Investigation of the catalytic wet peroxide oxidation of phenol over different types of Cu/ZSM-5 catalyst

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Abstract

In this work oxidation of phenol with hydrogen peroxide on Cu/ZSM-5 catalysts was studied. The catalysts samples were prepared by two different methods: by ionic exchange from the protonic form of commercial ZSM-5 zeolite, and by direct hydrothermal synthesis. Characterization of the catalysts extends to X-ray diffraction (XRD), while the adsorption techniques were used for the measurement of the specific surface area.

The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at the atmospheric pressure and the temperature range from 50 to 80 °C. The mass ratio of the active metal component on the zeolite was in the range of 1.62–3.24 wt.%. for catalyst prepared by direct hydrothermal synthesis and 2.23–3.52 wt.% for catalyst prepared by ion exchange method. The initial concentration of phenol and hydrogen peroxide was 0.01 and 0.1 mol dm^{-3}, respectively. The influence of different methods of Cu/ZSM-5 preparation on their catalytic performance was monitored in terms of phenol conversion and degree of metal leached into aqueous solution.
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1. 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 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, 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, e.g., adsorption processes, biological processes, incineration through dry way and processes of wet oxidation (WO), and of these only the WO processes show greater viability and relative efficiency when the contaminants are found in the diluted aqueous phase.

WO [1–3] can be defined as the oxidation of organic and inorganic compounds in an aqueous solution or suspension by air or oxygen (WAO) at high temperature and pressure: 150–200 °C and 2–15 MPa. In order to improve the conditions of such a process, homogenous and heterogeneous catalysts [1–11] were used. Catalytic wet air oxidation (CWAO) is an efficient technique to eliminate organic compounds such as phenols but reaction is performed at high operating pressure (1–10 MPa) and temperature (80–200 °C) makes investment rather costly.

The catalytic wet peroxide oxidation (CWPO) process first adapted from the classical Fenton's reagent allowed high oxidation efficiencies (up to 95%) under mild conditions ($T \leq 50$ °C, 0.1–0.3 MPa), using hydrogen peroxide and a homogeneous Fe^{2+} catalyst [2]. Even though the systems show an effective elimination of organic pollutants, two main drawbacks limit its application: a narrow range of pH, usually around 3.0 and the difficulties to recover the catalyst that may lead to a secondary pollution. The use of heterogeneous catalysts could be an alternative method of these problems. Recently, a great number of materials containing iron and copper as precursors supported/intercalated on/in oxides, clays, zeolite and polymers as active catalysts for Fenton-type reactions have been proposed to remove organic compounds [12–17]. These catalysts exhibit the advantages of heterogeneously catalyzed process and got

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Nomenclature

c_{HP}	hydrogen peroxide concentration (mol dm^{-3})
c_{Ph}	phenol concentration (mol dm^{-3})
E_a	activation energy (kJ mol^{-1})
k_{HP}	reaction rate constant for hydrogen peroxide decomposition (min^{-1})
k_{Ph}	reaction rate constant for phenol oxidation (dm^3 mol^{-1} min^{-1})
n	reaction order with respect to phenol
t	time (min)
T	temperature (°C)
w_{cat}	mass of catalyst (g)
Y_{Cu}	concentration of catalytic active sites (wt.%)

Fig. 1. XRD patterns of Cu/ZSM-5 catalyst prepared by ion exchange and direct hydrothermal synthesis, respectively.

