

INFLUENCE OF THERMAL TREATMENT ON CATALYTIC BEHAVIOR OF Cu/13X CATALYST IN CWPO OF PHENOL AQUEOUS SOLUTIONS

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ABSTRACT

Influence of postsynthesis thermal treatment of copper bearing 13X zeolite on its activity and stability in the catalytic wet peroxide oxidation of aqueous phenol solutions was investigated. The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at 353 K. The experimental results showed that total degradation of phenol can be achieved under mild operating conditions. The postsynthesis thermal treatment resulted in more stable catalyst in respect to stability of both catalysts' active metal component (copper) and support while the activity of catalysts in terms of TOC conversion remained unaltered.

Keywords: Catalytic oxidation, phenol, hydrogen peroxide, copper, zeolite.

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 wastewater containing phenol 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. Catalytic wet peroxide oxidation, known as CWPO process is one of the methods that can be used for the minimization of organic pollution in practice [1]. With the use of catalyst (homogeneous or heterogeneous) the process can be successfully operated under mild conditions with low energy consumption - atmospheric pressure and temperatures below 353 K. Zeolites modified with copper possess good catalytic properties when compared to the other types of heterogeneous catalysts tested in CWPO reaction [2,3]. Commercial zeolite type 13X was selected as catalyst support for copper cations in this research. Activity and stability of prepared catalyst was tested in catalytic wet peroxide oxidation of phenol in aqueous medium. Influence of postsynthesis treatment on their catalytic properties was investigated.

EXPERIMENTAL

The catalysts were prepared by ion exchange from commercial 13X zeolite (13X-APG Molsiv™ UOP Italy, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$, $w_{\text{N}_2\text{O}} = 20$ wt. %) by conventional method. 10 g of zeolite was ion exchanged with 0.015 M copper acetate solution after what the sample was filtered and dried overnight at room temperature. Postsynthesis thermal treatment consisted in calcination of prepared Cu/13X sample at 1273 K for 5h (ramp 5 K min⁻¹) in order to obtain zeolite based material that exhibit higher stability. The catalysts were characterized by BET, XRD, FTIR and AAS in order to obtain information about their physical and chemical properties. The catalytic tests were carried out in a stainless steel Parr reactor in batch

operation mode at atmospheric pressure at 353 K and stirrer speed 200 rpm. Phenol degradation experiments involved an aqueous phenol solution (200 cm³, 0.01 mol dm⁻³). The solid catalyst (0.5 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. The decreases in phenol and hydrogen peroxide concentrations were analytically monitored (UV-VIS spectrometry). Total organic carbon (TOC) was determined with TOC-V CSN Shimadzu analyzer from diluted reaction solutions.

RESULTS AND DISCUSSION

The physical and chemical properties of prepared catalysts are shown in table 1. The incorporation of copper on 13X zeolite did not have a significant effect on the measured surface area and pore volume since the values obtained for 13X and Cu/13X are in good accordance. On the other hand, thermal treatment caused the decrease of both BET surface area and pore volume (sample Cu/13X-K1273) due to a change in crystalline structure. Copper content of all samples was around 3.6 wt. % and wasn't affected by thermal treatment.

Table 1. Physical and chemical properties of prepared catalysts.

Sample	BET surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Mass loss after calcination (wt. %)	Cu content (wt. %)
13X	498.91	0.33	-	-
Cu/13X	494.67	0.31	-	3.59
Cu/13X-K1273	8.42	<0.01	21.8	3.58

To confirm structure and crystallinity, the samples were studied by X-ray diffraction (Fig. 1A). As can be seen, for 13X and Cu/13X sample all peak positions matched those reported for FAU structure [4] and no-impurity phase was observed. No shift in the peak positions and no significant diffraction lines assigned to any new phase are observed denoting that incorporation of copper into the zeolite framework via ion exchange method does not have an influence on the crystal structure of the zeolite which indicates that Cu²⁺ ions seem to be well dispersed in the zeolite framework [5]. The catalyst that was thermally treated at 1273 K exhibits a change in number, intensity and position of peaks what confirms that formation of new phase (identified as nepheline) occurred [6]. The high intensities of peaks and low background lines suggest high crystallinity of all samples.

