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CATALYTIC OXIDATION OF PHENOL IN AQUEOUS MEDIA OVER CuZSM-12 ZEOLITE

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Abstract

The catalytic oxidation of phenol over CuZSM-12 (SAR = 200) has been studied using a semi-batch slurry reactor at temperatures of 110, 120 and 130°C, and acidic neutral and basic pH. At 130°C, the phenol undergoes total conversion to carbon dioxide and water in 1.5 h. The kinetic parameters were evaluated using a modified homogeneous-heterogeneous model for the experimental data. Using this modified model, the activation energy for the catalytic oxidation process was *ca*. 90 kJ mol^{-1}.

Keywords: Phenol oxidation, CuZSM-12 zeolite, slurry reactor, kinetic model

INTRODUCTION

Catalytic oxidation of phenol in aqueous media is a very important process in the chemical, pharmaceutical and petrochemical industry. The main purpose of this catalytic process is the total conversion of fractions of phenol to carbon dioxide and water. The application of some oxidizing compounds for chemical

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oxidation, such as halogens, ozone and hydrogen peroxide has been previously reported [1-3]. However, they are expensive and cause environmental problems, for instance, the production of chlorophenols and ozone. Thus, the oxidation of aqueous solutions of organic compounds using air or oxygen over solid catalysts and moderate conditions seems to be very promising for the environment, where phenol is fully converted to water and carbon dioxide [4-7]. Akyurtlu *et al*. [4] and Pintar *et al*. [7] reported values higher than 90% of phenol conversion after 80 min of reaction, showing the efficiency of this process. Supported solid catalysts containing transition metals, mainly copper, cobalt and zinc in low concentrations are active materials for the oxidation process. The catalyst should be hydrophobic, resistant and stable in the presence of water. Sadana and Katzer [8,9] showed that CuO supported on alumina at 96-246^{o}C are active catalysts for phenol conversion, whereas unsupported CuO is inactive for this process. The use of zeolite CuZSM-5 (SAR = 63 and 143); CuY and CoAPO-5 has been reported [7]. The catalytic activity of these materials is related to the redox center located into the micropores of the zeolites. The present work deals with the application of CuZSM-12 (SAR = 200) as catalyst for total oxidation of phenol in aqueous media.

EXPERIMENTAL

The NaZSM-12 zeolite was synthesized according to the Ref. [10], which was adapted to obtain a sample with Silica/Alumina Ratio (SAR) of 200. The chemicals used as starting materials were silica gel (Merck), sodium hydroxide (Merck), pseudoboehmite (Catapal B – Vista) and methyltriethylammonium chloride (MTEACl – Sigma) as organic template. These reactants were combined to obtain a gel with the following molar composition: 20 MTEA : 10 Na_2O : 0.5 Al_2O_3 : 100 SiO_2 : 2000 H_2O [10]. After preparation of the gel, it was transferred to a PTFE lined stainless-steel autoclaves and heated at 140°C, in static conditions for 6 days. After synthesis, the material was calcined to remove the template, then ion exchanged with a 0.5 M $CuSO_4$ solution in the temperature of 80°C for 2 h. After this process, it was calcined again at 500°C for 3 h to generate the CuZSM-12 catalyst.

The catalytic tests were carried out in a semi-batch slurry reactor. The process occurred at temperatures of 110, 120 and 130^{o}C, at initial phenol concentration of 5.0 g L^{-1} (0.053 mol L^{-1}) and stirring at 1000 rpm, in presence of oxygen under a pressure of 6-7 atm, flowing at 500 mL min^{-1}. In order to verify the influence of the pH of the media, the phenol oxidation was also processed at 120^{o}C using pH values of 3.0 (acid), 7.0 (neutral) and 11.0 (basic). The conversion of phenol was monitored by gas chromatograph (Varian 3400-CX) using a DB-PETRO capillary column of 100 m and 0.25 mm of external

diameter, with a 0.5 μm of dimethylpolysiloxane film. To each experiment was used a mass of 0.45 g of catalyst. The catalyst-to-water mass ratio was 0.9. The carbon dioxide was determined by the reaction of this gas with a solution of barium hydroxide. Thus, the mass of barium carbonate was quantified and related to the amount of CO_2 generated during the process.

