: methylamine (Cu-Z-o) and sodium hydroxide (Cu-Z-B). Fe-ZSM-5 catalysts were synthesized either without mineralizing agent (Fe-Z-s) or with ammonium fluoride (Fe-Z-f). The metallic content of the synthesized materials varied between 0 and 1.8 wt.% and the Si/Al ratio varied from 32 to infinity. The type of mineralizing agent has a strong influence on the Cu or Fe species incorporated into ZSM-5. Cu<sup>I</sup> and Cu<sup>II</sup> predominated in Cu-ZSM-5 prepared with methylamine whereas Cu<sup>0</sup> clusters besides Cu<sup>I</sup> and Cu<sup>II</sup> were detected on Cu-Z-B. When copper and Al contents decreased in Cu-ZSM-5 catalysts catechol production was favored. Catechol was also preferably obtained over low iron loaded ZSM-5 prepared with NH<sub>4</sub>-F as mineralizing agent. Fe-Z-f samples contained both framework and extraframework iron species. The best reaction conditions found in this work to obtain high yields of catechol and hydroquinone are 1 mmol phenol, molar ratio phenol/H<sub>2</sub>O<sub>2</sub> = 3, catalyst = 20 mg, *T* = 80 °C, water = 5 g, reaction time = 4 h.

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## 1. Introduction

The incorporation of transition elements into framework positions of high silica zeolites and silicates has attracted much interest because it provides a novel means of obtaining high dispersions of these elements within the zeolite structure. Besides, the acidity generated is different from that associated with Al sites [1]. Transition metal ions have promising catalytic behavior in the oxidation of organic compounds and their stability toward dissociation and/or oxidative destruction is improved over their homogeneous counterparts [2]. Use of solid catalysts for selective oxidation of phenols, preferably at near ambient conditions and using clean oxidants like O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>, is a research area of great industrial importance. Hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub> using microporous titanosilicate, TS-1 and its commercial utilization by Enichem workers [3] is a major advance in this area. Hydroquinone (HQ) and catechol (CAT), widely used in chemical, pharmaceutical and food industries, are obtained

with high selectivity over TS-1 [4]. In the search for alternative catalysts, a wide variety of materials have been studied: metal oxides, supported metal complexes, hydrotalcite-like compounds, metal containing mesoporous materials, metal hydroxylphosphates and heteropoly compounds, among others [5,6]. However, titanosilicalites still continue to be the most important catalysts for this reaction. The narrow pores of TS-1 are necessary for the formation of hydroquinone and though catechol is formed on the external surface, it can also form in the pores of TS-1 [7]. In contrast to phenol hydroxylation over microporous TS-1 which is effectively carried out with methanol or acetone, organic solvents are not adequate for phenol hydroxylation over Cu-HMS [8,9], Cu-ZSM-5 [10], CoNiAl ternary hydrotalcites [11], Cu(II)<sup>+</sup>SiW<sub>12</sub> Keggin-type heteropoly compound [12], and CuM(II)M(III) ternary hydrotalcites [13]. The beneficial effect of water in phenol hydroxylation [14] over these catalysts has been ascribed to both phenol and H<sub>2</sub>O<sub>2</sub> simultaneously dissolving in water and approaching the active center. So, hydroxy radicals are generated, which are thought to be the active species involved in the hydroxylation reaction. Low valence transition metal ions such as Fe<sup>II</sup> and Cu<sup>II</sup> activate hydrogen

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peroxide to obtain free radicals [15–17]. Recently, the use of ZSM-5 containing copper or iron as active sites has been reported [18–20] for the wet peroxide oxidation of phenol from wastewaters. The activity and stability of the active Cu or Fe species was dependent on the preparation method. The objective of this work is to compare the activity of several Cu- and Fe-ZSM-5 catalysts for the aqueous phenol hydroxylation with  $\text{H}_2\text{O}_2$ . Different materials were hydrothermally synthesized by addition of the metal precursor in the synthesis gel using organic and inorganic mineralizing agents.

## 2. Experimental

### 2.1. Synthesis of Cu-ZSM-5 and Fe-ZSM-5

Cu-ZSM-5 was synthesized following the procedure reported by Gabelica and coworkers with tetrapropylammonium bromide, TBABr, as template [19]. Depending on the mineralizing agent used, methylamine or sodium hydroxide, two types of materials were obtained, coded Cu-Z-o or Cu-Z-B. The gel composition for Cu-Z-o was  $\text{Si}:0.28\text{TBABr}:2.1\text{CH}_3\text{NH}_2:x\text{Cu}:39\text{H}_2\text{O}:y\text{Al}$ , with  $x$  varying between  $6.57 \times 10^{-3}$  and 0.02 mol and  $y=0-0.03$  mol, and  $\text{Si}:0.28\text{TBABr}:0.27\text{NaOH}:0.03\text{Cu}:35\text{H}_2\text{O}$  for Cu-Z-B. To remove the organic template, all samples were calcined 5 h at  $600^\circ\text{C}$ , heating rate  $2^\circ\text{C}/\text{min}$ .

