I&EC research
Industrial & Engineering Chemistry Research
ARTICLE
pubs.acs.org/IECR

Catalytic Properties of Cu/13X Zeolite Based Catalyst in Catalytic Wet Peroxide Oxidation of Phenol

Karolina Maduna Valkaj,*[†] Andrea Katović,[‡] and Stanka Zrnčević[†]

[†]Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia
[‡]Department of Chemical Engineering and Materials, University of Calabria, Rende, Italy

ABSTRACT: Copper bearing 13X zeolite was prepared from commercial 13X zeolite via ion-exchange with copper acetate solutions. After the incorporation of copper, Cu/13X catalyst was exposed to post synthesis thermal treatment at different temperatures. The prepared catalysts were characterized by XRD and FTIR, while the adsorption techniques were used for the measurement of the specific surface area and pore volume. The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at atmospheric pressure in temperature range from 333 to 353 K. Influence of postsynthesis thermal treatment and reaction temperature on activity and stability of prepared catalysts in the catalytic wet oxidation process with hydrogen peroxide as oxidant was investigated. The experimental results showed that total degradation of phenol can be achieved under mild operating conditions at temperatures bellow 353 K. All catalysts exhibited higher activity in terms of hydrogen peroxide and phenol abatement with the increasing temperature of the reaction. The postsynthesis thermal treatment resulted in more stable catalyst with respect to stability of both catalysts' active metal component (copper) and support, while the activity of catalysts in terms of TOC conversion remained unaltered.

INTRODUCTION

The most important as well as the most vulnerable part of global ecosystem are surface waters. To this day numerous scientific investigations are conducted in order to develop new technologies to achieve effective purification of wastewaters polluted with organic compounds such as phenol and its derivatives. Due to its presence in various processes in the pharmaceutical, chemical, and petrochemical industries, 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 highest importance to constantly develop new and improve existing technologies in order to enhance wastewater treatment processes. Phenol can be removed from wastewater by physical, biological, and chemical treatment, while the choice of the method depends on source and quantity of the pollutant, quantity of wastewater to be purified, and desired reduction level of organic compounds as well as economical factors.[1] In most cases concentration of phenol in wastewaters is in the range of 1.5 to 4000 mg dm^{-3} which is too concentrated for direct biological treatment and, on the other hand, too diluted for some of the physical processes of wastewater treatment.[2] In such cases chemical methods of treatment are most applicable. Low-temperature, aqueous-phase heterogeneous catalytic oxidation of dissolved organic compounds is a potential route 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.[2−6] 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.[7−11] Zeolites modified with copper possess good catalytic properties when compared to the other types of heterogeneous catalysts tested in the CWPO reaction.[12−14] Based on the literature overview and actual trends in scientific research concerning development of new catalytic oxidation processes for treatment of wastewaters burdened with organic pollutants, commercial zeolite type 13X was selected as catalyst support for copper cations. Activity and stability of such prepared catalyst was tested in catalytic wet peroxide oxidation of phenol in aqueous medium. Influence of reaction temperature, synthesis, and postsynthesis treatment on catalytic properties was investigated. Special attention was directed toward evaluation of catalysts' stability in terms of copper leeching into the reaction mixture. Acquired experimental data were tested to a proposed kinetic model for phenol oxidation and hydrogen peroxide decomposition. The obtained kinetic parameters (estimated using Nelder-Mead method of nonlinear regression) were used for quantitative comparison of catalysts activity.

EXPERIMENTAL METHODS

Catalyst Synthesis. The catalysts were prepared by ion exchange from commercial 13X zeolite (13X-APG Molsiv UOP Italy, SiO_2/Al_2O_3 = 3.2, w_{N2O} = 20 wt %) by conventional method. Ten g of zeolite was ion exchanged with 0.015 M copper acetate solution in agitation, under 298 K over 2 h, after which the samples were filtered and dried overnight at room temperature. Postsynthesis thermal treatment consisted in calcination of

Received: November 3, 2010
Accepted: February 10, 2011
Revised: January 22, 2011
Published: March 10, 2011

Table 1. Physical and Chemical Properties of Prepared Catalysts

sample	method of preparation	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	ion exchange	494.67	0.31	-	3.6
Cu/13X-K773	ion exchange + calcination 773 K	446.85	0.30	2.02	3.7
Cu/13X-K1023	ion exchange + calcination 1023 K	9.27	0.02	21.6	3.4
Cu/13X-K1273	ion exchange + calcination 1273 K	8.42	<0.01	21.8	3.6

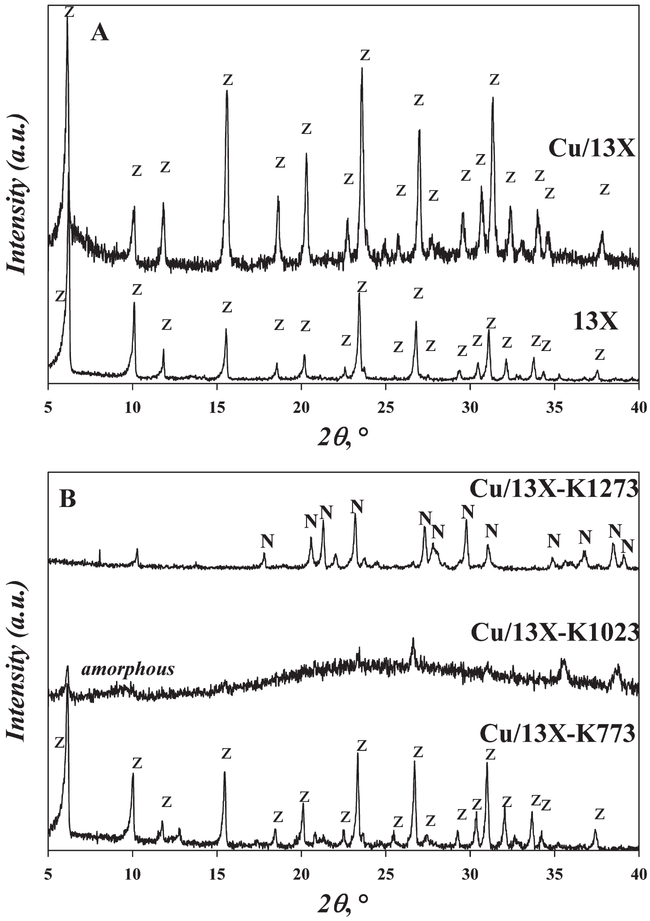

Figure 1. X-ray diffraction patterns of 13X and Cu/13X samples before (A) and after (B) thermal treatment (**Z** - zeolite, **N** – nepheline).