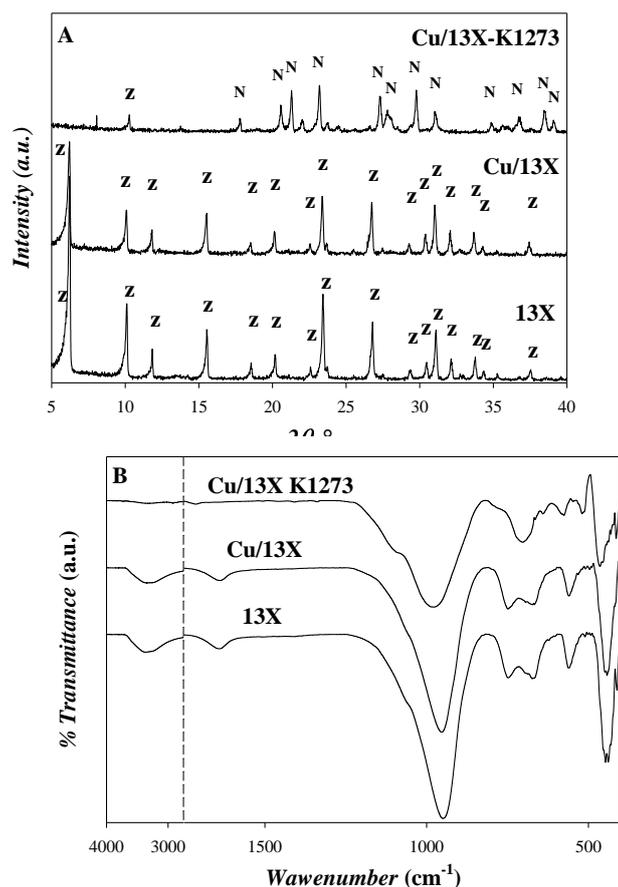


Figure 1. X-ray diffraction patterns (A) and ATR-IR spectra (B) of 13X, Cu/13X and Cu/13X-K1273 samples (Z - zeolite, N – nepheline).

The recorded ATR-IR spectra shown in Fig. 1B confirm that no structural changes of zeolitic framework occur during ion exchange treatment. Apart from bonds near 3350 and 1640 cm^{-1} that are assigned to O-H stretching vibration of water and/or OH group adsorbed in zeolite, IR spectra of 13X and Cu/13X samples consists of two classes of vibrations: internal vibrations of the framework TO_4 tetrahedron and vibrations related to external linkages between tetrahedra. The former, which are not sensitive to variations in framework type on IR spectra are expressed trough an asymmetric stretch around 1250-950 cm^{-1} , symmetric stretch around 720-650 cm^{-1} and T-O bend around 500-420 cm^{-1} . The latter, which are sensitive to the framework structure are double ring band around 650-500 cm^{-1} , pore opening band around 420-300 cm^{-1} , symmetric stretch around 820-750 cm^{-1} and an asymmetric stretch shoulder around 1150-1050 cm^{-1} [7]. The structural transformations of sample calcined at 1273 K observed by XRD analysis, on IR spectra are expressed by changes in position, number and appearance of bonds in the mid-infrared region (200-1300 cm^{-1}) as well as elimination of peaks at 3350 and 1640 cm^{-1} that are assigned to O-H stretching vibration.

At the beginning of catalytic evaluation of prepared catalysts a preliminary experiment was conducted which showed that in this experimental setup phenol can be oxidized with hydrogen peroxide without catalyst, but in that case, its conversion after 3 h of the reaction was only 20 % at 353 K (Fig. 2). The similar results were obtained using parent zeolite as catalyst before incorporation of copper took place (13X sample). The presence of copper on the zeolite (Cu/13X catalyst) had a significant effect on its activity in the CWPO process, drastically increasing the velocity and the extent of phenol removal. The complete oxidation of organic component can be achieved in the first 10 minutes of the reaction. The catalyst that

underwent thermal postsynthesis treatment showed inferior activity in regard to phenol oxidation and hydrogen peroxide decomposition.