The procedure developed by Sheldon and coworkers [21] was used to obtain Fe-Z-s, without mineralizing agent and that reported by Nagy and coworkers to prepare Fe-Z-f with  $\text{NH}_4\text{F}$  as mineralizing agent [22]. Gel compositions were  $\text{Si}:0.25\text{TPAOH}:x\text{Fe}:31\text{H}_2\text{O}:y\text{Al}$  for Fe-Z-s catalysts.  $x$  was varied between  $9.71 \times 10^{-3}$  and 0.02 mol,  $y=0-0.03$  mol. For Fe-Z-f catalysts  $\text{Si}:0.05\text{TPABr}:2.4\text{NH}_4\text{F}:x\text{Fe}:13\text{H}_2\text{O}:y\text{Al}$ .  $x$  varying between  $4.9 \times 10^{-4}$  and 0.03 mol and  $y=0-0.03$  mol. Template removal was done by calcining 10 h at  $550^\circ\text{C}$ ,  $2^\circ\text{C}/\text{min}$ .

### 2.2. Catalyst characterization

Chemical analysis of fresh catalysts was carried out by atomic absorption. Powder X-ray diffraction patterns were obtained in a Bruker AXS diffractometer generating Cu  $K\alpha$  radiation operating at 40 kV and 30 mA. Scanning was conducted from  $2\theta = 3-40^\circ$  and a step size of  $0.02^\circ$ . BET surface areas were determined in a Micromeritics ASAP 2010 sorptometer. IR spectra were recorded using a Bruker 22 (Mattson FT-IR 5000) spectrometer using intimate dilute mixtures of the zeolite samples in KBr. UV-vis experiments were performed on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer. The spectra were recorded in air against  $\text{BaSO}_4$ , in the 200–1000 nm wavelength range.

### 2.3. Catalytic activity measurements

Phenol hydroxylation with hydrogen peroxide was done under reflux in a three-necked flask surrounded by a heat-

ing mantle. The catalyst and an aqueous solution of phenol were mixed with a magnetic stirrer and heated to the desired temperature. To start the reaction, an aqueous  $\text{H}_2\text{O}_2$  solution (30% (w/v)) was then added in a single portion. After 4 h, the products were taken out and analyzed by GC on a SPB-50 capillary column either in a GC-FID or GC-MS.

## 3. Results and discussion

### 3.1. Catalyst characterization

#### 3.1.1. Chemical composition and X-ray diffraction

The Si/M (M = Cu or Fe) and Si/Al atomic ratios, as well as, metallic composition and color of the synthesized materials, are listed in Table 1. The surface area of selected samples was  $350 \text{ m}^2/\text{g}$ . As observed in Table 1 the copper content of samples prepared using methylamine as mineralizing agent (Cu-Z-o) varied between 0.05 and 1.15 wt.% depending on the amount of metal and aluminum precursors added to the synthesis gel. The final crystals exhibited a gray color. In general, the Si/Cu ratios of the final crystallized solids are higher than those of the corresponding gels. Particularly, when Al is not present in the synthesis gel the amount of copper in the solid is quite low. When Al was not present in the methylamine containing gel, Gabelica and coworkers could not detect Cu within individual MFI crystals by microprobe analysis. Instead, they found large octahedral crystals of  $\text{Cu}_2\text{O}$  intermixed with the MFI crystals by SEM [18]. Al was required to obtain high copper loadings into ZSM-5 prepared with methylamine as mineralizing agent. In contrast, for Al-free gels the efficiency of copper incorporation was higher when NaOH was the mineralizing agent, as observed for Cu-Z-B. However, it has been reported [20] that probably NaOH brings Cu as zeolite extraframework as well as dispersed copper oxide or hydroxyoxy insoluble polynuclear species, which would generate oxide particles on the external surface of the zeolite crystals upon calcination.

The gel Si/Fe atomic ratios of Fe-Z-s samples prepared in the absence of mineralizing agent were in most cases lower than those in the corresponding solids. In contrast, Fe-Z-f prepared in fluoride media contained Si/Fe ratios higher than those in the gels. As observed in Table 1, Fe containing catalysts were rusty-colored, suggesting the presence of extraframework Fe deposited outside the ZSM-5 crystallites. The only exception was the lower iron containing sample, Fe-Z-f1.

