Characterization and catalytic activity of ZSM-5 zeolite doped with iron and copper in the oxidation of phenol by hydrogen peroxide

Fatiha Talhaoui*, Fatiha Hamidi

Eco-Functional and Nanostructured Materials Laboratory, University of Science and Technology, Mohamed Boudiaf d'Oran, USTO, B.P.1505 Elmenaouar, Oran, Algeria, email: fatiha.talhaoui@univ-usto.dz (F. Talhaoui)

ABSTRACT

This work aims to develop catalysts based on ZSM-5 type zeolite and their application in the oxidation of phenol. The materials were synthesized using a method based on the crystallization of an aluminosilicate gel prepared from pure sources of silicon and aluminum. Iron and copper were introduced by ion exchange. The solids obtained were characterized by X-ray diffraction, infrared spectroscopy, and by scanning electron microscopy. The catalytic performance of samples was determined in terms of phenol conversion and by-product distribution. It has been found that these materials (Cu-ZSM-5, Fe-ZSM-5) are very active in the oxidation of phenol. Under the conditions of atmospheric pressure and at 70°C, higher phenol removal was obtained with ZSM-5 zeolite catalyst doped with iron [1,2]. The oxidation of phenol over the Fe-ZSM-5 catalyst produced carboxylic acids with a percentage greater than 68% and a negligible percentage of aromatics (almost equal to zero) compared to the Cu-ZSM-5 catalyst.

Keywords: Synthesis; Ion exchange; ZSM-5 zeolite; Iron; Copper; Phenol oxidation

1. Introduction

The last decades have been marked by a great environmental awareness; the huge necessity to protect natural environment has influenced both public opinion and political-economic world [3]. Environmental considerations and increasingly drastic standards in terms of pollution have led to designate some organic compounds such as phenolic ones to be strictly prohibited in water [4,5].

Therefore, previous studies were performed to assess the best catalyst resulting in less well, more efficient, more selective and less polluting products and processes [6,7]. Liquid phase oxidation processes involved soluble salts or transition metal complexes. These catalysts, which are often very expensive, have the disadvantage of being difficult to recover. In addition, their use requires the mandatory passage through a purification column to remove metals [8,9]. Furthermore, some chemists are simply trying to replace homogeneous catalysis with heterogeneous catalysis [10–12]. Transition metals, mainly iron, and copper are used as active phases. Many materials containing mainly iron, and copper as precursors supported on zeolites are proposed as catalysts for the oxidation of organic compounds [13,14].

The main reasons for this exceptional development of zeolite catalysts are the additional selectivity given to them by the size and shape of their cages, channels and pore openings (shape selectivity). This development influenced also the great diversity of zeolites synthesized, modification of composition and porosity, association in the desired form with active species, and the possible regeneration of catalyst and reduction of pollutant discharges.

ZSM-5 type zeolites are crystalline aluminosilicates, which have particular catalytic properties [15,16], a large specific surface area, and a uniform microporous structure whose pore size is perfectly calibrated (zeolites with medium pores), a high acidity and high thermal stability.

Several researchers have carried out studies on catalysts based on ZSM-5 zeolites on the oxidation reaction of

*Corresponding author.

phenol, for example Fajerwerg et al. [17] studied the effect of pH on the oxidation of phenol by hydrogen peroxide using Fe-ZSM-5 catalysts under mild conditions (T = 90°C; [phenol] = $7 \cdot 10^{-2}$ M; [H_2O_2] = $7 \cdot 10^{-1}$ M; $m_{catalyst}$ = 0.4 g L^{-1}; reaction time = 360 min). They found that the pH has a determining role on the conversion of phenol. They showed that pH = 5 is the optimal value for the total oxidation of phenol and the significant elimination of total organic carbon. For higher pH values, the system becomes less efficient. On the other hand, for lower values (pH < 3), the quantity of leached iron becomes significant. Karolina et al. [18] have investigated the activity and stability of Cu/Y5 and Cu/ZSM-5 catalysts in the oxidation of phenol with hydrogen peroxide in solution. Their study has revealed that the activity and the stability of a catalyst containing copper depend on the textural properties of the support and on several parameters such as the reaction temperature, and the method of preparation of the catalysts.

