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Oxidation of phenoliques products in liquid phase over Fe and Cu-ZSM5 in presence of peroxides

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Abstract : Iron and copper exchanged ZSM-5 has been prepared following several strategies of synthesis. The oxidative properties of exchanged zeolites (Cu_E-ZSM-5; Fe_E-ZSM-5) towards the liquid phase oxidation of phenols and P-cresols using peroxides (H₂O₂ 35%, SPC AND SBP) under mild reactions conditions (reflux of solvents and at atmospheric pressure) have been evaluated. Stoichiometric amount of peroxides was used for good oxidation efficiency. The catalytic performance was moni-

tored by the nature of active exchanged cations zeolites and the nature of used peroxide. In most cases, high yields of ketones have been obtained. The formed products were identified by gas-phase chromatography. © Global Scientific Inc.

Keywords : Phenol, Hydrogen Peroxides, Heterogeneous Catalyst, Fe-ZSM5, Cu-ZSM5, Oxidation.

INTRODUCTION

In the last few years, an increasing concern has risen due to the pouring of residual waters coming from industries that have organic toxic contaminants, with a negative impact on the ecosystem and mankind (toxicity, carcinogenic and mutant properties). Within these compounds, substituted phenols, pesticides, herbicides, among others stand out. Particularly the phenol (commonly chosen as "model" molecule for studies on the catalytic oxidation of organic compounds in diluted aqueous solutions) is

considered as one of the most toxic pollutants, harmful to human health and to water life. Hence causing an increase in the demand of oxygen in water sources and giving out unpleasant taste and smell in drinking water even when it is found in very small quantities. Several procedures have been developed to eliminate the organic contaminating compounds found in residual waters, for instance, adsorption processes, biological processes, cremation through dry way and processes of wet oxidation (WO), and of these only the WO processes show greater viability and relative efficiency. Considerable improvements have

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been proposed and performed, in order to oxidize organic pollutants into carbon dioxide or into products which are able to be eliminated by biological treatment. The catalytic oxidizing processes involving ozone, oxygen, hydrogen peroxide or a combination of them appear to be very attractive. Numerous papers and reviews especially on catalytic wet-air oxidation (CWAO) have been published. Different types of catalysts containing either non-noble metals such as copper or iron^[1-4] or noble metals (Pt, Ru,) supported on various types of carriers such as active carbons,^[5-7] titania^[8] and rare earth oxides^[7-9] have been proposed as promising catalytic materials. So, 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 generated acidity is different from that associated with Al sites^[10]. 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^[11]. The use of solid catalysts for selective oxidation of phenols, preferably at near ambient conditions and using clean oxidants like H₂O₂, sodium percarbonate (SPC) or sodium perborate (SPB) is a research area of great industrial importance. Hydroxylation of phenol with H₂O₂ using microporous titanosilicate, TS-1 and its commercial utilization by Enichem workers^[12] 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^[13]. In the search for alternative catalysts, a wide variety of materials have been studied: metal oxides, supported metal complexes, hydroxalcite-like compounds, metal-containing mesoporous materials, metal hydroxyphosphates and heteropoly compounds, among others^[14,15]. However, the TS-1 appears 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^[16]. 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^[17,18], Cu-ZSM-5^[19], CoNiAl ternary hydroxalcites^[20], Cu(II)+SiW₁₂ Keggin-type heteropoly compound^[21], and CuM(II)M(III) ternary hydroxalcites^[22].

Recently, the use of ZSM-5 containing copper or iron as active sites has been reported^[23-25] for the wet peroxide oxidation of phenol from wastewaters. The activity and stability of the active Cu or Fe species were dependent on the preparation method.

The aim of this study was double: firstly, it aimed to find a heterogeneous catalyst that will act efficiently for phenol degradation by promoting H₂O₂ decomposition to HO· radicals without producing inactive molecules. Secondly, it aimed to avoid any additional pollution, to minimize the concentration of transition metal ions generated in the solution during the reaction. For this purpose, a series of screening tests were conducted to oxidize phenol and p-cresol with different type of H₂O₂ as terminal oxidants. The activity of Cu- and Fe-ZSM-5 catalysts exchanged with lower content of Cu and Fe for the liquid phenol oxidation was performed.