The XRD patterns of Cu-ZSM-5 and Fe-ZSM-5 catalysts are shown in Figs. 1 and 2(a)–(b), respectively. Cu-Z-o samples show the characteristic XRD pattern of the MFI structure and no major structural changes were detected after Cu or Fe incorporation. The low background lines indicated high crystallinity of synthesized materials. Cu-ZSM-5 samples synthesized with NaOH as mineralizing agent show a peak at

Table 1  
Si/M (M = Cu or Fe), Si/Al atomic ratios of gels and crystalline Cu-ZSM-5 and Fe-ZSM-5 samples, as determined by atomic absorption

Catalyst	Si/M <sub>gel</sub>	Si/M <sub>MFI</sub>	Si/Al <sub>gel</sub>	Si/Al <sub>MFI</sub>	Cu or Fe <sub>MFI</sub> (wt.%)	Color
Cu-Z-o1	98	2058	79	88	0.05	Light blue
Cu-Z-o2	50	148	116	88	0.59	Gray
Cu-Z-o3	152	148	37	32	0.67	Gray
Cu-Z-o4	51	148	∞	∞	0.74	Dark gray
Cu-Z-o5	98	84	118	88	1.15	Gray
Cu-Z-B	47	61	∞	∞	1.59	Dark gray
ZSM-5	∞	∞	36	40	0	White
Fe-Z-s1	151	166	36	54	0.51	Light beige
Fe-Z-s2	101	143	37	54	0.71	Beige
Fe-Z-s3	103	86	122	54	0.96	Beige
Fe-Z-s4	51	48	∞	∞	1.58	Orange
Fe-Z-s5	51	48	36	34	1.70	Light brown
Fe-Z-s6	82	48	51	82	1.75	Light brown
Fe-Z-f1	2058	1820	88	901	0.05	White
Fe-Z-f2	148	328	88	901	0.28	Beige
Fe-Z-f3	33	64	∞	∞	1.09	Orange
Fe-Z-f4	33	64	32	901	1.31	Orange
Fe-Z-f5	33	64	88	390	1.47	Orange
ZSM-5	∞	∞	82	60	0	White

$2\theta = 26.8^\circ$  which was identified as silicon oxide type synthetic quartz (Powder Diffraction File, PDF 33–1161). No peaks corresponding to CuO phases at  $2\theta$  values of  $35.6^\circ$  and  $38.7^\circ$  [23,24] can be observed in Cu-ZSM-5 catalysts. Cu species in these samples might be highly dispersed either in the zeolite channels or in the external surface of the crystallites. In the Fe-Z-f1 sample no diffraction peaks due to ferric oxide and/or oxyhydroxide phases in the  $2\theta$  region  $12\text{--}18^\circ$  [13] neither around  $35.5^\circ$  due to  $\alpha\text{-Fe}_2\text{O}_3$  particles [25] appeared. However, the peak intensity around  $18^\circ$  is higher for Fe-Z-f2, Fe-Z-f4, and Fe-Z-f5 catalysts (see Fig. 2(b)). It could be due to iron oxides or oxyhydroxides, probably as a result of calcination.

### 3.1.2. UV–vis spectroscopy

The UV–vis reflectance spectra of Cu-ZSM-5 and Fe-Z-f catalysts are presented in Figs. 3 and 4, respectively. Copper containing catalysts, except Cu-Z-o3, showed an absorption

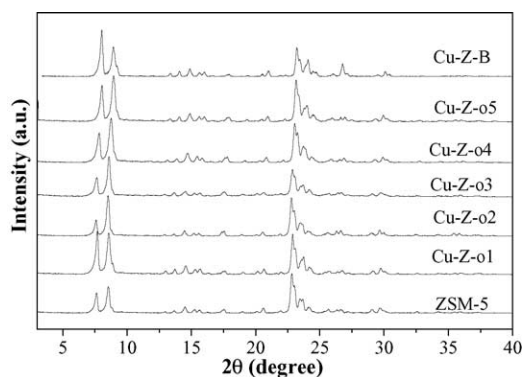


Fig. 1. Powder X-ray diffraction patterns for fresh Cu-ZSM-5 catalysts synthesized with methylamine and NaOH as mineralizing agents.

band at 212 nm corresponding to  $\text{Cu}^{\text{I}}$  [26]. Also, d–d transitions of octahedral  $\text{Cu}^{2+}$  with O-containing ligands is observed at 250 nm for Cu-Z-B and at 232 nm for Cu-Z-o3 and Cu-Z-o4. The latter band has been attributed to  $\text{CTO} \rightarrow \text{tran}$

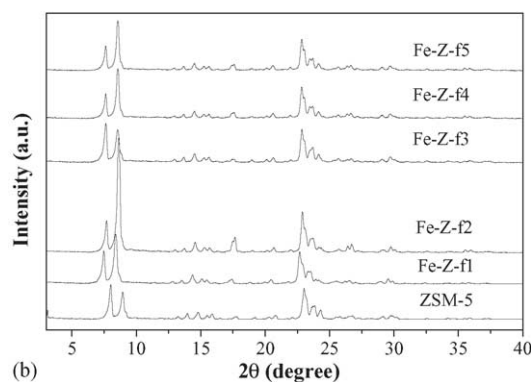
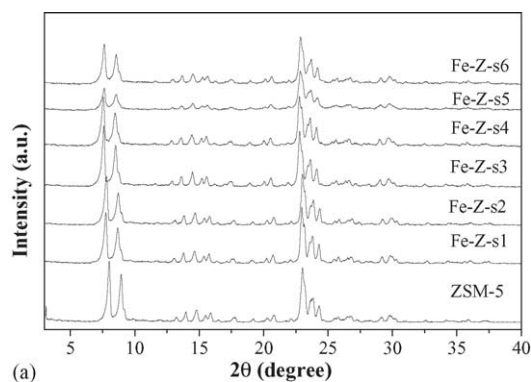


Fig. 2. Powder X-ray diffraction patterns of (a) fresh Fe-ZSM-5 synthesized without mineralizing agent, Fe-Z-s and (b) fresh Fe-ZSM-5 synthesized with  $\text{NH}_4\text{F}$  as mineralizing agent, Fe-Z-f.