RESULTS AND DISCUSSION

The crystalline phase of the catalyst by X-ray diffraction, (Shimadzu XRD 6000), chemical analysis by X-ray fluorescence using dispersive energy (Shimadzu EDX-800) and morphology of the crystals by scanning electron microscopy (Philips ESEM microscope), showed that the crystalline phase was obtained, for a typical MTW (Mobil Twelve) structure, with the main XRD peaks at 2-theta of 7.36; 8.80; 20.88; 22.88 and 23.20 degrees [10-12]. From the catalytic experiments, were obtained results of conversion of phenol as a function of temperature and time of reaction as well as the effect of pH of the media.

As can be visualized in Fig. 1, the phenol oxidation increases with the temperature and time, with conversion degree ranging from 40 to 100% for 120 min of reaction. It is clearly observed an induction period on the process at the beginning of the reaction. This phenomena was also reported by Sadana and Katzer [8,9], Pintar *et al*. [7,13] and Santos *et al*. [14], and it is associated to free radicals produced in the aqueous media, due to the reaction between phenol and CuZSM-12, proposed as follows:

$$\text{H-R-OH} + \text{CuZSM-12} \rightarrow \text{H---*R=O} + \text{*H---CuZSM-12} \quad (1)$$

$$\text{*OH---CuZSM-12} + \text{H-R-OH} \rightarrow \text{H---*R=O} + \text{HOH} + \text{CuZSM-12} \quad (2)$$

The H-R-OH species refers to phenol. Equations (1) and (2) indicate reactions of initialization. The free radicals react with oxygen from liquid phase, giving rise to peroxides and hydroperoxides, which are the most reactive species for hydrocarbon oxidation in aqueous media.

The SiO_2/Al_2O_3 ratio of 200 favors the hydrophobic character of the zeolite, increasing the adsorption capacity of the material, and consequently the rate of reaction. Figure 2 shows the amount of barium carbonate obtained at the end of experiment. This fact confirmed the efficiency of the CuZSM-12 as catalyst for total oxidation of phenol. According to the literature [13,14], the rate of reaction is strongly influenced by the initial pH value of the solution. This influence was verified on the catalytic tests at temperature of 120°C at pH = 3 (acid), neutral and pH = 11 (basic), as observed in the Fig. 3.

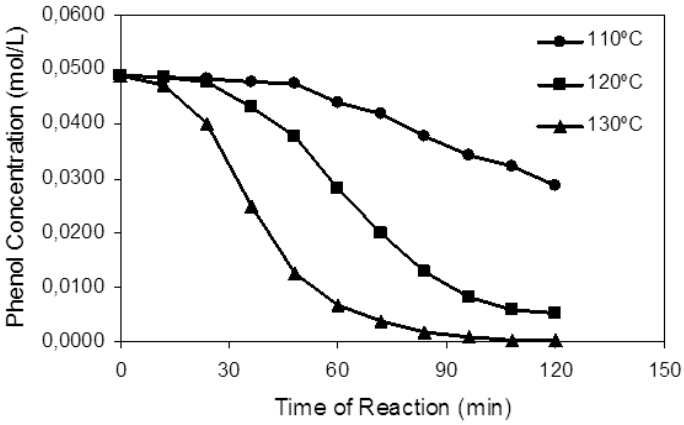

Fig. 1. Temperature effect on decreasing of phenol concentration as a function of time of process

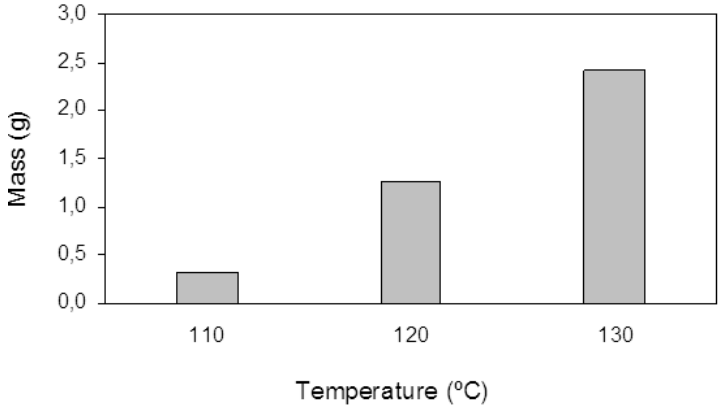

Fig. 2. Effect of the temperature on the formation of barium carbonate

According to the obtained data, the rate of phenol oxidation is a function of the acidity. The results suggest that the electrostatic field generated by the acid media on the zeolite activates the free radicals and the catalytic activity for total oxidation of phenol to CO_2 and water. The basic media decreases the catalytic activity for the process. It is suggested that the hydroxyl group coordinates to

copper, producing $Cu(OH)^+$ complexes which are non-reactive species in the oxidation process. The intercept of curves of neutral and basic media at 60 min shows that there exists an equilibrium between free radicals and copper complexes in this media. As shown in Fig. 4, for the final process of the phenol oxidation, the total mass of barium carbonate was quantified as an indicative function of CO_2 production.