The concept we have tried to develop was to improve the catalytic efficiency of the process by combining a porous support and an active phase in order to increase the concentration of organic compounds close to the H₂O₂ activation sites and therefore to enhance both the oxidation rate and the efficiency of the use of H₂O₂.

EXPERIMENTAL

Catalyst preparation

ZSM-5 synthesized as described elsewhere^[26] using sodium silicate and tetrapropylammonium bromide (TPABr) from Merck, aluminium sulfate from Fluka, potassium fluoride from Aldrich and deionized water has the following molar composition:

100 SiO₂, 1 Al₂O₃, 10 K₂O, 27 Na₂O, 5 TPA₂O, 7000 H₂O. The treatment of ZSM-5 (2 g) with 1 M NaCl solution (200 mL x 2) at room temperature for 24 h led to Na-ZSM-5. An aqueous 0.1M solution of Cu(NO₃)₂ and separately of Fe(NO₃)₃ (40 mL) at pH 5 (adjusted with aqueous MeNH₂) was added to

Na-ZSM-5; heating this mixture at 70 °C for 2 h led to the ion-exchanged zeolites.

The resulting Fe-ZSM-5 and Cu-ZSM5 zeolites were filtered, carefully washed with deionized water, and then dried at 80°C overnight.

Catalyst characterization

Cu-ZSM-5 and Fe-ZSM5 were characterized by powder X-ray diffraction using a Philips PW 1801/29 diffractometer with Cu K α radiation.

The chemical analysis of the catalyst solids was carried out through the use of the X-rays fluorescence technique (using a Philips Magix apparatus). Selected areas were analyzed by EDX, which showed that Cu and Fe was regularly distributed at the zeolite framework. TEM images were obtained by using a Philips XL30 FEG apparatus. The BET surface area was measured with an ASAP 2010 instrument.

Oxidation procedure

Blank test

In the absence of active cations, case of Na-ZSM-5, phenol was adsorbed in the pore volume of solid catalysts, but not oxidized even in the presence of hydrogen peroxide.

Oxidation of phenol and P-Cresol

A mixture of Cu-ZSM-5 or Fe-ZSM5 catalysts (20 mg), oxidants 8 mmole (35% aqueous H₂O₂, SPC (Na₂CO₃·1.5 H₂O₂) and SPB (Na₂B₂O₄(OH)₄), substrate 1 mmole (phenol, p-cresol) in PhMe (20 mL) was stirred at 80°C under air atmosphere during 8 hours. After cooling to room temperature, the mixture was filtered over a small pad of alumina. Evaporation of the solvent followed by chromatography of the residue led to the oxidized compound, which was identified by gas chromatography phase (CPG).

RESULTS AND DISCUSSION

Catalyst properties

The intensity of the main peaks of Cu-ZSM-5 and Fe-ZSM5 with that of Na-ZSM-5 indicated the absence of alteration of the zeolite structure in the course of the ion exchanges (Figures 1, 2, 3). Scan-