prepared Cu/13X samples at temperatures of 773, 1023, and 1273 K for 5 h (ramp 5 K min^{-1}) in order to obtain zeolite based materials that exhibit higher stability to the loss of active metal component during the reaction.

Catalyst Characterization. Textural characterization of the catalyst samples was performed by means of nitrogen adsorption/desorption isotherms at 77 K using Micromeritics ASAP 2000 instrument. 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 CuKα radiation operating at 40 kV and 30 mA. The patterns were recorded over $5° < 2\theta < 40°$ range using a step size of 0.02°. Framework ATR-IR spectra were recorded using an infrared spectrometer (Perkin-Elmer Spectrum 100 FTIR Spectrometer) in the range of 400–4000 cm^{-1}. Stability of used catalysts was monitored trough the extent of copper leaching as well as the

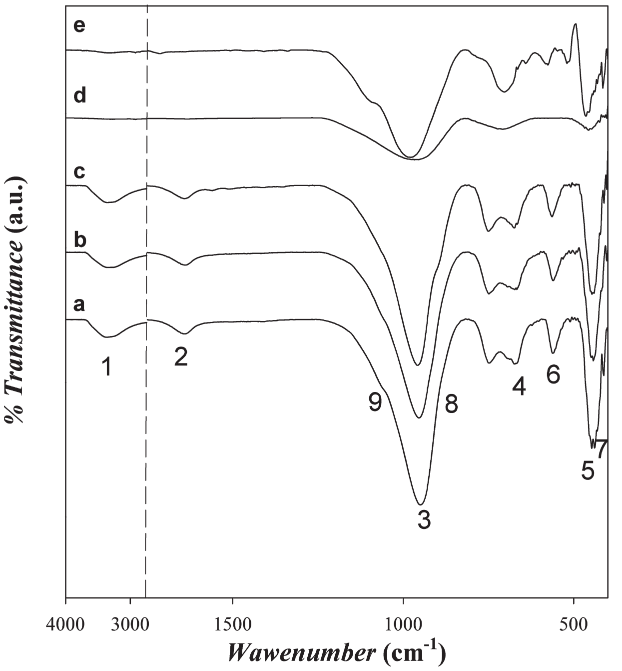

Figure 2. IR spectra of 13X (a), Cu/13X (b), Cu/13X-K773 (c), Cu/13X-K1023 (d), and Cu/13X-K1273 (e). Legend: 1 and 2 – OH stretching vibrations (1640 and 3350 cm^{-1}); 3–5 – internal vibrations of the framework TO4 tetrahedron (1250–950 cm^{-1}, 720–650 cm^{-1}, 500–420 cm^{-1}); 6–9 – vibrations related to external linkages between tetrahedra (1150–1050 cm^{-1}, 820–750 cm^{-1}, 650–500 cm^{-1}, 420–300 cm^{-1}).

stability of zeolite support. Copper content on fresh and used catalyst and in the reaction mixture was determined by atomic absorption spectrometry using Perkin-Elmer AAS 3110. Stability of catalysts' support was checked using XRD and FTIR analysis.

Catalytic Evaluation. The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at atmospheric pressure, temperature range 333–353 K, and stirrer speed 200 rpm. Phenol degradation experiments involved an aqueous phenol solution (200 cm^3, 0.01 mol dm^{-3}). The solid catalyst (0.5 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 that initiated the reaction. Aliquots were withdrawn during the reaction course at selected time, filtered by means of 0.2 μm 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. Total organic carbon (TOC) was determined with