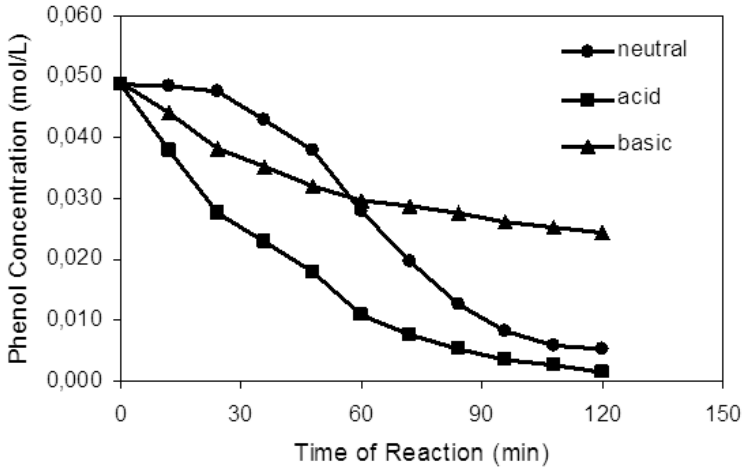

Fig. 3. Effect of the pH of the media on the phenol concentration at the temperature of 120°C

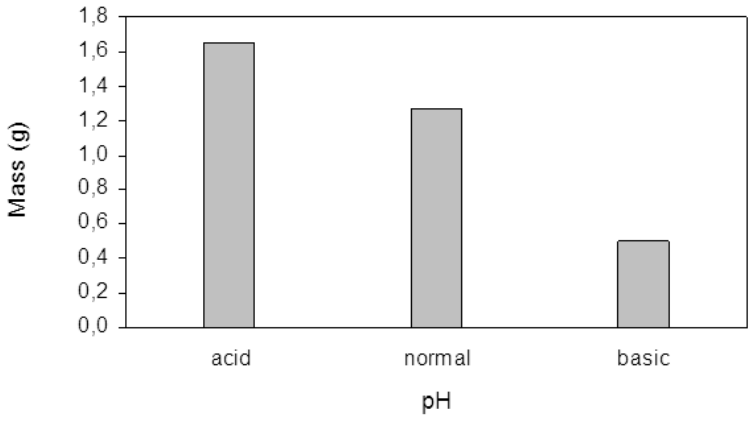

Fig. 4. Effect of pH of the media on the formation of barium carbonate

The catalytic oxidation of phenol in aqueous media in a slurry reactor occurs according to a heterogeneous-homogeneous autocatalytic mechanism involving free radicals. This model is characterized by the following rate equation as a function of the reactant concentration: according the following:

$$ln\left(\frac{C_{fe,o}\cdot\left(c_o - C_{fe}\right)}{C_{fe}\cdot\left(c_o - C_{fe,o}\right)}\right) = k^{*}\cdot c_o \cdot C_{cat.}\cdot t \qquad (3)$$

where: $C_{fe,o}$ is the initial concentration of phenol (mol/L); C_{fe} is the concentration of phenol (mol/L); c_o is a constant; k^* is the apparent heterogeneous rate constant ($L/g_{cat}.min$); $C_{cat.}$ is the catalyst concentration (g_{cat}/L); and t is the time (min). Due to the difficulty to identify the intermediates of the reaction, the constant c_o was assumed to be 10% higher than the initial concentration of phenol. In Fig. 5, the plot obtained from Eq. (3) is shown. The kinetic model for the experimental data fits this equation. This is evident from the straight line observed for different temperatures of the oxidation process. From the slope of each line (Fig. 5), the value of k* is determined from the Arrhenius equation $ln(k^*)=ln(A)/(Ea/RT)$, plotting $ln(k^*)$ against (1/T), as shown in Fig. 6, the activation energy (Ea) and the pre-exponential factor (A) were obtained as 90.0 kJ/mol and $1.97x10^{11}$ L/(gcat min) for phenol oxidation.