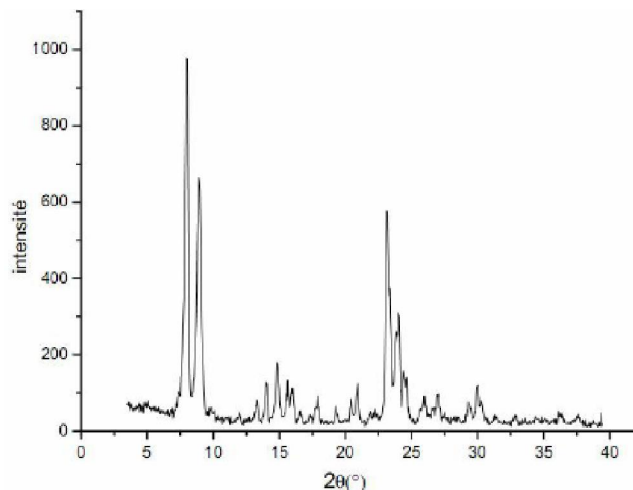


Figure 1 : DRX diffractogramms of Na-ZSM-5

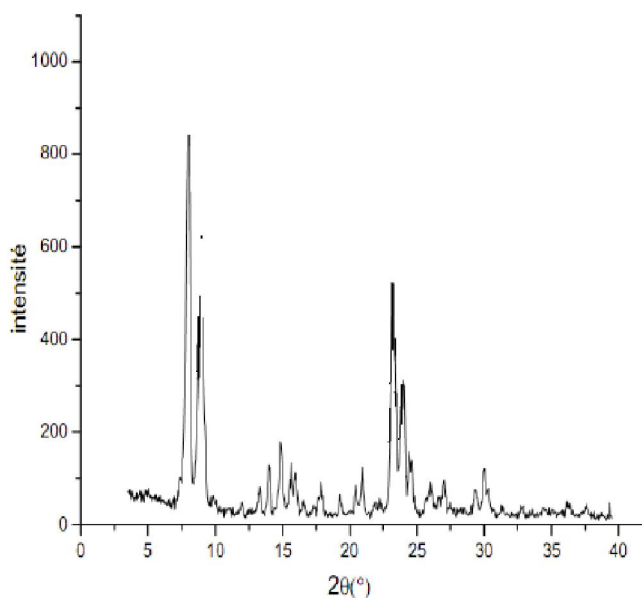


Figure 2 : DRX diffractogramms of Cu-ZSM-5

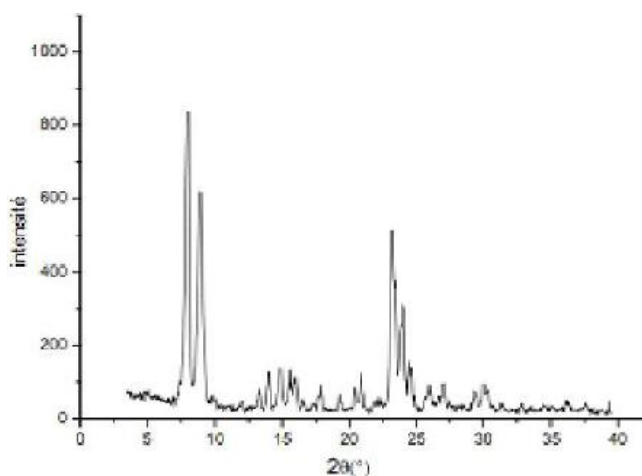


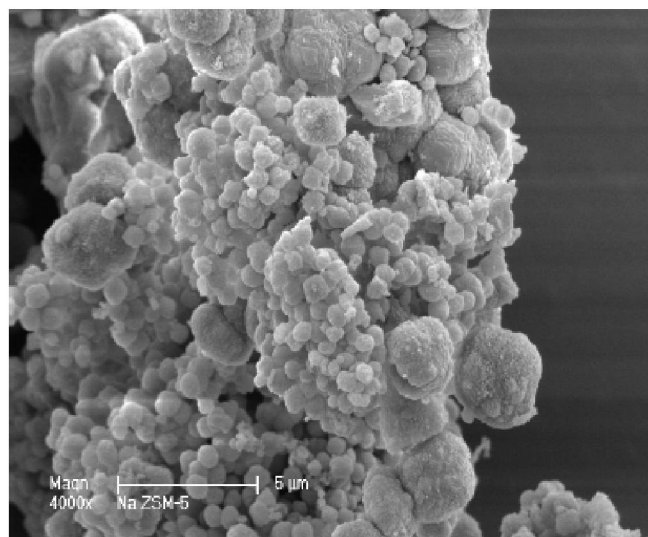
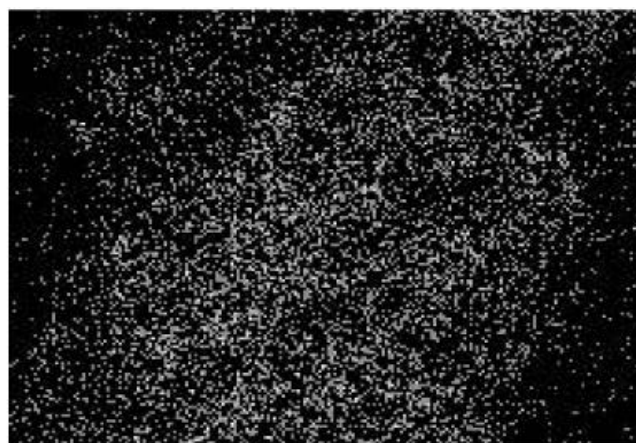
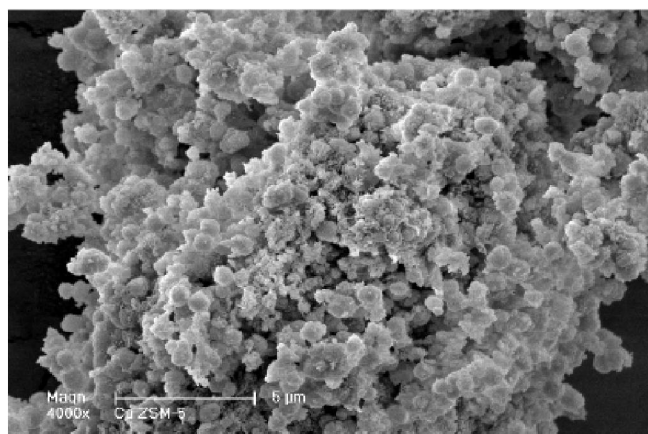
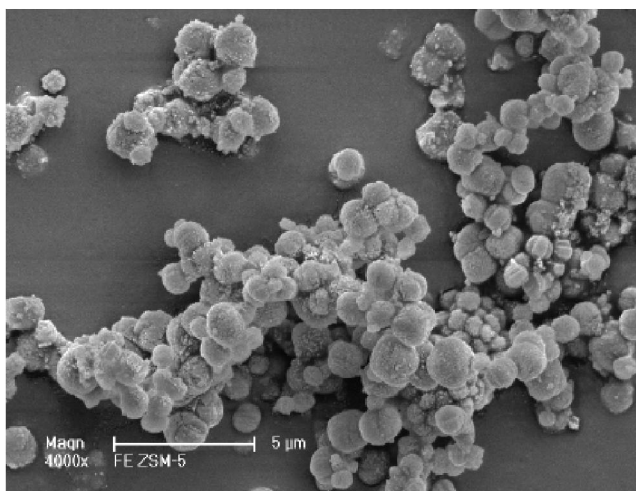
Figure 3 : DRX diffractogramms of Fe-ZSM-5

ning electron microscopy of Cu-ZSM-5 and Fe-

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TABLE 1 : Variation of the cell parameters of the exchanged ZSM-5 and its exchanged forms

Samples	a (Å)	b (Å)	c (Å)	V (Å) ³
Calcined ZSM5	20.10	19.81	13.28	5287,84
Na-ZSM-5	19.99	19.72	13.16	5187,70
Cu-ZSM-5	20.10	19.89	13.30	5317,19
Fe-ZSM-5	20.16	19.94	13.34	5362,55


Figure 4 : Image MEB of Na-ZSM-5

Cuivre Ka1
Figure 6 : Analysis of the copper ions EDAX insertion CuZSM5

Figure 5 : Image MEB of Cu-ZSM-5

Figure 7 : Image MEB of Fe-ZSM-5

ZSM5 crystals showed, a sphere like morphology and a crystal size of 1 or 2 μm size with uniform dispersion of Cu and Fe in the framework of the zeolite. The BET surface area was 460 m² g⁻¹ for Cu-ZSM-5 and 490 m² g⁻¹ for Fe-ZSM-5. The chemical compositions of the unit cells of the Fe-ZSM-5 (Fe_{3.51}K_{0.06}Na_{0.2}(Al_{1.47}Si_{44.4}O_{50.5})) and that of Cu-ZSM-5 (Cu₁K_{0.532}Na_{0.24}(Al_{1.3}Si_{44.5}O_{52.3})) were determined by X-ray fluorescence