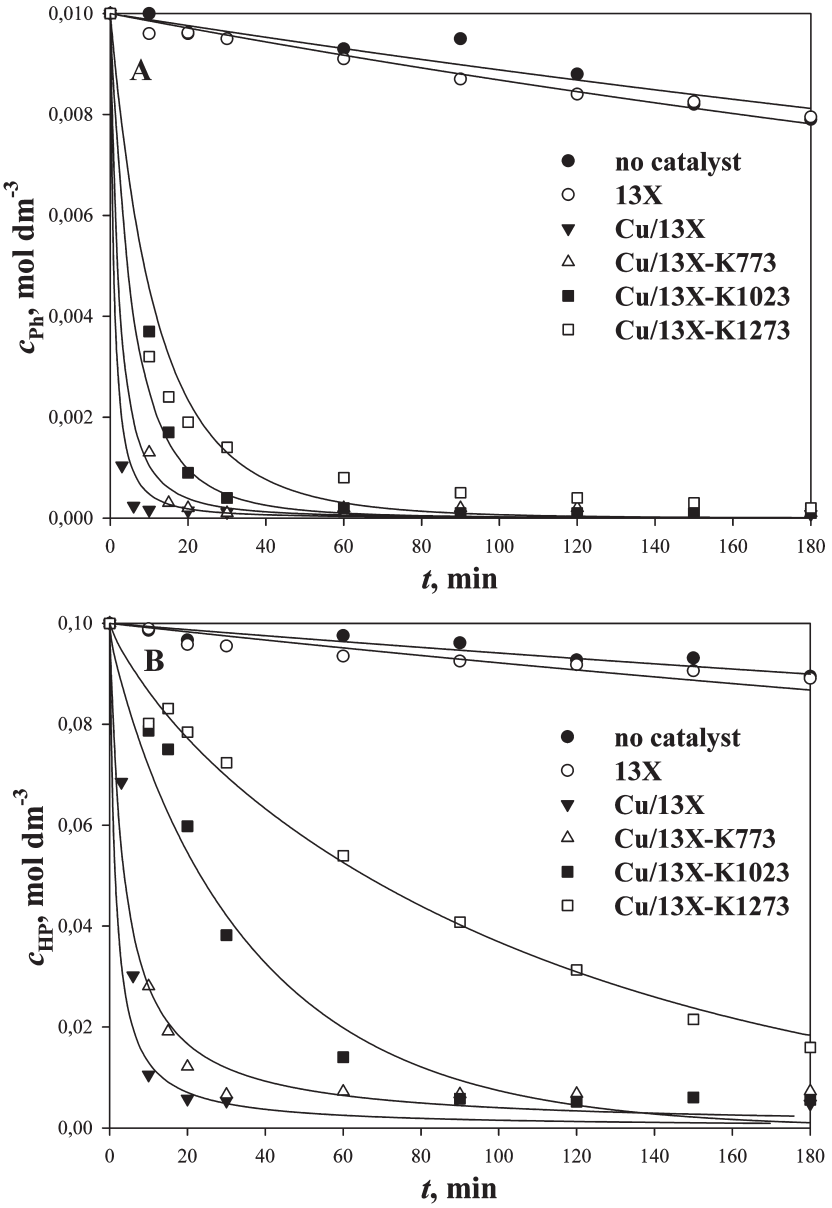

Figure 3. Activity of prepared catalysts in the CWPO reaction at 353 K: phenol removal (A) and hydrogen peroxide decomposition (B) (m_{CAT} = 0.5 g dm^{-3}, $c_{Ph,0}$ = 0.01 mol dm^{-3}, $c_{HP,0}$ = 0.1 mol dm^{-3}, w_{Cu} ~ 3.5 wt %, symbols — experimental data, lines — theoretical data: mathematical modeling results).

TOC-V CSN Shimadzu analyzer from diluted reaction solutions. Reaction products were analyzed by HPLC (Shimadzu Prominence LC-20AT) with UV/vis detector (at 210 and 254 nm) using C18 5 μm column (Waters Spherisorb ODS2, 150 × 4.6 mm) and 1−2.75 cm^3 min^{-1} of 25 mM KH_2PO_4 solution buffered at pH 2.7 as a mobile phase.

The adsorption tests were carried out on a similar manner. The solid catalyst (0.5 g dm^{-3}) was suspended in the phenol solution under continuous stirring. After the reaction mixture was heated to the desired temperature measurement of phenol concentration commenced in order to observe if there is any disappearance of phenol due to adsorption on catalyst.

■ RESULTS AND DISCUSSION

In Table 1 physical and chemical properties of prepared catalysts are shown. 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, as shown in Table 1, the thermal treatment caused the decrease of both BET surface area and pore volume (samples Cu/13X-K773, Cu/13X-K1023, Cu/13X-K1273). The change of physical properties, including the loss of mass during heating, was specially pronounced in catalysts calcined at 1023 and 1273 K, which can be attributed to ceramization process that occurs during thermal treatment in the course of which a change in crystalline structure occurs. Copper content of all samples was around 3.5 wt % and was not affected by thermal treatment.

To confirm structure and crystallinity, the samples were studied by X-ray diffraction (Figure 1). In the XRD patterns of 13X and Cu/13X samples presented in Figure 1A, all peak positions matched those reported for the FAU structure[15] and no-impurity phase was observed. No shift in the peak positions

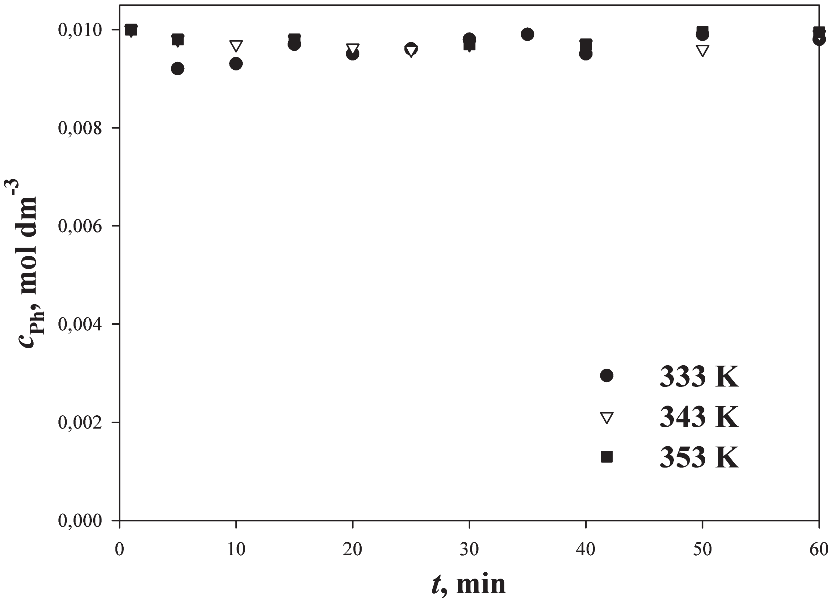

Figure 4. Phenol adsorption test over Cu/13X catalyst ($T = 333-353$ K, $m_{CAT} = 0.5$ g dm^{-3}, $c_{Ph,0} = 0.01$ mol dm^{-3}, $c_{HP,0} = 0.1$ mol dm^{-3}, $w_{Cu} \sim 3.5$ wt %).