Aziz et al. [19] have used Fe-ZSM-5 prepared with two different iron sources (ferric ammonium citrate and FeCl$_3$); phenol oxidation results have shown that Fe-ZSM-5 synthesized from a gel prepared with a new iron complex, ferric ammonium citrate, has better catalytic performance compared to Fe-ZSM-5 material prepared by FeCl$_3$.

The main objective of this study is to develop catalysts based on ZSM-5 zeolite exchanged with copper and iron. The synthesis and characterization of ZSM-5 zeolite were carried out in this research. The preparation of zeolites doped with copper and iron were performed by ion exchange. Hence, a catalytic application was carried out.

2. Experimental

2.1. Reagents

Sodium silicate solution (29.1% SiO_2, 9.1% Na_2O, 61.8% H_2O; Sigma-Aldrich), aluminum sulfate (Al$_2$(SO$_4$)$_3$·18H$_2$O; Sigma-Aldrich), soda (prolabo) and tetrapropylammonium bromide were purchased from (Sigma-Aldrich). Sodium chloride and iron and copper chloride were purchased from (Merck).

2.2. Preparation of M$^+$-ZSM-5 catalysts

The procedure used for the synthesis of ZSM-5 zeolite crystals (MFI) was developed from the experience gained in the laboratory.

The Na-ZSM5 that we used for the ion exchange is ZSM-5 zeolite synthesized at 160°C for 48 h from a gel of stoichiometric composition of NaAlO$_2$: 25, SiO$_2$: 3.1 Na$_2$O: 3.1 TPA$_2$: 280 H$_2$O.

The preparation of the zeolite gel was carried out according to the method of Yoo et al. [20], which consists in the addition of an aqueous solution of sodium silicate into sodium hydroxide dissolved in distilled water with stirring. Then, the aluminum sulfate and organic agent (tetrapropylammonium bromide) dissolved in distilled water were added successively in the mixture.

The gel obtained was crystallized in an autoclave at a temperature of 150°C for 48 h. The product obtained was then filtered, washed, dried and calcined at 450°C for 8 h.

The zeolite synthesized previously was subjected to a saturation of 1 M solution of sodium chloride at room temperature.

The Na-ZSM-5 zeolite obtained after saturation is brought into contact with solutions of iron and copper chlorides with a concentration of 0.05 M. The cation exchange experiments were carried out at room temperature under stirring for 24 h.

The initial ion exchange was followed by several exchanges under the same conditions. The solids obtained after the exchange reactions were filtered and washed several times with deionized water. The final products were dried at 80°C for 12 h.

2.3. Characterization

The structural characterization of zeolites was important as the catalytic and adsorption properties were closely related to the size and configuration of the channels of zeolites.

Thus, a first characterization was carried out by X-ray diffraction by using a Philips PW 1710 powder diffractometer, K$_\alpha$ radiation of copper and intensity of 30 mA.

The results obtained were then compared with those obtained by scanning electron microscopy (SEM). The size and morphology of zeolites were observed under scanning electron microscope (SEM) (Philips EM420 T), and Fourier-transform infrared spectroscopy (FTIR, ATR Platinum diamond spectrophotometer). Copper and iron content on catalysts was determined from solutions obtained by atomic absorption spectrometry using PerkinElmer AAS 3110, and nitrogen adsorption measurements were carried out on a Micromeritics ASAP 2100 device, after degassing the samples at 250°C for 15 h under vacuum.

2.4. Catalytic reaction

The catalytic tests of degradation of phenol in aqueous solution were carried out in a tricole flask placed in an oil bath. The oxidation of the phenol was carried by the addition of 200 mL of phenol (0.01 mol L^{-1}) into the flask, in the presence of 0.1 g L^{-1} of catalyst. When the mixture reaching the desired temperature, hydrogen peroxide (0.1 mol L^{-1} of H$_2$O$_2$) was added under vigorously stirring at a constant temperature (70°C) for 4 h. The pH was adjusted and controlled at the set point value (pH = 4.8 ± 0.1) by injection of KOH (1 M) or H$_2$SO$_4$ (0.5 M) with pumps connected to a pH regulator.