The cell parameters calculated from the crystallographic data, showed that the structure was slightly

modified (TABLE 1). Such changes can be explained by the penetration of the ion Cu II and Fe III in the framework zeolite. In the passage from the form Na-ZSM-5 to the form Cu-ZSM-5 and Fe-ZSM-5, the cell parameters a and b have increased, this growth indicate the penetration of the ions of copper and of iron in the two channels types a and b (rectilinear tunnels with the openings quasi-circular (5Å° X 5,Å°), and in zigzag channels with the elliptic openings (5,1Å° X 5,Å°).

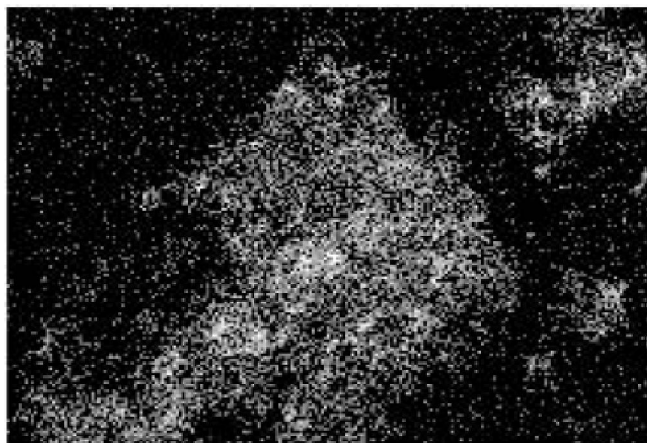
Detailed analysis of the spectrum given by the MEB were determined by X-ray fluorescence

Analysis EDAX by electronic scan microscopy also gives information about the dispersion of copper and iron in the framework of zeolite. Copper and iron are dispersed in a uniform way; they are well occluded in the framework of zeolite (Figure 6,8).

Images M.E.B presented on (Figures 5,7, 8) shows that the formed crystals are of spherical morphology, which notify that the iron and copper exchanged ZSM-5 not altered the structure, this is by the way with the analysis given by DRX.

Analysis EDAX by electronic scan microscopy also gives information about the dispersion of copper in the framework of zeolite. Copper is dispersed in a uniform way; it is well occluded in the framework of zeolite (Figure 7).

Image MEB presented on (Figure 7) shows that the formed crystals are of spherical morphology,



Fer Ka1

Figure 8 : Analysis of iron ions EDAX insertion FeZSM5

which notify that the iron exchanged with ZSM-5 not altered the structure, this is by the way with the analysis given by DRX

Analysis EDAX by electronic scan microscopy confirms that iron is not well dispersed in the zeolite framework, and a certain iron content remains occluded in the extra framework.

The analysis by x-ray fluorescence highlighted the chemical composition of our samples (TABLE 2) and confirmed the presence of its components. It was noted that the major part of catalysts was in the form of silica and oxygen, the Si/Al ratio varied between 30.2 and 34.23 % and this confirmed the characteristic of the richness of the zeolite prepared in fluoride medium. The metal content of synthesized materials was 1% of copper and 3.51% of iron. This is in good agreement with the results given by the MEB spectra.

Activity in the oxidation of phenol and P-cresol in liquid phase

The potential of Cu-ZSM-5 and Fe-ZSM5 as oxidative catalyst was separately examined using the phenol as p-cresol as substrates. The use of (35% aqueous H_2O_2 , SPC ($Na_2CO_3 \cdot 1.5 H_2O_2$) and SPB ($Na_2B_2O_4(OH)_4$), as terminal oxidants in toluene at $80^\circ C$ led to the oxidation of the substrates in good yields (TABLE 3, Entries 1–6) for phenol and (TABLE 4, entries 7-12) for p-cresol

The following experiments consist on the oxidation of phenols and p-cresol and the formation of the novel products according to the oxidant introduced into the reactional mixture (TABLES 3,4).