and no significant diffraction lines assigned to any new phase are observed. The high intensities of peaks and low background lines suggest high crystallinity of copper bearing 13X zeolite 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. These results indicate that Cu^{2+} ions seem to be well dispersed in the zeolite framework.[16]

Copper bearing zeolite calcined at 773 K retains the crystal structure of FAU zeolite, while the catalysts that were thermally treated at 1023 and 1273 K exhibit a change in number, intensity, and position of peaks (Figure 1B) indicating that Cu/13X sample shows thermal stability up to 773 K. By further heating, Cu/13X catalyst undergoes phase transformations: amorphization (1023 K) and recrystallization of new phase (1273 K) that was identified as nepheline - anhydrous analogue of zeolite.[17] The fact that there is no peak attributable to copper cations on any of the diffractograms presented in Figure 1 A and B implies that the copper is very dispersed into the zeolite framework and that no Cu-containing phase was formed during postsynthesis thermal treatment. The change in dominant crystal phase of samples thermally treated at temperatures higher than 773 K is accompanied by a significant drop in measured BET surface area and pore volume as presented in Table 1.

Structural transitions of calcined copper bearing 13X zeolites were additionally monitored using FT-IR spectroscopy. The recorded IR spectra shown in Figure 2 indicate that no structural change of zeolitic framework occurs during ion exchange treatment and heating up to 773 K. 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, Cu/13X, and Cu/13X-K773 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 through 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}.[18] The structural transformations of samples calcined at 1023 and 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. Upon further heating to 1023 K, parallel with the loss of crystallinity, disappearance of structure sensitive bands near 1065, 750, and 560 cm^{-1} is observed, while the internal tetrahedral vibrations near 950, 710, and 460 cm^{-1} remain with minor changes in breadth and position[18] indicating a Si/Al content of amorphous material similar to that in the parent zeolite. The appearance of new bands near 640, 580, and 520 cm^{-1} in Cu/13X-K1273 sample confirms structural changes associated with the formation of new crystal phase identified by XRD as nepheline.

A preliminary set of experiments were performed in order to investigate the effect of phenol adsorption on reaction rate, to compare uncatalyzed and catalyzed phenol oxidation and the behavior of the Cu bearing zeolites and pure zeolites. As can be seen in Figure 3 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. Similar results were obtained using parent zeolite as catalyst before incorporation of copper (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 rate and the extent of phenol removal. A complete degradation of phenol can thus be achieved in the first 10 min of the reaction. The catalysts that underwent thermal postsynthesis treatment showed inferior activity in regard to phenol oxidation and hydrogen peroxide decomposition. The activity decreased with increasing temperature of calcination showing that structural changes that were expressed through the reduction of pore volume and surface area affected the catalytic properties.

To ensure that the phenol removal took place only by oxidation, the set of experiments were performed to discriminate the effect of phenol adsorption on reaction rate. These experiments

Table 2. Kinetic Properties of Prepared Catalysts in the CWPO Reaction Carried at 353 K[a]

catalyst	kinetic parameters k_{Ph} (dm^3 mol^{-1} min^{-1})	k_{HP} (min^{-1})	rmsd (%)	TOC abatement at t_{RT} = 180 min (wt %)	copper leached at t_{RT} = 180 min (wt %)
no catalyst	0.01	0.01	1.55	-	-
13X	0.01	0.01	1.65	-	-
Cu/13X	10.20	6.19	2.25	53.5	66
Cu/13X-K773	7.54	3.00	0.19	52.2	36
Cu/13X-K1023	1.83	0.58	3.16	54.0	68
Cu/13X-K1273	0.89	0.15	3.07	52.6	19

[a] Reaction conditions: m_{CAT} = 0.5 g dm^{-3}, $c_{Ph,0}$ = 0.01 mol dm^{-3}, $c_{HP,0}$ = 0.1 mol dm^{-3}, w_{Cu} ~ 3.5 mas. %.

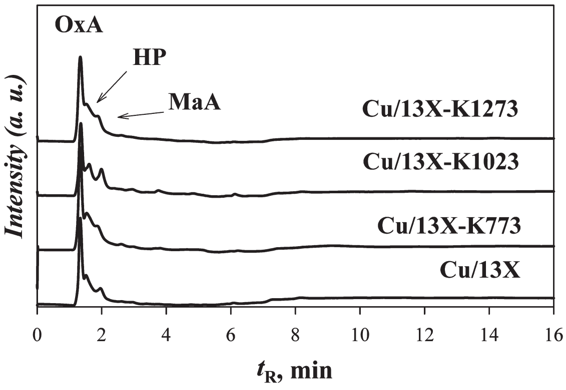

Figure 5. HPLC chromatograms of reaction mixtures after 180 min of reaction (T = 353 K, m_{CAT} = 0.5 g dm^{-3}, $c_{Ph,0}$ = 0.01 mol dm^{-3}, $c_{HP,0}$ = 0.1 mol dm^{-3}, w_{Cu} ~ 3.5 wt %, OxA — oxalic acid, HP — hydrogen peroxide, MaA — maleic acid).

were carried out without the oxidant at three different temperatures over the catalyst with the highest surface area (Cu/13X catalyst, S_{BET} = 494.67 m^2 g^{-1}). As can be seen in Figure 4 in the absence of hydrogen peroxide the disappearance of phenol was almost negligible, allowing the conclusion that phenol was being transformed only by reaction.

TOC conversions presented in Table 2 were similar for all catalysts indicating that despite the lower oxidation rate of phenol, oxidation of the CWPO intermediates occurred 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 (OH•) that are for the most part occupied in the ineffective side reactions such as formation of hydroperoxyl radicals (OH_2•) 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.[19] On the other hand, when the decomposition of hydrogen peroxide is slower, a 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.