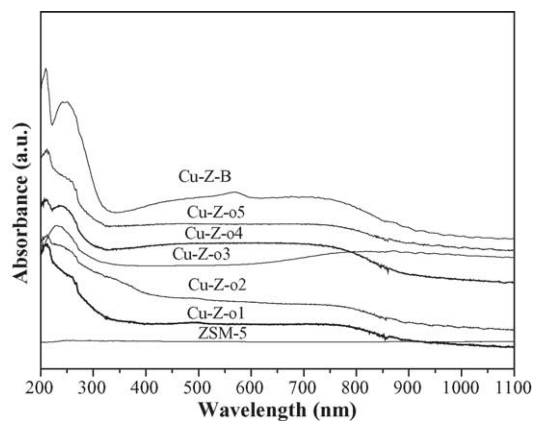


Fig. 3. Diffuse reflectance, UV-vis spectra of fresh Cu-ZSM-5 catalysts synthesized with methylamine and NaOH as mineralizing agents.

sitions of isolated  $\text{Cu}^{\text{II}}$  ions in coordination with lattice oxygen [27]. The other samples (Cu-Z-o1, Cu-Z-o2, Cu-Z-o5) exhibit a shoulder around 250 nm. A broad band observed in the 670–1000 nm range for all Cu-ZSM-5 samples have been attributed to  $\text{Cu}^{\text{II}}$  ions octahedrally coordinated and is typical of metal oxide structures [28]. An additional band at 568 nm assigned to  $\text{Cu}^{\text{I}}$  [26] is also observed in Cu-Z-B. On the basis of this data, it is confirmed that the use of NaOH as mineralizing agent generates copper metal clusters in addition to  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  species. However, no copper clusters are detected by UV-vis in samples prepared with methylamine as mineralizer.

UV-vis of Fe-Z-f catalysts exhibited a strong absorption in the 200–350 nm range due to metal-oxygen charge transfer [21]. The band at 247 nm in the calcined white material, Fe-Z-f1, has been attributed to both octahedral and tetrahedral complexes [21]. This band is broadened and shifted towards higher wavelengths as the iron composition increases. High Fe loaded materials show a band around 280 nm that corresponds to the absorption of octahedral complexes of iron in extraframework positions [21]; these materials also show a band around 316 and 324 nm, which are related with d-d tran-

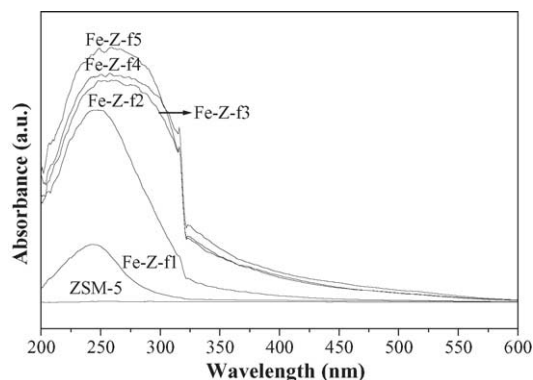


Fig. 4. Diffuse reflectance, UV-vis spectra of fresh Fe-ZSM-5 synthesized with  $\text{NH}_4\text{F}$  as mineralizing agent, Fe-Z-f.

sitions or octahedral  $\text{Fe}^{3+}$  present in small clusters [29,30] and superparamagnetic/ferromagnetic iron oxide clusters [31], respectively. Therefore, in the rusty-colored samples iron may be present as isolated or clustered iron oxide species [32].

### 3.1.3. Infrared spectroscopy

Fig. 5 shows the framework vibration region of fresh Cu-ZSM-5 catalysts. IR bands between 958 and 961  $\text{cm}^{-1}$  are observed in the synthesized Cu-ZSM-5 materials containing Cu between 0.05 and 0.74 wt.% which are attributed to  $\text{Cu}^{\text{I}}$  [33]. This band is absent in Cu-Z-o5 and appears rather shifted to higher wavelengths in Cu-Z-B. Bands in the 918–923  $\text{cm}^{-1}$  range due to  $\text{Cu}^{\text{II}}$  (isolated and oxygen bridged) perturbations of asymmetric internal zeolite stretching vibrations are not observed [33]. Sachtler and coworkers [33] found that these bands are highly sensitive to pretreatment or experimental conditions.