The concentrations of the reaction products were determined by high performance liquid chromatography. We used as controls: phenol, catechol (99%, Alfa Aesar), hydroquinone (99%, Alfa Aesar), maleic acid (98%, Alfa Aesar), oxalic acid (98%, Alfa Aesar) and formic acid (98%, Alfa Aesar). These products were analyzed by HPLC under the same conditions to identify the oxidation products by comparing the retention times with them.

The method of calculating relative percentages is based on the results of the chromatography; in a first step, the retention times of the most intense peaks of the chromatogram are selected, in the table provided with the chromatogram, the corresponding surfaces are taken. For each peak selected,

the sum of these surfaces is added, which equals 100%, and by the rule of three, the relative percentages of each product are calculated.

The conversion rate of phenol (Conv) is the overall conversion rate of this reagent. It is calculated according to the following equation where $[PhOH]_0$ and $[PhOH]_t$ are respectively the phenol concentrations of the initial solution and of the analyzed sample.

$$\mathrm{Conv}\left(\%\right) = \frac{\left[PhOH\right]_0 - \left[PhOH\right]_t}{\left[PhOH\right]_0} \times 100 \qquad (1)$$

In order to evaluate the phenol conversion rate achievable by non-catalyzed thermal oxidation, a blank test (in the absence of catalyst) was carried out. This reaction was also carried out in the presence of hydrogen peroxide to determine the influence of the metallic phase on the support.

3. Results and discussion

3.1. Characterization of ZSM-5 catalysts by XRD

The structures of the different ZSM-5 solids obtained were analyzed and identified.

Among the different techniques used, X-ray diffraction is an excellent method for detecting the structure of crystalline phases. The diffractograms (Fig. 1) show all the characteristic peaks of an MFI type zeolite [21]. The peaks are intense, which means that the samples are well crystallized. The catalysts present an orthorhombic symmetry whose spatial crystallographic group is the Pnma by three regions, the first between 7.5° and 10°, the second between 12° and 16° and the last for an angle 2θ between 22° and 26° [22], the most intense peak is attributed to the family of plants around (101) at 7.5° and 8°, three less intense peaks are attributed to the families (501) (303) and (133) respectively [23], the decrease in the intensity of the intense hkl peaks mentioned above of the exchanged solids compared to the Na-ZSM-5 solid is due to the replacement sodium cations by copper and iron cations. It was also expected that more pore cavities in the zeolite would be blocked by the addition of metal ions.
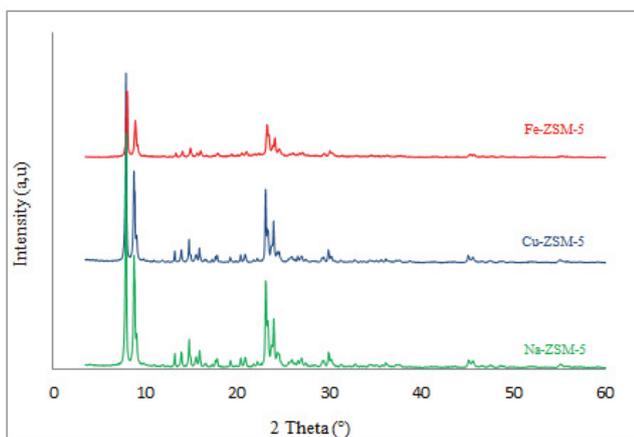
No additional phase was observed after ion exchange. It should also be noted that no phase corresponding to copper and iron was observed. This is strongly related to the low metal content contained in the zeolite and also due to the high dispersion of cations on the surface of the zeolite. We can therefore conclude that the structure of the zeolite is preserved after the exchange.

3.2. Characterization of ZSM-5 catalysts by infrared spectroscopy

The infrared spectra of ZSM-5 zeolites obtained before and after exchange with copper and iron show all the bands relating to the characteristic vibrations of ZSM-5 type zeolite [24], with a displacement of bands due to ion exchange. According to Fig. 2, the characterization of ZSM-5 synthesized and solids exchanged with copper and iron by infrared spectroscopy reveals bands at 545.73 cm^{-1} attributed to vibrations of structural units of six tetrahedron (5-1) complexes of MFI type zeolite. A large asymmetric elongation vibration band at 1,067.94 cm^{-1} and a symmetrical elongation vibration band at 628.96 cm^{-1} can be attributed to the internal Si–O–Al bond, as the bands at 797.47 and 1,224.75 cm^{-1} are due to the bonds of primary structural units. The band shifting recorded is due to the exchange of sodium cations with of copper, and iron cations [25,26].