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). It is presumed that the leaching of copper cations during the reaction is in connection with the presence of organic acids that are formed as intermediate products.[20,21] In Figure 5 the HPLC chromatograms of the reaction mixtures taken at the end of the reaction at t_{RT} = 180 min are presented. In all cases the composition of the final solution was similar consisting of oxalic and maleic acid (~20 mg dm^{-3} and <1 mg dm^{-3}, respectively) and small quantities of the remaining hydrogen peroxide. The measured values of copper leached into the

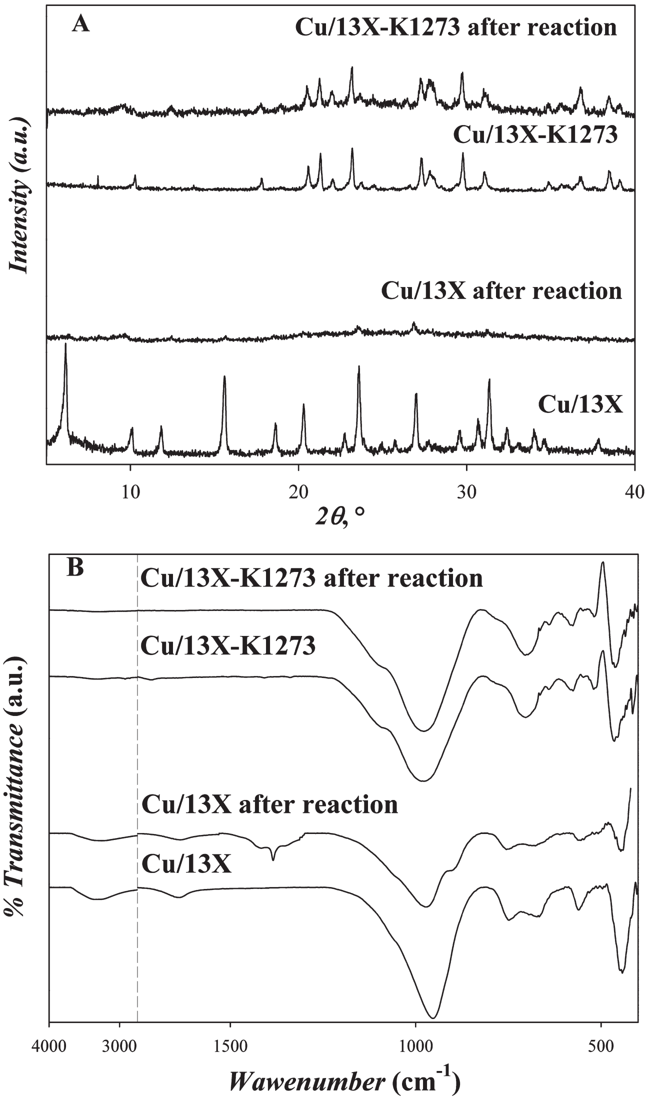

Figure 6. Stability of catalyst support in the CWPO reaction for Cu/13X and Cu/13X-K1273 catalysts: XRD analysis (A) and ATR-FTIR analysis (B).