IR spectra in the framework vibration region of Fe-Z-s catalysts are shown in Fig. 6(a). Between 855 and 882  $\text{cm}^{-1}$ , a band which has been assigned to isolated  $[\text{FeO}_4]$  units [34] can be observed. Besides, since all Fe-Z-s materials are rusty-colored, it may suggest that these samples contain some framework and also extraframework  $\text{Fe}^{3+}$  even though, the latter band is not detected in the IR spectra of Fe-Z-f catalysts (see Fig. 6(b)). Rather, Si-OH stretching bands at 1001, 988, 992, 969, and 974  $\text{cm}^{-1}$  are observed in Fe-Z-f1 through Fe-Z-f5, respectively. The higher the iron content the lower the wavenumber which this band is observed. Therefore, extraframework iron appears to be the predominant species in Fe-ZSM-5 prepared with or without an inorganic mineralizer.

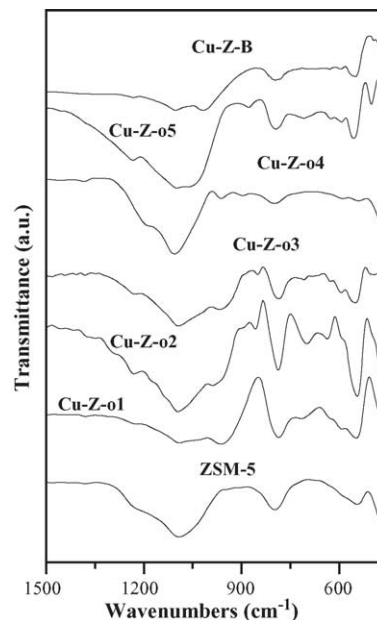


Fig. 5. Infrared spectra of fresh Cu-ZSM-5 catalysts synthesized with methylamine and NaOH as mineralizing agents.

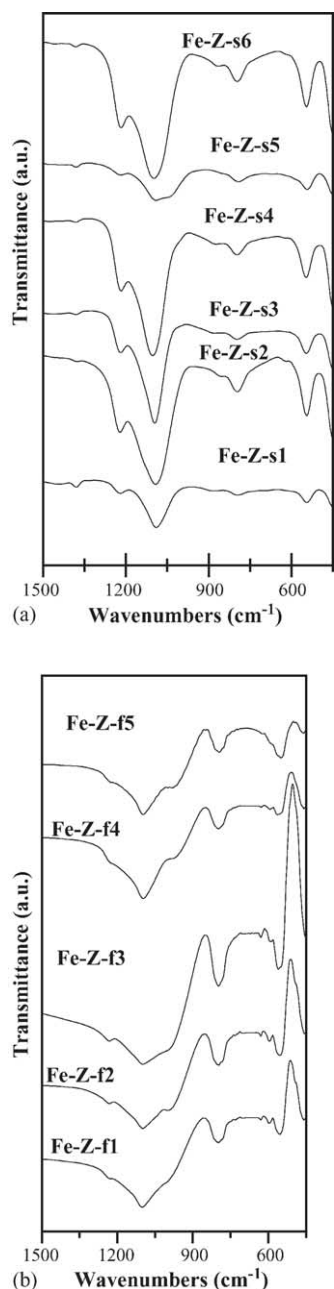


Fig. 6. Infrared spectra of (a) fresh Fe-ZSM-5 catalysts synthesized without mineralizing agent, Fe-Z-s and (b) fresh Fe-ZSM-5 catalysts synthesized with  $\text{NH}_4\text{F}$  as mineralizing agent, Fe-Z-f.

### 3.2. Phenol hydroxylation over Cu-ZSM-5 catalysts

#### 3.2.1. Influence of the Si/Al and Si/Cu ratios

Before examining the effect of different parameters influencing phenol hydroxylation, it was necessary to determine the optimum amount of water on phenol hydroxylation over Cu-ZSM-5 catalysts. The highest phenol conversion, catechol selectivity and CAT/HQ ratio were obtained with 5 g of water. Therefore, in the following experiments the reaction conditions were: 1 mmol phenol, molar ratio

Table 2  
Effect of Si/Al and Si/Cu atomic ratios on the catalytic activity of Cu-Z-o catalysts in phenol hydroxylation

Catalyst	Si/Al	Cu (wt.%)	Conversion (%)	Selectivity (%)		CAT/HQ
				CAT	HQ	
Cu-Z-o1	88	0.05	18.6	60	40	1.5
Cu-Z-o2	88	0.59	17.9	63	37	1.7
Cu-Z-o3	32	0.67	23.5	67	33	2.0
Cu-Z-o4	$\infty$	0.74	13.8	60	40	1.4
Cu-Z-o5	88	1.15	19.4	62	38	1.6

CAT: catechol; HQ: hydroquinone. Reaction conditions: 1 mmol phenol, 5 g water,  $80^\circ\text{C}$ , 20 mg catalyst, phenol/ $\text{H}_2\text{O}_2$  = 3, reaction time = 4 h.

phenol/ $\text{H}_2\text{O}_2$  = 3, catalyst = 20 mg,  $T = 80^\circ\text{C}$ , water = 5 g, and reaction time = 4 h.