3.3. Scanning electron microscopy

The micrography of different ZSM-5 zeolites (Fig. 3) is very similar to that reported in the literature of MFI zeolite. The aggregates of small crystals characteristic of ZSM-5 zeolite observed have regular and well-defined geometric shapes. This micrograph shows a single crystalline phase and the absence of an amorphous phase indicating the complete crystallization of sample.

The physicochemical properties of the catalysts used in this study are given in Table 1. The copper and iron content of the catalysts was determined from solutions obtained by atomic absorption spectrometry. According to the results, the copper content present in the catalyst Cu-ZSM-5 is equal to 3.1 wt.%, while the iron content

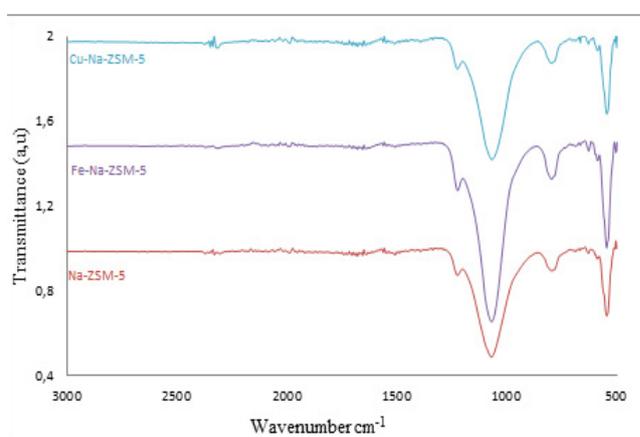Fig. 1. X-ray diffraction of different ZSM-5 zeolites.

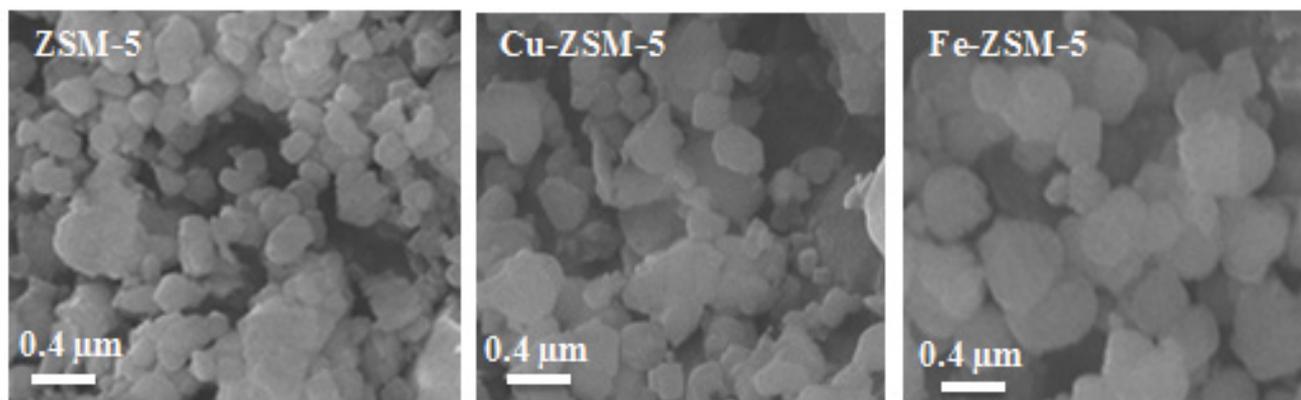Fig. 2. Infrared spectrum of ZSM-5 catalysts.

Fig. 3. SEM of different ZSM-5 catalysts.

Table 1
Physico-chemical properties of ZSM-5, Cu-ZSM-5, and Fe-ZSM-5 samples

	Si/Al	Cu (wt.%)	Fe (wt.%)	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	D_{pores} (nm)
ZSM-5	50			400	0.25	4.1
Cu-ZSM-5	50	3.1		352	0.19	2.6
Fe-ZSM-5	50		2.5	289	0.21	3.0

present in the catalyst Fe/ZSM5 is equal to 2.5 wt.% (all species included). The tests showed that the Brunauer–Emmett–Teller (BET) surface and the micropore volume of the zeolites decreased when the copper and iron loading was added. The pure ZSM-5 sample showed the highest BET area (400 m^2 g^{-1}), while the lowest BET area was found for the Fe-ZSM-5 sample (289 m^2 g^{-1}). The Cu-ZSM-5 sample has the second largest BET surface area (352 m^2 g^{-1}).