relatively higher oxidation efficiency as well as a lower sensitivity to pH compared with homogeneous catalysts at the same reaction conditions. However, most of them could not be used due to its lack of stability in aqueous media. A leaching of the active elements or/and the support was often observed [10,13].
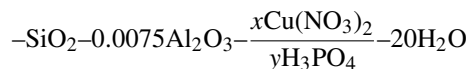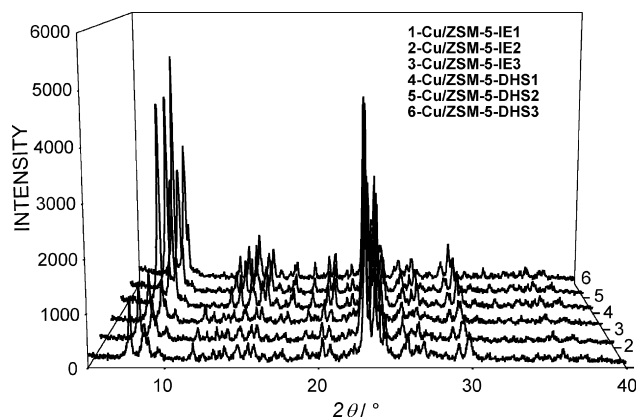
The present article is devoted to the investigation of the influence of different methods of preparation of Cu/ZSM-5 on the catalytic activity and stability in the wet oxidation of phenol by hydrogen peroxide.

2. Experimental

2.1. Preparation of catalysts

The catalyst samples were prepared by two different methods: by direct hydrothermal synthesis (code: DHS) and by ion exchange (code: IE) from the protonic form of ZSM-5. In the first case, Cu/ZSM-5 zeolites were synthesized from gels with Si/Cu ratios varying from 29 to 67. Synthesis was carried out using high purity chemicals Na$_2$O, TPABr, SiO$_2$, Al$_2$O$_3$, Cu(NO$_3$)$_2$, and H$_3$PO$_4$ to prepare gel with composition (in mol) as follows:

0.16Na$_2$O–0.08TPABr

$$-SiO_2-0.0075Al_2O_3-\frac{xCu(NO_3)_2}{yH_3PO_4}-20H_2O$$

where x varied in the range from 0.015 to 0.035 and y from 0.045 to 0.105. The Cu/ZSM-5 samples were crystallized in autoclave at 70 °C for 72 h. After the crystallization, the solids were washed with distilled water until reaching pH 7, and then dried at room temperature, before to be calcined at 550 °C for 5 h.

Me-H-ZSM-5 samples of metal bearing zeolites were obtained by ion-exchange treatment with 1 M solution of NH$_4$Cl at 80 °C for 2 h in order to exchange the sodium cation and to prepare the zeolites in the protonic form. The post-synthesis thermal treatment consisted in the calcinations of the samples at 550 °C for at least 5 h.

In the second case Cu/ZSM-5 was prepared by the ion exchange of protonic form of commercial ZSM-5 zeolite. Ionic exchange was carried out at 25 °C in aqueous solution of Cu(CH$_3$OO)$_2$ over 24 h. After filtration and washing with redistilled water the sample was dried overnight at 100 °C.

Crystalline structure of the Cu/ZSM-5 zeolites prepared by both methods was checked by X-ray diffraction analysis. XRD patterns were obtained with Philips PW 1065 diffractometer using Ni-filtered Cu Kα radiation. In the XRD patterns (Fig. 1), all peak positions matched those reported for ZSM-5 structure [18] and no-impurity phase was observed.

Textural characterization of the catalyst samples was performed by means of nitrogen adsorption/desorption isotherms at −96 °C using Micromeritics ASAP 2000 instrument. Before measuring the samples were degasified at 200 °C for 24 h. Software program included BET and Langmuir surface area analysis, t-plot analysis (Harkins and Jura equation for determination of statistical thickness of the adsorbed layer) and pore size distribution according Barett–Joyner–Halende model. The main characteristics of Cu/ZSM-5 samples prepared on both ways were given in Table 1.

The stability of the catalyst samples to leaching of the active metal ingredient was verified by atomic absorption of the filtered solution samples.

Table 1
The main characteristic of Cu/ZSM-5 catalysts

Method of preparation	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore diameter (nm)	Cu content (wt.%)
Cu/ZSM5-DHS1	408.47	0.28	2.75	1.62
Cu/ZSM5-DHS2	397.94	0.26	2.63	2.75
Cu/ZSM5-DHS3	391.55	0.23	2.37	3.24
Cu/ZSM5-IE1	293.91	0.15	2.01	2.23
Cu/ZSM5-IE2	299.59	0.15	2.03	2.48
Cu/ZSM5-IE3	300.45	0.15	2.03	3.52