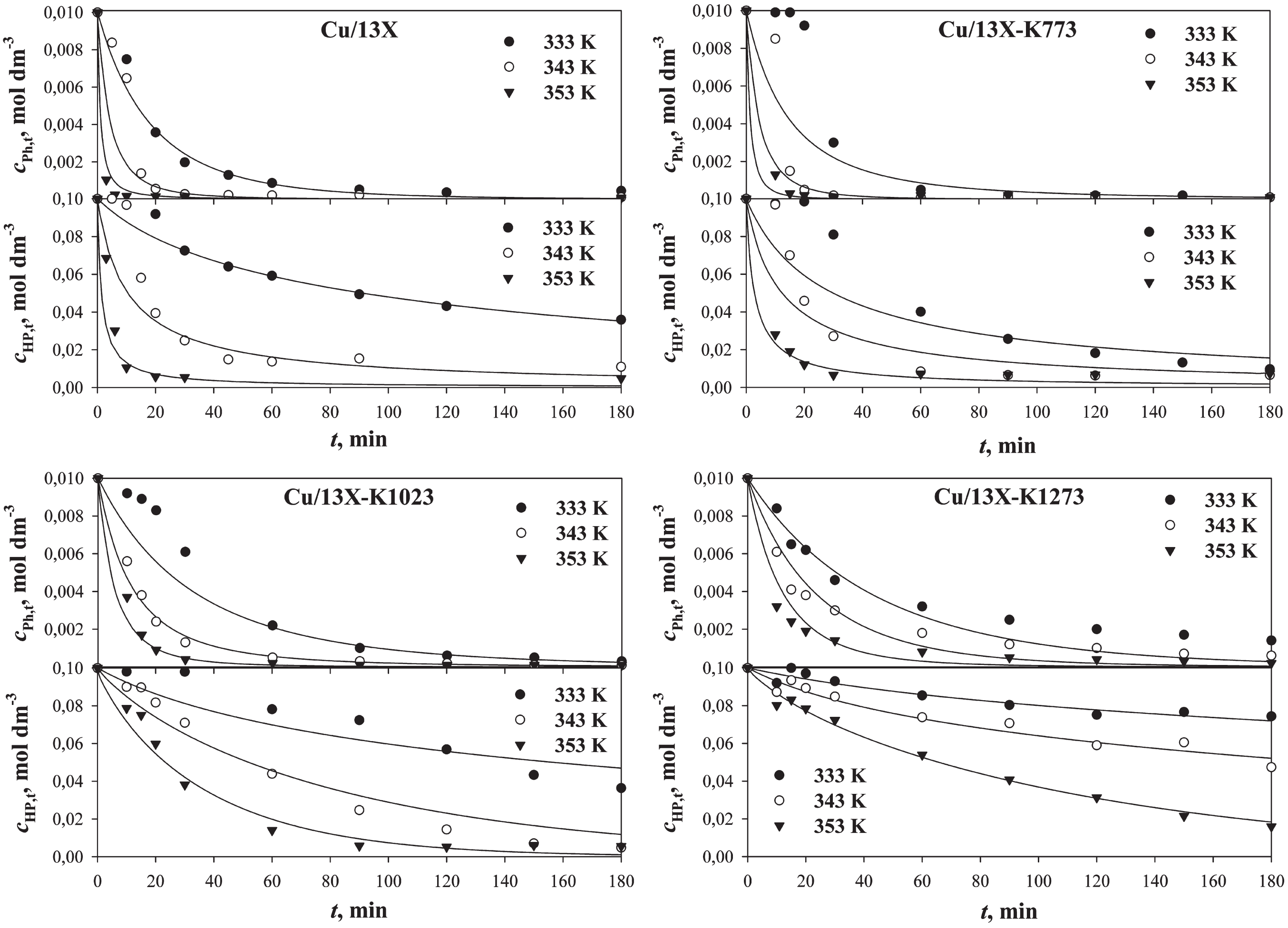

Figure 7. Influence of temperature on phenol removal and hydrogen peroxide decomposition over Cu/13X, Cu/13X-K773, Cu/13X-K1073, and Cu/13X-K1273 catalysts (m_{CAT} = 0.5 g dm^{-3}, $c_{Ph,0}$ = 0.01 mol dm^{-3}, $c_{HP,0}$ = 0.1 mol dm^{-3}, w_{Cu} ∼ 3.5 wt %, symbols — experimental data, lines — theoretical data).

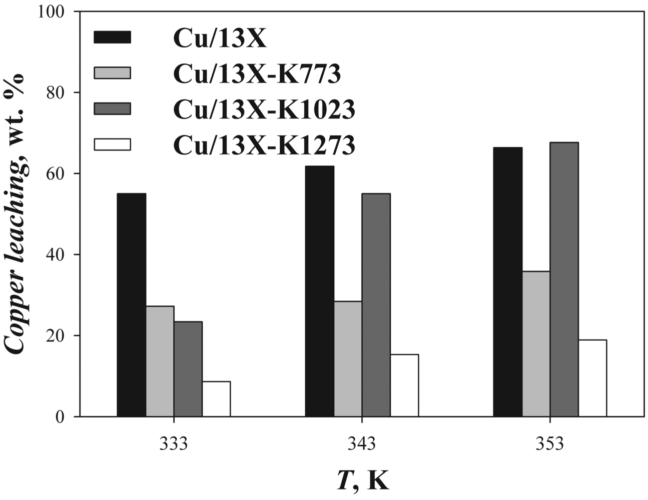

Figure 8. Influence of temperature on copper leaching for Cu/13X, Cu/13X-K773, Cu/13X-K1073, and Cu/13X-K1273 catalysts.

reaction mixture presented in Table 2 were different for all catalysts even if the concentration of oxalic acid in the reaction mixture was similar. These results indicate that the presence of organic acids is not the only factor affecting the extent of copper leaching from catalyst' surface. Cu/13X-K1023 catalyst showed the lowest stability toward resistance to copper leaching that can be connected to the loss of coherent crystal structure during the postsynthesis thermal treatment. The best results were obtained for the Cu/13X-K1273 catalyst showing that by postsynthesis thermal treatment that consists in heating of the copper bearing catalyst at 1273 K for 5 h, the catalyst stability in the CWPO reaction can be enhanced by several times with unvaried activity in terms of TOC conversion.

For an evaluation of stability of catalysts' support XRD and FTIR analysis were applied. A comparison of XRD diffractograms of Cu/13X and Cu/13X-K1273 catalysts before and after the reaction is presented in Figure 6. 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 the 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. Bearing that in mind, the increase in catalysts stability with respect to copper leaching after the thermal treatment can be attributed to the stabilization of catalyst support that occurs during calcination. FTIR analysis of Cu/13X

Table 3. Influence of Postsynthesis Thermal Treatment on Oxidation Rate of Phenol and Decomposition Rate of Hydrogen Peroxide at Different Temperatures

	k_{Ph} (dm^3 mol^{-1} min^{-1})			k_{HP} (min^{-1})			E_a (kJ mol^{-1})	
catalyst	333 K	343 K	353 K	333 K	343 K	353 K	Ph	HP
Cu/13X	0.56	2.43	10.20	0.09	0.82	6.19	141.8	204.9
rmsd (%)	1.24	2.33	2.25	1.24	2.33	2.25		
Cu/13X-K773	0.70	2.32	7.54	0.25	0.69	3.00	115.8	122.1
rmsd (%)	2.68	3.16	2.41	2.68	3.16	2.41		
Cu/13X-K1023	0.32	0.88	1.83	0.05	0.22	0.58	86.0	115.8
rmsd (%)	3.32	3.32	3.16	3.32	3.32	3.16		
Cu/13X-K1273	0.19	0.44	0.89	0.01	0.04	0.15	75.5	115.6
rmsd (%)	2.80	2.28	3.07	2.80	2.28	3.07		

and Cu/13X-K1273 before and after reaction confirms the structural change of noncalcined catalyst exhibited by the changes in the framework sensitive section of IR spectra (800−200 cm^{-1}) as well as appearance of new bands in the range of 1500−1200 cm^{-1}. In the IR spectra of the thermally treated Cu/13X-K1273 catalyst no changes in the entire spectral range are observed confirming its stability and resistance to adsorption of intermediate products of the CWPO reaction.

