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

K. Maduna Valkaj [a], A. Katovic [b], S. Zrnčević [a,*]

[a] *Faculty of Chemical Engineering and Technology, University of Zagreb, Croatia*
[b] *Universita della Calabria, Dip. Ingegneria Chimica e dei Materiali, Rende, Italy*

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.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Wastewater treatment; Pollutant degradation; CWPO; Catalyst preparation; Cu/ZSM-5; Phenol oxidation; Kinetics; Modeling

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

* Corresponding author.
  E-mail address: szrnce@pierre.fkit.hr (S. Zrnčević).

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].
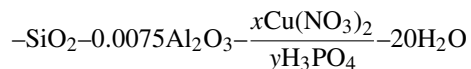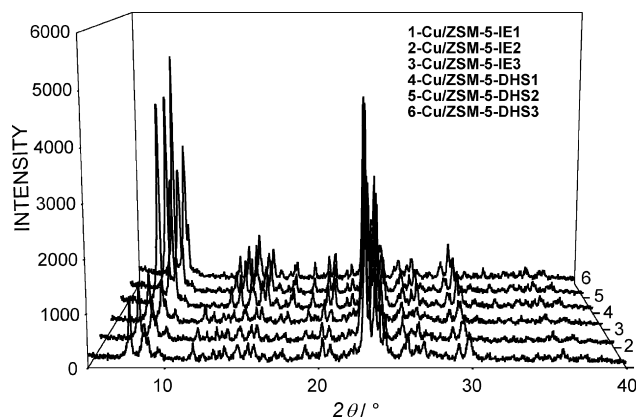
The present article is devoted to the investigation of the influence of different methods of preparation of Cu/ZSM-5 on the catalytic activity and stability in the wet oxidation of phenol by hydrogen peroxide.

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

2.2. Catalytic experiments

The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at atmospheric pressure, the temperature range from 50 to 80 °C and stirrer speed 200 rpm. 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. 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 which 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 absorbance at 510 nm wavelengths by standard 4-aminoantipyrine colorimetric method. Hydrogen peroxide was detected by titration with Na$_2$SO$_3$ with an excess of KI in the acidic medium.

3. Results and discussion

In order to check whether the recorded conversion was exclusively due to the metal ions leached from the Cu/ZSM-5 catalysts (after 3 h having been 4.8% for sample prepared by IE method and 3.2% for sample prepared by DHS method), the solution activity was tested after catalyst filtration and repeated addition of phenol and hydrogen peroxide in the concentration used before catalytic test. In the absence of the catalyst (filtered solution) phenol conversion was below 5% in 300 min as opposed to its conversion of around 80% in the presence of the solid catalyst. That showed that the fraction of copper leached from the catalyst was not capable of destroying the organic pollutant. Also, activity of the re-used and fresh catalysts was practically equal, indicating absence of significant deactivation.

In heterogeneous catalysis, intrinsic kinetics can be evaluated only if the external or internal mass transfer resistances are minimized. When external mass transfer controls the reaction rate, the most important factor is the speed of stirrer. In the present investigation external mass transfer was of negligible importance at the stirrer speed higher than 150 rpm. The internal mass transfer was also not limiting step, because proportionality between rate constant for phenol oxidation and catalyst loading and concentration of catalytic active material were obtained.

The operating temperature is an important variable in the phenol wet peroxide oxidation. Figs. 2–5 show normalized concentrations of the remaining phenol and hydrogen peroxide versus time in the experiments performed at different temperatures on catalysts prepared by direct hydrothermal synthesis and ion exchange method.

As shown in Figs. 2–5, an elevated temperature increases the rate and degree of phenol oxidation and hydrogen peroxide decomposition. Also, it can be noticed that the activity of Cu/ZSM-5 catalyst prepared by direct hydrothermal synthesis is
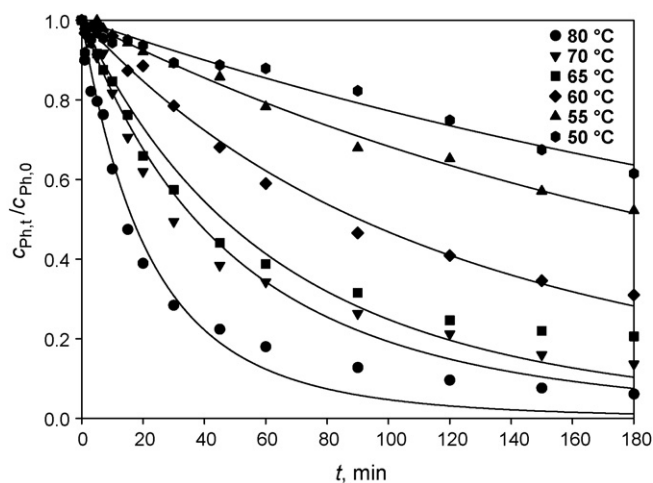

