

CATALYTIC WET PEROXIDE OXIDATION OF PHENOL OVER COPPER CONTAINING ZEOLITES

Karolina Maduna Valkaj, Ozren Wittine, Stanka Zrnčević

Faculty of Chemical Engineering and Technology, University of Zagreb
Marulićev trg 19, 10000 Zagreb
E-mail: kmaduna@fkit.hr

INTRODUCTION

Due to its presence in various processes in pharmaceutical, chemical and petrochemical industry, where it is used either as reagent, intermediate substance or solvent, phenol is known as one of the most common organic water pollutants. Its high toxicity and suspected mutagenic and carcinogenic properties prohibit the release of untreated phenolic wastewater into the natural recipients. Therefore, it is of the most importance to constantly develop new and improve existing technologies in order to enhance wastewater treatment processes.

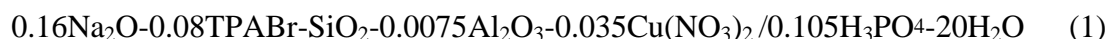
Low-temperature, aqueous-phase heterogeneous catalytic oxidation of dissolved organic compounds is a potential means for remediation of contaminated industrial effluents and other wastewater streams. The abatement of phenol in water can be most successfully conducted in the catalytic wet oxidation process with hydrogen peroxide as oxidant (*CWPO process*) [1,2]. Using zeolites that contain copper as catalytic active sites, total degradation of phenol can be achieved under mild operating conditions at temperatures below 100 °C and atmospheric pressure [3-5].

In this article catalytic properties of copper containing ZSM5, Y5 and 13X zeolites were investigated in heterogeneous catalytic wet peroxide oxidation of aqueous phenolic solutions. Influence of synthesis and post synthesis methods, framework type, copper loading and reaction parameters were studied. Special attention was directed towards evaluation of catalysts' stability in terms of copper leaching into reaction mixture.

EXPERIMENTAL

Catalyst synthesis

The catalysts were prepared by two different methods: direct hydrothermal synthesis (code *DHS*) and ion exchange (code *IE*) from the protonic forms of ZSM5, Y5 and 13X zeolites. In the first case, Cu/ZSM5 zeolite was synthesized from gel using high purity chemicals (Na₂O, TPABr, SiO₂, Al₂O₃, Cu(NO₃)₂ and H₃PO₄). The composition of gel was as follows:



The crystallization took place in an autoclave at 170 °C during 72h. Cu/H-ZSM5 sample of metal bearing zeolites was obtained post synthesis by ion exchange treatment with 1 M ammonium chloride solution, after what the catalyst underwent calcination at 773 K throughout 5h.

In the second case Cu/ZSM5, Cu/Y5 and Cu/13X zeolites were prepared by the ion exchange of protonic form of commercial ZSM5 (*Leuna Werke*), Y5 (*Süd Chemie*) and 13X (*UOP*) zeolites. The first step involved ion exchange with 1M sodium nitrate solution while

the second step involved ion exchange with copper acetate solution, what was carried out at 25 °C over 24 hours after what the samples were dried overnight at room temperature.

The Cu/13X sample was exposed to calcination at extreme temperature (1000 °C for 5h) in order to obtain zeolite based ceramic material that exhibited higher stability to the loss of active metal component during the reaction.

Catalyst characterization

Crystalline structures of all prepared catalysts were checked by X-ray diffraction analysis. XRD patterns were obtained with Philips PW 1830 diffractometer using Ni-filtered CuK_α radiation operating at 40 kV and 30 mA. The patterns were recorded over $5^\circ < 2\theta < 40^\circ$ range using a step size of 0.02° .

Textural characterization of the catalyst samples was performed by means of nitrogen adsorption/desorption isotherms at -96°C using Micromeritics ASAP 2000 instrument.

Copper content on catalysts was determined from solutions obtained by atomic absorption spectrometry using Perkin Elmer AAS 3110.

Catalytic evaluation

The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at atmospheric pressure, temperature of 70°C and stirrer speed 200 rpm. Phenol degradation experiments involved an aqueous phenol solution (200 cm^3 , 0.01 mol dm^{-3}). The solid catalyst (0.1 g dm^{-3}) was suspended in the solution under continuous stirring. After the reaction mixture was heated to the desired temperature hydrogen peroxide (0.1 mol dm^{-3}) was added what initiated the reaction. Aliquots were withdrawn during the reaction course at selected time, filtered by means of $0.2\ \mu\text{m}$ nylon membrane to analyze the reaction mixture. The decreases in phenol concentration, as well as the decomposition of hydrogen peroxide were analytically monitored. Phenol was detected and measured by UV/VIS absorbance at 510 nm wavelengths by standard 4-aminoantipyrine colorimetric method. Hydrogen peroxide was detected by UV/VIS absorbance at 450 nm by ammonium-metavanadate colorimetric method.

RESULTS AND DISCUSSION

In the Table 1 physical and chemical properties of prepared catalysts are shown. Copper content of all samples was around 3 wt. %, while the measured surface area differed for every zeolite type. Extremely low BET surface area of Cu/13X sample can be attributed to ceramization process.