The influence of the reaction temperature on the rate of phenol removal and hydrogen peroxide decomposition as well as intensity of copper leaching was investigated for all catalysts. In Figure 7 concentrations of the remaining phenol and hydrogen peroxide versus time in the experiments performed at different temperatures for Cu/13X, Cu/13X-K773, Cu/13X-K1023, and Cu/13X-K1273 catalysts are presented. As expected, the increase of the reaction temperature considerably increases the reaction rate and the extent of both phenol removal and hydrogen peroxide decomposition for all catalysts. When the reaction is conducted at lower temperatures upon the addition of hydrogen peroxide, an induction period appears during which the decomposition of hydrogen peroxide is slowed resulting in low phenol conversions. The induction period of the CWPO reaction refers to the time needed for a threshold quantity of hydroxyl radicals to be formed to start the oxidation of phenol. As can be seen from Figure 7 the induction period is present at lower reaction temperatures for all catalysts but Cu/13X-K1273 indicating that the structural changes that occurred during calcination at 1273 K affected its catalytic performance in the CWPO reaction.

In Figure 8 the influence of postsynthesis thermal treatment on the intensity of copper leaching during the CWPO reaction at different temperatures is presented. The stability measurements showed that thermal treatment stabilizes the catalyst since the leaching of copper is significantly lower for the calcined catalysts at all temperatures. It can be concluded that the promising catalyst in the reaction of phenol oxidation in a diluted aqueous solution with hydrogen peroxide is Cu/13X calcined at 1273 K, because at mild reaction conditions (T = 353 K, atmospheric pressure, initial H_2O_2 concentration below stoichiometric, and the reaction time of 3 h) this catalyst allows complete elimination of phenol and other aromatic compounds with acceptable TOC conversion and without significant leaching of copper ions from the zeolite matrix.

The obtained experimental data were tested to a proposed kinetic model for phenol oxidation and hydrogen peroxide decomposition

$$-\frac{dc_{Ph}}{dt} = k_{Ph}c_{Ph}c_{HP} \quad (1)$$

$$-\frac{dc_{HP}}{dt} = k_{HP}c_{HP} + k_{Ph}c_{Ph}c_{HP} \quad (2)$$

The parameters of kinetic model were estimated using the Nelder-Mead method of nonlinear regression in MATLAB-Simulink program package. The residual sum of squares calculated from the difference between the experimental and predicted concentrations was minimized in the regression. The rate of phenol oxidation is first order toward the concentration of phenol and first order toward the concentration of H_2O_2. The rate of H_2O_2 decomposition is the sum of rates of phenol oxidation and peroxide decomposition. The results of mathematic modeling are presented as lines in Figures 4 and 7. As can be seen, the proposed model adequately fits the experimental data. The maximum deflection from the model refers to the data obtained during the induction period of the reaction because the effects that caused hydroxyl radicals hold-up are not included into the main assumptions of the mathematical model.

In Table 3 the influence of postsynthesis thermal treatment on the rate of phenol oxidation and hydrogen peroxide decomposition at different temperatures is presented. It can be seen that postsynthesis thermal treatment influences reaction rates of phenol oxidation and hydrogen peroxide decomposition by decreasing them throughout the whole temperature range. Calculated apparent activation energies are in the range from 75.5 to 141.8 kJ mol^{-1} for phenol oxidation and from 115.6 to 204.9 kJ mol^{-1} for hydrogen peroxide decomposition, which is in accordance with previously reported results.[12,13,22−26]

CONCLUDING REMARKS

In this work influence of post synthesis thermal treatment and reaction temperature was investigated on the catalytic properties of zeolite based copper bearing catalysts. Catalysts' activity depends on the conditions of post synthesis thermal treatment and it decreases with the increase of calcination temperature in the respect of reaction rates of phenol oxidation and H_2O_2 decomposition. The TOC abatement in the CWPO reactions at 353 K for all catalysts remains unaffected by post synthesis treatment. The catalysts that were calcined at higher temperatures exhibit significantly higher stability of both active metal component and catalyst's support showing greater resistance to leaching and adsorption of intermediate products of reaction.

The most promising catalyst in the reaction of phenol oxidation in a diluted aqueous solution with hydrogen peroxide is Cu/13X calcined at 1273 K, because at mild reaction conditions (T = 353 K, atmospheric pressure, initial H_2O_2 concentration below stoichiometric, and the reaction time of 3 h), this catalyst allows complete elimination of phenol and other aromatic compounds with acceptable TOC conversion and without significant leaching of copper ions from the zeolite matrix.

The rate of phenol oxidation and hydrogen peroxide decomposition increases with the increase of reaction temperature for all catalysts. The rate of phenol oxidation is first order toward the concentration of phenol and first order toward the concentration of H_2O_2. The rate of H_2O_2 decomposition is the sum of rates of phenol oxidation and peroxide decomposition.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 00385 1 4597 134. Fax: 00385 1 4597 133. E-mail: kmaduna@fkit.hr. Corresponding author address: Department of Reaction Engineering and Catalysis, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia.

■ ACKNOWLEDGMENT

The authors thank the Ministry of Science, Education and Sports and Hrvatske vode d.d. for the financial support of this study.

■ SYMBOLS

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})
rmsd	root mean square deviation
S_{BET}	BET surface area
t	time (min)
t_R	retention time (min)
t_{RT}	reaction time (min)
T	temperature (K)
m_{CAT}	mass of catalyst (g)

■ REFERENCES

(1) Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, C. Technologies for the Removal of Phenol from Fluid Streams: A Short Review of Recent Developments. *J. Hazard. Mater.* **2008**, *160*, 265.

(2) *The NALCO Water Handbook*; Kremmer, F. N., Eds.; McGraw Hill: New York, 1988.

(3) Melero, J. A.; Martinez, F.; Botas, J. A.; Molina, R.; Pariente, M. I. Heterogeneous Catalytic Wet Peroxide Oxidation Systems for the Treatment of an Industrial Pharmaceutical Wastewater. *Water Res.* **2009**, *43*, 4010.