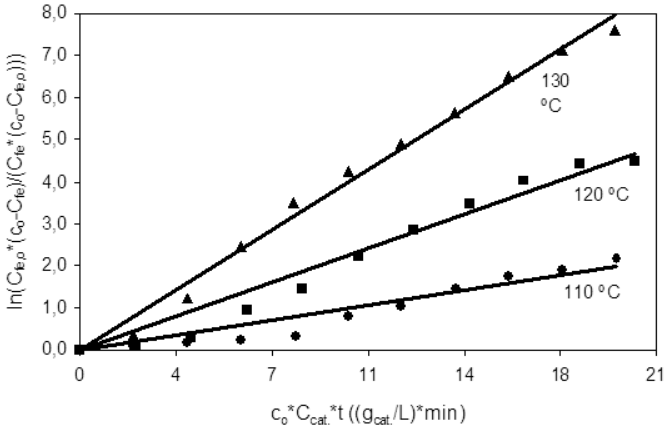

Fig. 5. Autocatalytic kinetic model for the oxidation different temperatures

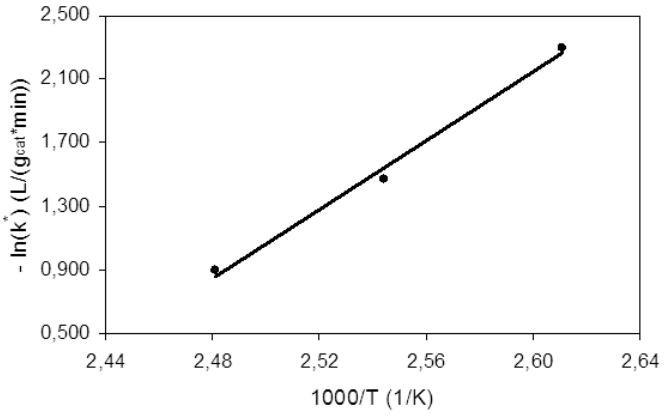

Fig. 6. Arrhenius plot for phenol oxidation

CONCLUSIONS

The CuZSM-12 zeolite proved to be a good catalyst for the total oxidation of phenol in aqueous media at relatively low temperatures in a semi-batch slurry reactor. The Silica/Alumina ratio of 200 was used in order to combine the hydrophobic property with acidity of the catalyst. By adjusting the pH it was observed that acidic media favor the formation of free radicals, increasing the degree of phenol conversion. The experimental phenol concentrations as a function of time were adjusted using an autocatalytic heterogeneous-homogeneous model. Combining this model with the Arrhenius equation yielded an activation energy of *ca*. 90 kJ/mol for the oxidation of phenol.

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REFERENCES

1. Y. Yamamoto, E. Niki, H. Shiokawa, Y. Kamiya: *J. Org. Chem.*, **44**, 2137 (1979).
2. A. Fortuny, C. Ferrer, C. Bengoa, J. Font, A. Fabregat: *Catal. Today*, **24**, 79 (1995).

3. E. Plattner, C. Comninellis: *Process technology for water treatment*, p. 205. Plenum, New York 1988.
4. J.F. Akyurtlu, A. Akyurtlu, S. Kovenklioglu: *Catal. Today*, **40**, 343 (1998).
5. A. Pintar, J. Levec: *J. Catal.*, **135**, 435 (1992).
6. A. Alejandre, F. Medina, P. Salagre, A. Fabregat, J.E. Sueiras: *Appl. Catal. B: Environmental*, **18**, 307 (1998).
7. A. Pintar, G. Bercic, J. Batista, J. Levec: *Stud. Surf. Sci. Catal.*, **110**, 633 (1997).
8. A. Sadana, J.R. Katzer: *Ind. & Eng. Chem. Fund.*, **13**, 127 (1974).
9. A. Sadana, J.R. Katzer: *J. Catal.*, **35**, 140 (1974).
10. H. Robson: *Microp. Mat.*, **22**, 551 (1998).
11. W.M. Meier, D.H. Olson, C. Baerlocher: *Atlas of Zeolite Structure Type*s. Elsevier; New York 1996.
12. A.O.S. Silva, M.J.B. Souza, J.M.F.B. Aquino, V.J. Fernandes Jr., A.S. Araujo: *J. Therm. Anal. Calor.*, **75**, 699 (2004).
13. A. Pintar, J. Levec: *Chem. Eng. Sci.*, **49**, 4391 (1994).
14. A. Santos, E. Barroso, F. García-Ochoa: *Catal. Today*, **48**, 109 (1999).