Table 1. Physico-chemical properties of calcined Cu/ZSM-5 samples

Sample	Method of preparation	BET surface area ($\text{m}^2\text{ g}^{-1}$)	Cu content (% wt)
Cu/ZSM5-DHS	direct hydrothermal synthesis	391.45	3,24
Cu/ZSM5-IE	ion exchange	300.45	3,52
Cu/Y5	ion exchange	576.69	3,54
Cu/13X pellet	ion exchange + ceramization	-	2,73
Cu/13X powder	ion exchange + ceramization + grinding	3	2,73

To confirm structure and crystallinity, the samples were studied by X-ray diffraction. In the XRD patterns (Fig. 1), all peak positions matched those reported for MFI and FAU structure [6] and no-impurity phase was observed. XRD patterns of Cu/13X and Cu/ZSM5-IE samples show that incorporation of copper into the zeolite framework via ion exchange method does not have an influence on the crystallinity and structure of the zeolites, while the ceramization process does. The high intensities of all peaks and low background lines indicate the high crystallinity of all prepared zeolites (Fig. 1).

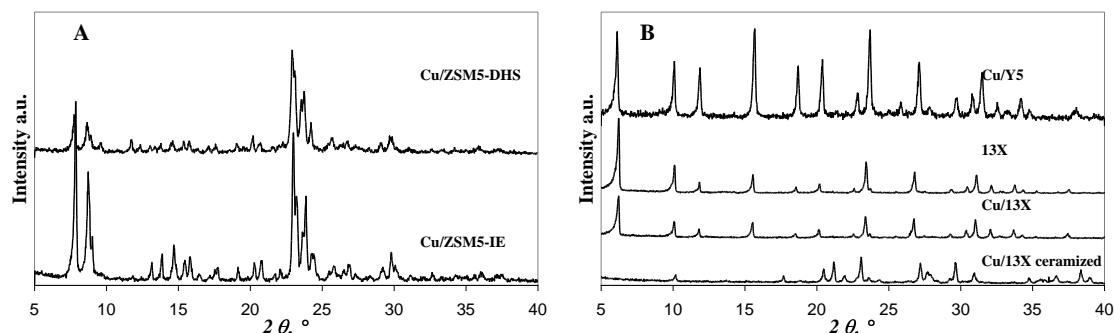


Figure 1. X-ray diffraction patterns of Cu/ZSM5-DHS and Cu/ZSM5-IE catalysts (A) and FAU type catalyst Cu/Y5 and Cu/13X powder (B).

At the beginning of catalytic evaluation of prepared catalysts a preliminary experiment was conducted which showed that phenol can be oxidized with hydrogen peroxide without the catalyst, but in that case, its conversion after 3 h of the reaction was around 20%. As can be seen from Fig. 2 the highest activity in terms of both phenol oxidation and hydrogen peroxide decomposition exhibits Cu/Y5 catalyst. This is in accordance with the fact that this sample has the highest measured surface area, as well as copper loading.

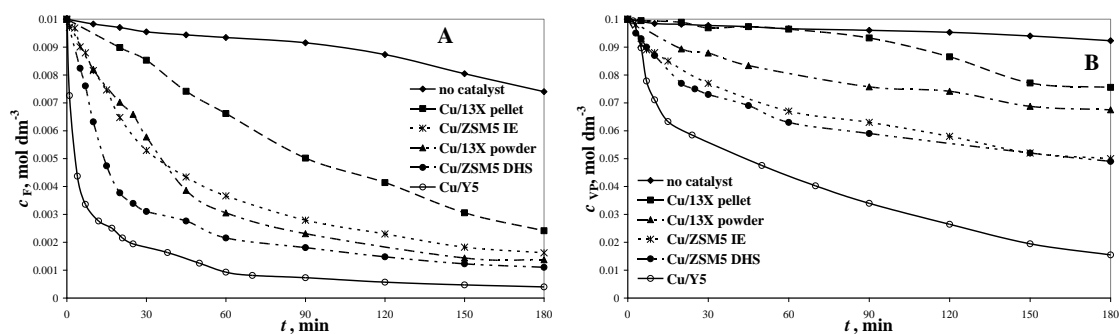


Figure 2. Phenol oxidation (A) and hydrogen peroxide decomposition (B) over different zeolites containing copper ($c_F = 0.01 \text{ mol dm}^{-3}$, $c_{VP} = 0.1 \text{ mol dm}^{-3}$, $T = 343 \text{ K}$, $w_{\text{cat}} = 0.1 \text{ g dm}^{-3}$, $w_{\text{Cu/13X pellet}} = 0.5 \text{ g dm}^{-3}$).

If we compare the two Cu/ZSM5 catalysts prepared by two different methods of synthesis, it can be seen that the activity of the catalyst prepared by DHS method is significantly higher. The powdered form of ceramized Cu/13X catalyst showed noticeable activity when compared to other samples despite its lower copper content and surface area. The pelleted form of ceramized Cu/13X catalyst had the lowest activity of all, no doubt due to occurrence of intraphase diffusion.