3.4. Catalytic activity

The materials obtained were analyzed by HPLC high pressure liquid phase chromatography. To identify the products of the oxidation reaction of phenol, we made a comparison between the retention times of the reaction products with the retention time of phenol, hydroquinone, catechol, maleic acid, oxalic acid and formic acid.

The appearance of peaks in HPLC chromatograms (not shown here) follows an order of polarity. In general the order of polarity of phenol and its derivatives in a non-polar column is as follows: from most polar to least polar. The most polar are the carboxylic acids, then alcohols (phenol), and lastly the less polar ones, that is, ketones and aldehydes.

First of all, when we carried out the oxidation of phenol by H_2O_2 without the presence of catalyst, we concluded after 4 h of reaction, that hydrogen peroxide can oxidize phenol but with a conversion rate reached of 35%, this means that the oxidation reaction requires the presence of the catalyst and the oxidant to obtain excellent results.

The comparison of results obtained during the experiments performed on different forms of ZSM-5 zeolite mentioned that the reactions carried out with doped ZSM-5 zeolites produced higher phenol conversion rates than those obtained with pure ZSM-5 zeolite [27] (Fig. 4a). The redox

properties of transition metal cations, e.g. copper and iron species, favor the production of active hydroxyl radicals in the presence of hydrogen peroxide. These radicals are responsible for the degradation and mineralization of organic compounds [28,29].

The higher catalytic performance obtained with iron-exchanged ZSM-5 zeolite means better utilization of the oxidant. This shows that the nature of the active iron species and the textural properties of the zeolite may be responsible for the more efficient use of the oxidant and the highest rate of phenol degradation. Which can be related to the thermodynamic properties and in particular the electrochemical properties of iron compared to copper [30–33]. Similar results on the catalytic activity of copper on phenol decomposition have been reported in the literature [34,35].

At pH close to 5 (4.8), the catalytic results clearly show that the phenol has been almost completely eliminated with the Fe-ZSM-5 and Cu-ZSM-5 catalysts, which means that the hydrogen hydroxide degrades to hydroxyl radicals which help convert phenol into a by-product. Fajerwerg et al. [17] also concluded that a pH of 5 was the optimum value for the degradation of phenol by H_2O_2 with iron used as a catalyst.