For the oxidation of phenol with the oxidant H_2O_2 a change of colour after the addition of H_2O_2 and

TABLE 2 : Chemical analysis of the ZSM-5 unit cells and its exchanged forms with copper and iron

	Na-ZSM5	CuZSM5	Fe-ZSM5
Si %	44.4	44.5	44.4
Al %	1.47	1.3	1.47
Na %	1.25	0.24	0.2
O %	52.5	52.3	50.5
K %	0.23	0.532	0.06
Cu %		1	
Fe %			3.51
Si/Al %	30.20	34.23	30.20

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TABLE 3 : Cu-ZSM5 and Fe-ZSM5 catalyzed oxidation of phenol

Entry	Catalyst	Oxidant	Conversion%	Formed product		
				Yields %		
				Hydroquinone	Cathecol	Benzoquinone
1	Cu-ZSM-5	35% aq. H ₂ O ₂	85	50	20	15
2	Cu-ZSM-5	SPC	80	35	45	-
3	Cu-ZSM-5	SPB	75	35	40	-
4	Fe-ZSM-5	35% aq. H ₂ O ₂	65	20	35	10
5	Fe-ZSM-5	SPC	95	40	55	-
6	Fe-ZSM	SBP	85	30	55	-

TABLE 4 : Cu-ZSM5 and Fe-ZSM5 catalyzed oxidation of p-cresol

Entry	Catalyst	Oxidant	Conversion %	Formed product		
				Yields %		
				4 methyl hydroquinone	4 methyl cathecol	Benzoquinone
7	Cu-ZSM-5	35% aq. H ₂ O ₂	90	50	40	
8	Cu-ZSM-5	SPC	85	55	30	
9	Cu-ZSM-5	SPB	75	25	50	
10	Fe-ZSM-5	35% aq. H ₂ O ₂	80	50	30	
11	Fe-ZSM-5	SPC	95	50	45	
12	Fe-ZSM-5	SBP	80	30	50	

was observed, this colour becomes darker while heating until obtaining a red rust colour at the end of the reaction. The use of SPC led to obtaining a transparent solution. The SBP identically gives transparent solutions after filtration. For the total of these experiments, we could prove the strong effectiveness of the oxidants SPC and SBP and H₂O₂ (35%), on the conversion of the quantities of phenols, all oxidants used in our case are very active, the products formed are Hydroquinone and Cathecol, but in the case of H₂O₂ (35%) as terminal oxidant, in addition to the two preceding products, there is formation of benzoquinone in slight quantity.

But in the case of p-cresol it show to be more active. However the Fe-ZSM-5 seem more active than Cu-ZSM-5, this is granted to the high specific area of Fe-ZSM-5

The best results were obtained by using the SPC and the SBP as well as Fe-ZSM-5 with all phenols.

CONCLUSIONS

Several oxidative tests were done using phenol, p-cresol as target pollutants. The oxidation was con-

tinuously conducted under reflux conditions using the exchanged Cu and Fe-ZSM5 as catalyst. The moderate conditions were used as low temperature 80°C and atmospheric pressure to carry out these experiments. The time of reactions was fixed to 8 hours for all experiments.

When the exchanged Cu and Fe-ZSM-5 were used in the presence of hydrogen peroxide at appropriate pH value about 6, phenol is quickly oxidized into intermediate products such as hydroquinone, cathecol and in some cases benzoquinone was observed. For the case P-cresol, the products formed are 4-methyl hydroquinone, 4-methyl cathecol and also the benzoquinone was observed. The formation of hydroquinone (HQ) and cathecol (CAT) is major advance in this area, because these products are widely used in chemistry and pharmaceutical industries

The reactivity of the target pollutants was different depending on the operating conditions and catalyst behaviour. It seems that the use of solid hydrogen peroxide (SPC and SBP) as terminal oxidant gives better results than aqueous hydrogen peroxide does. Hence the Fe-ZSM5 gives the better re-

sults than the Cu-ZM5 does due to its great specific area.

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