Table 2 illustrates the effect of the Si/Al and Si/Cu ratios in phenol conversion and selectivity to the major partial oxidation products: catechol and hydroquinone. At a constant Si/Al = 88, phenol conversion is not significantly affected by the Cu content. As can be observed in Table 2, phenol conversion over the catalyst with the highest copper content (Cu-Z-o5) was similar to that obtained over the catalyst with the lowest Cu content (Cu-Z-o1). CAT and CAT/HQ ratio slightly decreased with the Cu content. No products were detected over the ZSM-5 carrier. Therefore, the presence of copper species is necessary to obtain active catalysts for phenol hydroxylation.

Phenol conversion increased by decreasing the Si/Al ratio of Cu-ZSM-5 catalysts. Cu-Z-o3 having a Si/Al ratio of 32 exhibited the highest phenol conversion and Cu-Z-o4 prepared with no Al precursor shows the lowest activity. It is known that the simultaneous presence of aluminum and transition metal ions in zeolites generates strong acid sites. Therefore, in agreement with previous reports [35], acid catalysis is involved in phenol hydroxylation. The acidity effect on phenol hydroxylation is also evidenced with the hydrogen form Y zeolite which was active itself on this reaction due to its acidity [36,37].

#### 3.2.2. Influence of phenol to $\text{H}_2\text{O}_2$ molar ratio

To better elucidate the behavior of materials prepared with different mineralizing agents the most active materials Cu-Z-o3 and Cu-Z-B, obtained with methylamine and NaOH, respectively, were chosen as representative catalysts for phenol hydroxylation. The effect of phenol/ $\text{H}_2\text{O}_2$  molar ratio on the conversion efficiency of Cu-Z-o3 and Cu-Z-B catalysts is illustrated in Fig. 7. It is clear that Cu-Z-B is much more active than Cu-Z-o3 for different phenol/ $\text{H}_2\text{O}_2$  ratios. Wang et al. reported that not only isolated  $\text{Cu}^{\text{II}}$  species but also a small amount of clustered  $\text{Cu}^{\text{II}}$  species are necessary to improve the selectivity and the effective conversion of  $\text{H}_2\text{O}_2$  [38]. The higher activity of Cu-Z-B could be owing to the clustered copper species which are not present in Cu-ZSM-5 catalysts prepared with methylamine.

For large concentrations of  $\text{H}_2\text{O}_2$  phenol conversion increased over both Cu-Z-o3 and Cu-Z-B catalysts. CAT/HQ

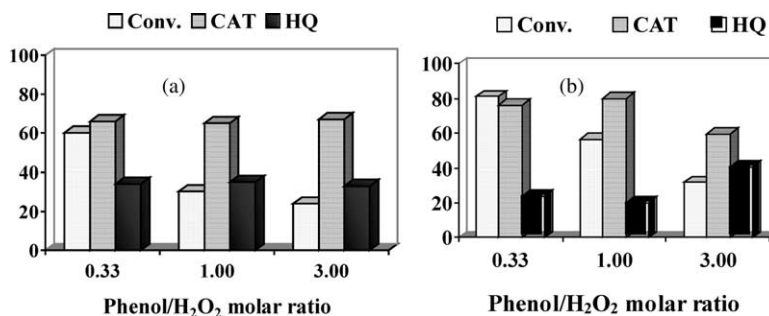


Fig. 7. Effect of phenol/H<sub>2</sub>O<sub>2</sub> molar ratios on conversion over Cu-ZSM-5 catalysts for phenol hydroxylation: (a) Cu-Z-o3; (b) Cu-Z-B. Reaction conditions: 1 mmol phenol, 5 g water, 80 °C, 20 mg catalyst, reaction time = 4 h.

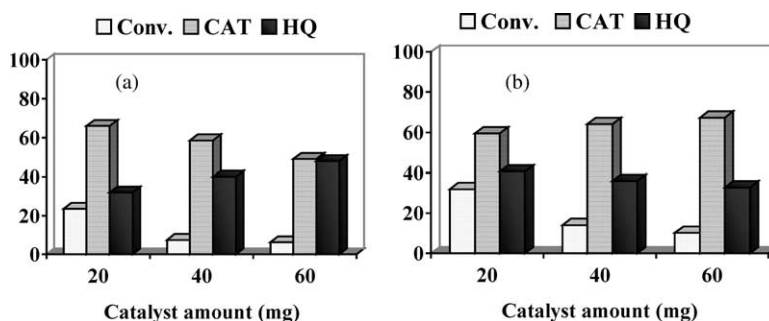


Fig. 8. Effect of catalyst amount on the catalytic activity of Cu-ZSM-5 catalysts for phenol hydroxylation: (a) Cu-Z-o3; (b) Cu-Z-B. Reaction conditions: 1 mmol phenol, 5 g water, 80 °C, phenol/H<sub>2</sub>O<sub>2</sub> = 3, reaction time = 4 h.