The distribution and the relative percentage of the by-products of the phenol oxidation reaction obtained on the catalysts based on pure zeolite-ZSM-5 and exchanged with copper and iron, are represented in Fig. 4b. These results show the appearance of degradation products, different percentages depending on the nature of the catalyst used, the catalytic activity of each fraction differs according to the composition of the latter. The catalyst based on natural ZSM-5 and exchanged with iron and copper gives a mixture of two products, which would be probably carboxylic acids and
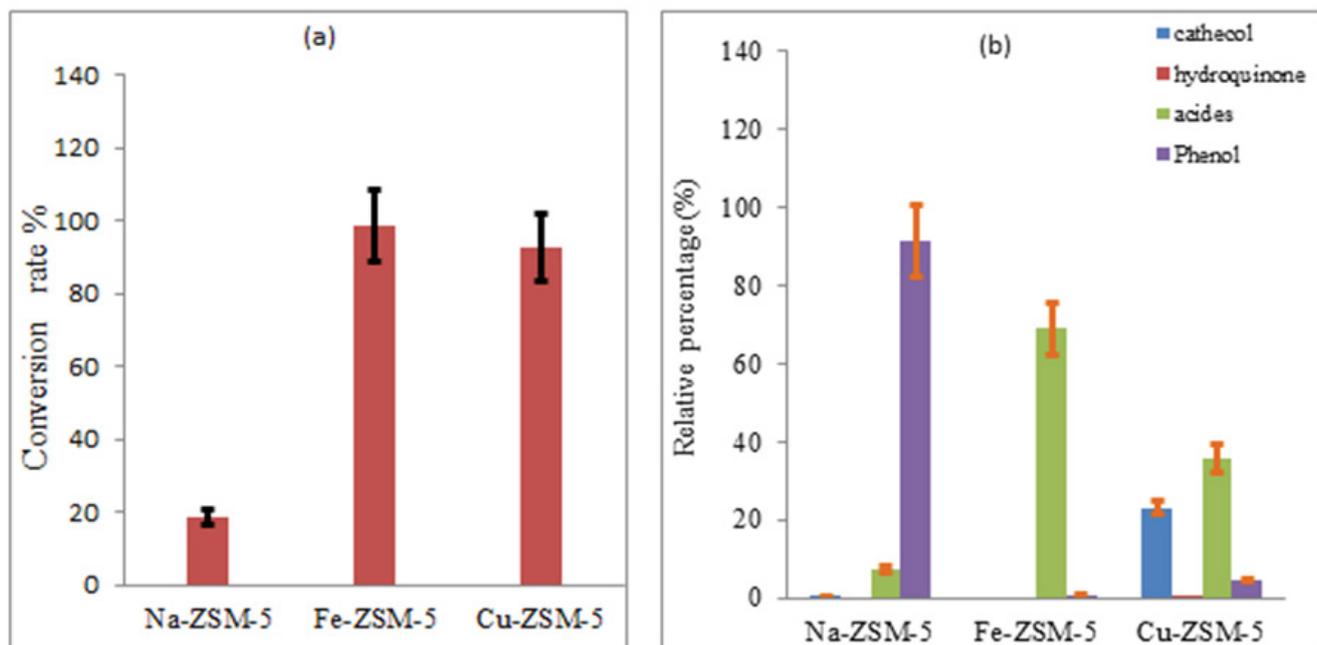
Fig. 4. (a) Conversion rate of phenol on ZSM-5 catalysts and (b) distribution of by-products by ZSM-5 catalysts. (t = 240 min, T = 70°C, C_{Ph} = 0.01 mol dm^{-3}, C_{H2O2} = 0.10 mol dm^{-3}, m_{cat} = 0.1 g dm^{-3}, pH = 4.8).

aromatic compounds with a percentage of the acids of 7.25% for the natural zeolite and 35.8% for the ZSM-5 modified with copper and a percentage of 68.87% for the ZSM-5 modified with iron respectively. We can say that these catalysts have a selectivity for acids.

4. Conclusion

During this work, catalysts based on ZSM-5 zeolite were prepared and characterized; their catalytic properties were tested in the oxidation reaction of phenol by hydrogen peroxide. The main results obtained are as follows:

- The study revealed that the activity of a catalyst containing copper and iron depends on the textural properties of the support and on several parameters such as the reaction temperature, and the method of preparation of the catalysts
- The pure ZSM-5 catalyst has a phenol conversion rate of 18%, while the Cu-ZSM-5 and Fe-ZSM-5 samples have conversion rates of 93% and 99%, respectively. The observation that pure ZSM-5 sample removes a small amount of phenol may be due to adsorption on pores and channels, as it does not contain metal ions; therefore, the only possibility is adsorption. The phenol removal capabilities of different materials show that the highest phenol removal capability is that of the Fe-ZSM-5 sample. The catalytic activity of Fe-ZSM-5 catalyst is higher than that of Cu/ZSM-5. This can be attributed to limitation by the diffusion of molecules into the pores of ZSM-5.
- At pHs close to 5, almost complete conversion of phenol was observed, meaning that hydrogen peroxide degrades to hydroxyl radicals that help phenol convert to a by-product, as shown by Fajerwerg et al. [17].

As prospects, concerning the phenol oxidation process in an aqueous medium, a great deal of work must be provided in order to improve the stability and the activity of the shaped catalysts, by the use of more resistant supports (for example: catalysts based on ZSM-5 zeolite exchanged with transition metals) and by modifying and optimizing the catalyst preparation method. Once this stage will be completed, it would be interesting to consider the treatment of real effluents. Finally, work on wet oxidation (OVHC) with hydrogen peroxide and in the presence of zeolites revealed a significant impact of the mode of decomposition of the by-products on the performance of the process. It would therefore be relevant to study the influence of the experimental conditions on this reaction.

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