(4) Carriazo, J. G.; Molina, R.; Moreno, S. A Study on Al and Al—Ce—Fe Pillaring Species and Their Catalytic Potential as They Are Supported on a Bentonite. *Appl. Catal., A* **2008**, *334*, 168.

(5) Gogate, P. R.; Pandit, A. B. A Review of Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions. *Adv. Environ. Res.* **2004**, *8*, 501.

(6) Gogate, P. R.; Pandit, A. B. A Review of Imperative Technologies for Wastewater Treatment II: Hybrid Methods. *Adv. Environ. Res.* **2004**, *8*, 553.

(7) Liotta, L. F.; Gruttadauria, M.; Di Carlo, G.; Perrini, G.; Librando, V. Heterogeneous Catalytic Degradation of Phenolic Substrates: Catalysts Activity. *J. Hazard. Mater.* **2009**, *162*, 588.

(8) Liou, R.-M.; Chen, S.-H. CuO Impregnated Activated Carbon for Catalytic Wet Peroxide Oxidation of Phenol. *J. Hazard. Mater.* **2009**, *172*, 498.

(9) Catrinescu, C.; Teodosiu, C.; Macoveanu, M.; Miehe-Brendlé, J.; Le Dred, R. Catalytic Wet Peroxide Oxidation of Phenol Over Fe-Exchanged Pillared Beidellite. *Water Res.* **2003**, *37*, 1154.

(10) Guelou, E.; Barrault, J.; Fournier, J.; Tatibouët, J. M. Active Iron Species In The Catalytic Wet Peroxide Oxidation of Phenol Over Pillared Clays Containing Iron. *Appl. Catal., B* **2003**, *44*, 1.

(11) Carriazo, J. G.; Guelou, E.; Barrault, J.; Tatibouët, J. M.; Molina, R.; Moreno, S. Catalytic Wet Peroxide Oxidation of Phenol By Pillared Clays Containingal—Ce—Fe. *Water Res.* **2005**, *39*, 3891.

(12) Zrnčević, S.; Gomzi, Z. CWPO: An Environmental Solution for Pollutant Removal from Wastewater. *Ind. Eng. Chem. Res.* **2005**, *44*, 6110.

(13) Maduna Valkaj, K.; Katovic, A.; Zrnčević, S. Investigation of the Catalytic Wet Peroxide Oxidation of Phenol Over Different Types of Cu/ZSM-5 Catalysts. *J. Hazard. Mater.* **2007**, *144*, 663.

(14) Maduna Valkaj, K.; Katovic, A.; Tomašić, V.; Zrnčević, S. Characterization and Activity of Cu/ZSM5 Catalysts for the Oxidation of Phenol with Hydrogen Peroxide. *Chem. Eng. Technol.* **2008**, *31*, 398.

(15) Treacy, M. M. J.; Higgins, J. B.; von Ballmos, R. *Collection of Simulated XRD Powder Patterns for Zeolite*; Elsevier: London, 1996.

(16) Benaliouche, F.; Boucheffa, Y.; Ayrault, P.; Mignard, S.; Magnoux, P. NH3-TPD and FTIR Spectroscopy of Pyridine Adsorption Studies for Characterization of Ag- and Cu-Exchanged X Zeolites. *Microporous Mesoporous Mater.* **2008**, *111*, 80.

(17) Khaleghian-Moghadam, R.; Seydeyn-Azad, F. A Study on the Thermal Behavior of Low Silica X-Type Zeolite Ion-Exchanged with Alkaline Earth Cations. *Microporous Mesoporous Mater.* **2009**, *120*, 285.

(18) Flanigen, E.; et al. Infrared Structural Studies of Zeolite Frameworks. In *Molecular Sieve eolites-I, Advances in Chemistry, Vol.* 101; Flanigen, E. M., Khatami, H., Eds.; American Chemical Society: 1971.

(19) Kondru, A. K.; Kumar, P.; Chand, S. Catalytic Wet Peroxide Oxidation of Azo Dye (Congo Red) Using Modified Y Zeolite As Catalyst. *J. Hazard. Mater.* **2009**, *166*, 342.

(20) Santos, A.; Yustos, P.; Quintanilla, A.; Rodriguez, S.; Garcıa-Ochoa, F. Route of the Catalytic Oxidation of Phenol in Aqueous Phase. *Appl. Catal., B* **2002**, *39*, 97.

(21) Santos, A.; Yustos, P.; Quintanilla, J.; Ruiz, G.; Garcia-Ochoa., F. Study of the Copper Leaching in the Wet Oxidation of Phenol with CuO-Based Catalysts: Causes and Effects. *Appl. Catal., B* **2005**, *61*, 323.

(22) Pruden, B. B.; Le, H. Wet Air Oxidation of Soluble Components in Waste Water. *Can. J. Chem. Eng.* **1976**, *54*, 319.

(23) Ota, H.; Goto, S.; Teshima, H. Liquid-Phase Oxidation of Phenol in Rotating Catalytic Basket Reactor. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 180.

(24) Willms, R. S.; Balinsky, A. M.; Reible, D. D.; Wetzel, D. M.; Harison, D. P. Aqueous Phase Oxidation: Rate Enhancement Studies. *Ind. Eng. Chem. Res.* **1987**, *26*, 606.

(25) Jaulin, L.; Chornet, E. High Shear Jet-Mixers As Two-Phase Reactors: An Application To the Oxidation of Phenol in Aqueous Media. *Can. J. Chem. Eng.* **1987**, *65*, 64.

(26) Perez-Benito, J. F. Reaction Pathways in the Decomposition of Hydrogen Peroxide Catalyzed By Copper(II). *J. Inorg. Biochem.* **2004**, *98*, 430.