ratio was almost constant over Cu-Z-o3 probably due to the lack of interconversion and/or consecutive reactions [14]. However, CAT/HQ increased by increasing H<sub>2</sub>O<sub>2</sub> on Cu-Z-B. Presumably, Cu species are located mainly on the surface of the ZSM-5 crystals. Therefore, once H<sub>2</sub>O<sub>2</sub> is added, phenol molecules are oxidized over the Cu species outside the channels to give catechol, the most thermodynamically favored isomer [8]. Considering that the maximum phenol conversion is 33% or 100% when phenol/H<sub>2</sub>O<sub>2</sub> = 3 or 1, the conversion efficiency is higher for phenol/H<sub>2</sub>O<sub>2</sub> = 3. Therefore, the phenol/H<sub>2</sub>O<sub>2</sub> (mole ratio) should be high for maximum utilization of H<sub>2</sub>O<sub>2</sub> in the conversion of phenol to HQ + CAT.

### 3.2.3. Influence of the amount of catalyst

The effect of catalyst amount on the conversion efficiency of Cu-Z-o3 and Cu-Z-B catalysts is shown in Fig. 8. Phenol hydroxylation did not occur in the absence of catalyst or over ZSM-5 support but it decreased when catalyst content was increased from 20 to 60 mg. The lower conversion obtained when the catalyst amount was higher than 20 mg is attributed to the favorable H<sub>2</sub>O<sub>2</sub> decomposition instead of phenol hydroxylation.

### 3.2.4. Influence of temperature

Fig. 9 compares the catalytic activity of Cu-Z-o3 and Cu-Z-B at different reaction temperatures. Phenol conversion increased with temperature up to 80 °C but it decreased at a higher temperature, i.e. 90 °C. The same trend was also reported over Cu-HMS [7]. The presence of a maximum may

be due to a competitive thermal decomposition of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O and O<sub>2</sub> at higher temperatures. CAT selectivity did not change much by increasing temperature while HQ selectivity increased.

### 3.3. Phenol hydroxylation over Fe-ZSM-5 catalysts

Fe-ZSM-5 catalysts were tested under the best reaction conditions found in this work for Cu-ZSM-5 catalysts: 1 mmol phenol, molar ratio phenol/H<sub>2</sub>O<sub>2</sub> = 3, catalyst = 20 mg, *T* = 80 °C, water = 5 g, reaction time = 4 h. The effect of Si/Al and Si/Fe atomic ratios on the conversion of phenol and selectivity to CAT and HQ over Fe-Z-f catalysts is listed in Table 3. From Table 3 it can be observed that phenol conversion increased with Fe content over Fe-Z-f catalysts with constant Si/Al = 901. However, the highest CAT and CAT/HQ ratio was obtained over the catalyst that

Table 3

Effect of Si/Al and Si/Fe atomic ratios on catalytic activity of Fe-Z-f catalysts in phenol hydroxylation

Catalyst	Si/Al	Si/Fe	Conversion (%)	Selectivity (%)		CAT/HQ
				CAT	HQ	
Fe-Z-f1	901	1820	23.1	73.6	26.4	2.8
Fe-Z-f2	901	328	27.7	55.4	44.6	1.2
Fe-Z-f3	∞	64	18.4	65.8	34.2	1.9
Fe-Z-f4	901	64	27.9	61.9	38.1	1.6
Fe-Z-f5	390	64	32.9	60.5	39.5	1.5

Reaction conditions: 1 mmol phenol, 5 g water, 20 mg catalyst, phenol/H<sub>2</sub>O<sub>2</sub> = 3, 80 °C, reaction time = 4 h.

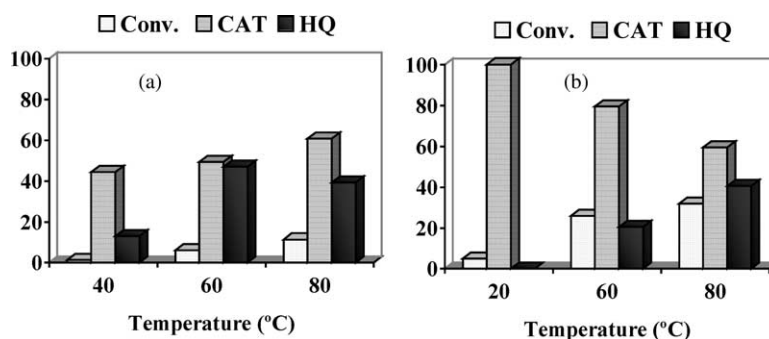


Fig. 9. Effect of temperature on the catalytic activity of Cu-ZSM-5 catalysts for phenol hydroxylation: (a) Cu-Z-o3; (b) Cu-Z-B. Reaction conditions: 1 mmol phenol, 5 g water, 20 mg catalyst, phenol/H<sub>2</sub>O<sub>2</sub> = 3, reaction time = 4 h.