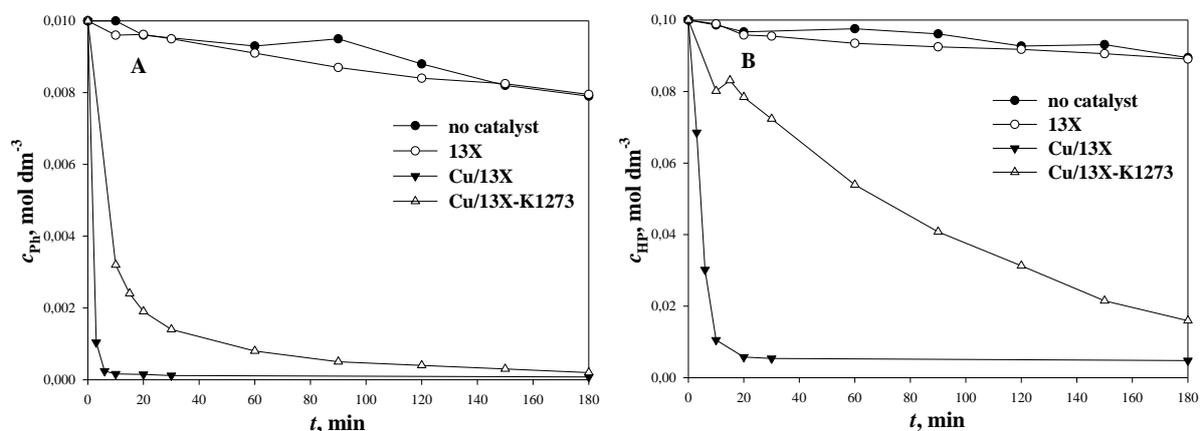


Figure 2. Activity of prepared catalysts in CWPO reaction at 353 K: phenol removal (A) and hydrogen peroxide decomposition (B) ($m_{CAT} = 0.5 \text{ g dm}^{-3}$, $c_{Ph,0} = 0.01 \text{ mol dm}^{-3}$, $c_{HP,0} = 0.1 \text{ mol dm}^{-3}$, $w_{Cu} \sim 3.5 \text{ wt. \%}$)

Nevertheless, TOC conversions presented on Fig. 3A were similar for both catalysts indicating that despite the lower oxidation rate of phenol, oxidation of the CWPO intermediates was to the same extent. These results can be explained with the fact that in the reactions with the most active catalysts hydrogen peroxide decomposes too fast generating high quantities of hydroxyl radicals ($\text{OH}\cdot$) that are for the most part occupied in the ineffective side reactions such as formation of hydroperoxyl radicals ($\text{OH}_2\cdot$) or decomposition. The hydroperoxyl radicals are less reactive and do not contribute to the oxidation of phenol and organic intermediates present in the reaction mixture [8]. On the other hand, when the decomposition of hydrogen peroxide is slower, major part of the formed hydroxyl radicals is engaged in the reactions with the organics, minimizing the extent of undesired side reactions and leading to a comparable TOC abatement.

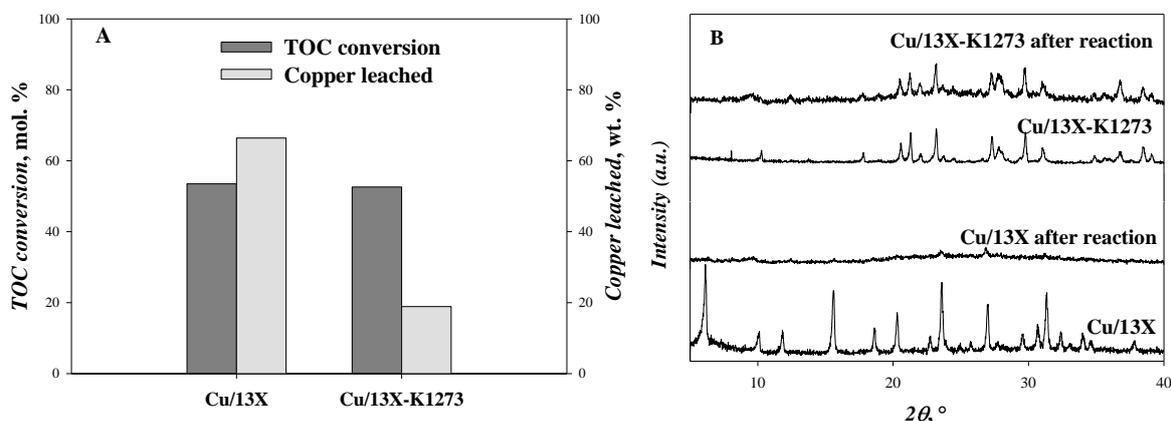


Figure 3. Stability of prepared catalysts: TOC conversions and copper leaching (A) and XRD analysis (B)

The stability of prepared catalysts in the CWPO reaction was investigated by monitoring the stability of both components of the catalyst: active metal component (copper cations) and the support (zeolite). The stability measurements showed that thermal treatment stabilizes the catalyst since the leaching of copper is significantly lower for the calcined catalysts (Fig. 3A). A comparison of XRD diffractograms of Cu/13X and Cu/13X-K1273 catalyst before and after reaction is presented on Fig. 3B. The results showed that during the CWPO reaction the zeolitic Cu/13X catalyst completely transforms from crystalline into amorphous material, with no major reference intensity peaks in the 2θ angle range from 5 to 40° . After the thermal treatment at 1273 K copper bearing Cu/123X-K1273 catalyst retains its

crystal structure in the CWPO reaction yielding all the major peaks of dominant nepheline crystal phase comparable to the catalyst before reaction.

CONCLUSION

In this work influence of postsynthesis thermal treatment on the catalytic properties of zeolite based copper bearing catalysts was investigated. Catalysts' activity decreases after calcination in the respect of reaction rates of phenol oxidation and H₂O₂ decomposition, while the TOC abatement for both catalysts remains unaffected. Stability of active metal component and catalyst's support was significantly improved by postsynthesis thermal treatment.

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