Catalyst' stability in terms of copper leaching is presented on Fig. 3. The tests showed that the leaching of copper depends strongly of the pH of reaction mixture. With the progression of reaction the intermediates form, such as organic acids that lowers the pH value of reaction mixture. It has been reported that oxalic acid specially favors the process of leaching since it forms stabile complexes with the metal released to the reaction mixture. The highest stability exhibited ceramized catalysts, indicating that the process of ceramization has a positive influence on the stability of catalysts. The Cu/ZSM5 zeolite prepared by DHS method, although very active, has poor stability since active metal component almost completely left its structure during the reaction. On the other hand Cu/ZSM5 and Cu/Y5 catalysts that were prepared by IE method showed stronger resistance to leaching of copper from its' surface.

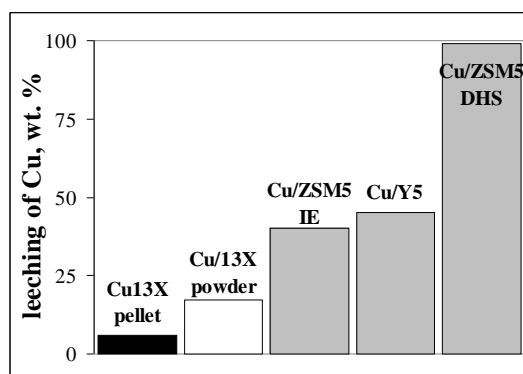


Figure 3. Leaching of copper from catalyst surface into reaction mixture ($c_F = 0.01 \text{ mol dm}^{-3}$, $c_{VP} = 0.1 \text{ mol dm}^{-3}$, $T = 343 \text{ K}$, $w_{\text{cat}} = 0.1 \text{ g dm}^{-3}$, $w_{\text{Cu/13X pellet}} = 0.5 \text{ g dm}^{-3}$).

CONCLUSION

The present work describes wet oxidation of aqueous solutions of phenol with hydrogen peroxide using different types of heterogeneous copper bearing zeolites under mild conditions. From the presented data it can be concluded that all catalysts showed good activity in terms of destruction of phenol and decomposition of hydrogen peroxide. However, stability of zeolites remains a challenging issue. Only the ceramized samples showed acceptable resistance to copper leaching. Further investigation on this aspect of catalysts' catalytic performance is currently being conducted.

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KATALITIČKA MOKRA OKSIDACIJA VODIKOVIM PEROKSIDOM UZ ZEOLITE SA BAKROM KAO KATALITIČKI AKTIVNOM TVARI

Karolina Maduna Valkaj, Ozren Wittine, Stanka Zrnčević

Fakultet kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu
Marulićev trg 19, 10000 Zagreb
E-mail: kmaduna@fkit.hr

SAŽETAK

Zbog toga što se fenol često upotrebljava u različitim industrijskim procesima, bilo kao reaktant, međuprodukt ili otapalo, zamjetna je i njegova prisutnost u otpadnim vodama tih procesa. Kako je fenol izrazito toksičan spoj za koji se smatra da posjeduje i mutagena i kancerogena svojstva, zabranjeno je nekontrolirano ispuštanje u okoliš svih otpadnih voda koje ga mogu sadržavati. Zato je od izuzetne važnosti stalno razvijati nove i usavršavati postojeće tehnologije kako bi se unaprijedile sadašnje metode obrade industrijskih otpadnih voda.

Katalitička oksidacija otopljenih organskih tvari u vodi uz heterogene katalizatore koja se provodi pri blagim reakcijskim uvjetima potencijalno je rješenje problema zagađenih industrijskih i municipalnih otpadnih voda. Uklanjanje fenola u vodi može se vrlo uspješno provesti procesom katalitičke mokre oksidacije sa vodikovim peroksidom (*CWPO proces*) [1,2]. Korištenjem zeolitnih katalizatora koji sadrže bakar kao aktivnu komponentu, potpunu oksidaciju fenola je moguće postići i pri blagim reakcijskim uvjetima: atmosferskom tlaku i temperaturama ispod 100 °C [3-5].

U ovom radu su ispitivane katalitičke značajke Cu/ZSM5, Cu/Y5 i Cu/13X zeolita u heterogenokatalitičkoj reakciji oksidacije fenola vodikovim peroksidom. Ispitivan je utjecaj različitih metoda pripreme i obrade katalizatora, tipa zeolita nosioca katalitički aktivne komponente, sadržaja bakra na zeolitu i reakcijskih uvjeta. Posebna pozornost usmjerena je istraživanju stabilnosti pripremljenih katalizatora u smislu ispitivanja intenziteta otpuštanja katalitički aktivne komponente – bakra tijekom reakcije sa zeolita u reakcijsku smjesu.

Ključne riječi: Obrada otpadnih voda; CWPO; priprava katalizatora; Cu/ZSM5; Cu/Y5; Cu/13X; Oksidacija fenola;