Table 4

Catalytic activity of Cu-Z-B and Fe-Z-f5 compared with several Cu and Fe catalysts reported in the literature<sup>a</sup>

Catalyst	Conversion (%)	Selectivity (%)		CAT/HQ	Reference
		CAT	HQ		
CuNiAl ternary hydroxalates <sup>b</sup>	13.8	54.3	45.7	1.2	[14]
CuCoAl ternary hydroxalates <sup>b</sup>	14.9	67.1	32.9	2.0	[23]
CuNaY <sup>c</sup>	17.4	47.7	17.2	2.8	[38]
Cu-Bi-V-O <sup>d</sup>	23.1	55.0	42.7	1.3	[42]
Copper hydroxyphosphate Cu <sub>2</sub> (OH)PO <sub>4</sub> <sup>e</sup>	28.3	52.2	46.7	1.1	[43]
Cu-Z-B <sup>f</sup>	31.9	60	40	1.5	This work
Ferritin <sup>g</sup>	11.5	78.8	21.2	3.7	[44]
Fe-Mg-Si-O <sup>h</sup>	24.5	53.6	45.9	1.2	[6]
Fe-ZSM-5 <sup>f</sup>	32.9	60.5	39.5	1.5	This work

<sup>a</sup> Phenol/H<sub>2</sub>O<sub>2</sub> = 3, 80 °C, water as solvent, reaction time = 4 h.

<sup>b</sup> 65 °C, reaction time = 2 h, 10 mg catalyst, 10 ml water, 1 g phenol.

<sup>c</sup> 50 °C, reaction time = 5 h, 2 g phenol, 60 ml water, 200 mg catalyst.

<sup>d</sup> 1.7 g phenol, 15 ml water, 85 mg catalyst.

<sup>e</sup> 80 mg catalyst, 15 ml water, 20.4 mmol phenol.

<sup>f</sup> 20 mg catalyst, 5 ml water, 1 mmol phenol.

<sup>g</sup> 1 g phenol, 10 g water, 50 mg catalyst.

<sup>h</sup> 5.6 g phenol, reaction time = 0.5 h, 50 ml water, 0.28 g catalyst.

had the lowest Fe content (Fe-Z-f1). The UV–vis spectra of the white material Fe-Z-f1 indicate that Fe may be present in tetrahedral framework position. Interestingly, with constant Si/Fe = 64 phenol conversion increased with Al content (Fe-Z-f5). Also, as observed over Cu-ZSM-5 catalysts, acid catalysis is involved in phenol hydroxylation. In addition, since Fe-Z-f5 contains framework and extraframework Fe, we conclude that both types of iron species could catalyze phenol hydroxylation. Phu and coworkers also found that both framework and extraframework Fe catalyzed the oxidation reaction of phenol in aqueous solution and framework Fe can catalyze the complete phenol oxidation into CO<sub>2</sub> [20]. In general, there is no agreement whether framework or extraframework iron is the active species for this reaction. For example, over Fe-MCM-48, it has been suggested that the active centers are framework isolated Fe<sup>3+</sup> [31].

On the other hand, Fe-Z-s catalysts exhibited very low activity (less than 1% conversion) for phenol hydroxylation. Therefore, the use of NH<sub>4</sub>F as a mineralizing agent in the direct synthesis of Fe-ZSM-5 is very important to obtain active Fe species for phenol hydroxylation. In the fluoride

route the pH is between 6.5 and 7.0. Under these conditions Fe(III) species are supposed to be mononuclear, because the products were absolutely free of extraframework iron-oxide/hydroxide [39]. Fe zeolites synthesized in the presence of fluoride salts were previously obtained. The authors probed that in these samples iron species did not precipitate as hydroxides [40,41].

For comparison purposes, the performance of Cu- and Fe-containing catalysts previously reported [6,14,23,35,42–44] together with our best Cu and Fe-ZSM-5 samples are listed in Table 4. From this table it can be observed that our Cu-Z-B and Fe-Z-f5 materials gave higher conversions and comparable selectivities.

#### 4. Conclusions

Under the conditions of this study, hydrothermally synthesized Cu- and Fe-ZSM-5 catalysts are active for hydroxylation of phenol provided an adequate mineralizer is used. The use of NaOH as mineralizing agent in the gel precur-

sor of Cu-ZSM-5 catalysts generates copper metal clusters in addition to Cu<sup>I</sup> and Cu<sup>II</sup> species which efficiently activate H<sub>2</sub>O<sub>2</sub>. On the other hand, NH<sub>4</sub>F in the synthesis gel of iron containing ZSM-5 was appropriate for obtaining Fe<sup>3+</sup> in the zeolite framework. However, the most active Fe-ZSM-5 catalyst contained extraframework iron. Finally, the presence of Al was required to obtain high phenol conversion over both, Cu- and Fe-ZSM-5 catalysts.

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