Fig. 2. Influence of temperature on phenol removal on Cu/ZSM-5 catalyst prepared by direct hydrothermal synthesis ($c_{HP} = 0.1$ mol dm^{-3}, $c_{Ph} = 0.01$ mol dm^{-3}, $w_{cat} = 0.1$ g dm^{-3}, $Y_{Cu} = 1.62$ wt.%).
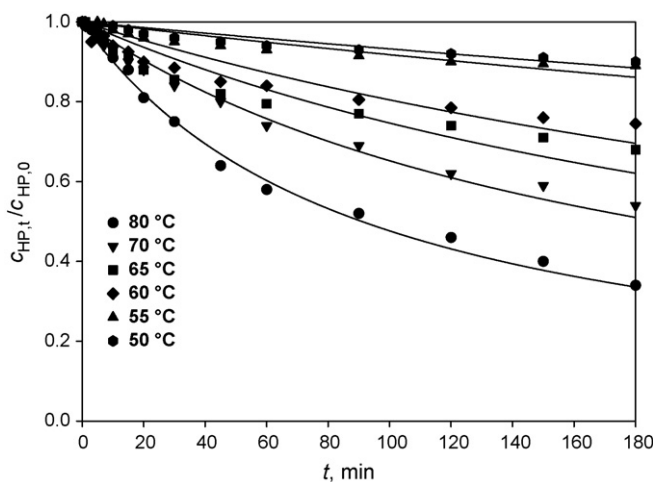

Fig. 3. Influence of temperature on hydrogen peroxide decomposition on Cu/ZSM-5 catalyst prepared by direct hydrothermal synthesis ($c_{HP} = 0.1$ mol dm^{-3}, $c_{Ph} = 0.01$ mol dm^{-3}, $w_{cat} = 0.1$ g dm^{-3}, $Y_{Cu} = 1.62$ wt.%).
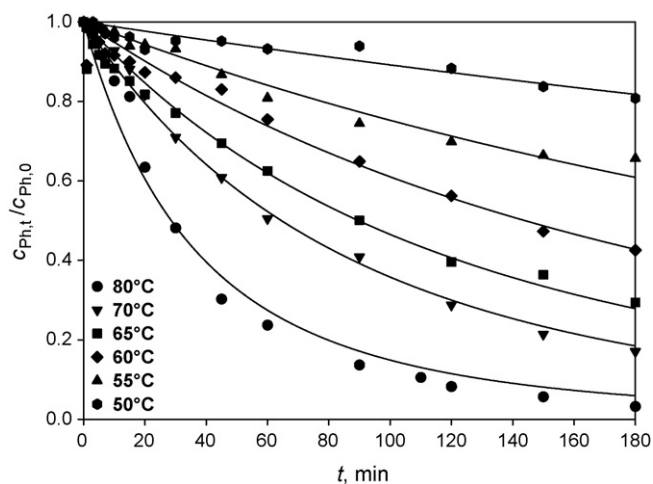

Fig. 4. Influence of temperature on phenol removal on Cu/ZSM-5 catalyst prepared by ion exchange method ($c_{HP} = 0.1$ mol dm^{-3}, $c_{Ph} = 0.01$ mol dm^{-3}, $w_{cat} = 0.1$ g dm^{-3}, $Y_{Cu} = 2.53$ wt.%).
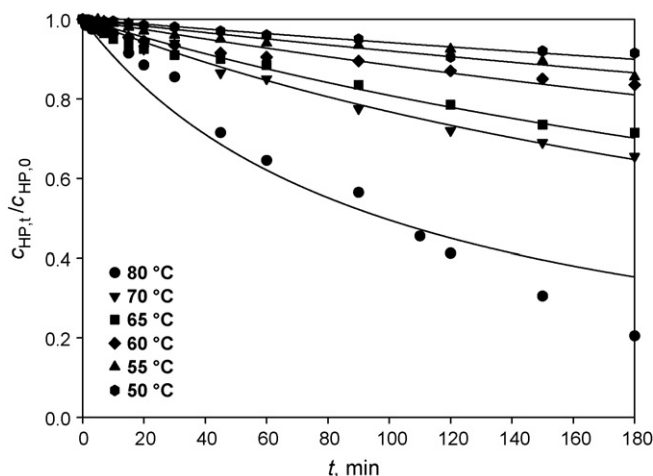
Fig. 5. Influence of temperature on hydrogen peroxide decomposition on Cu/ZSM-5 catalyst prepared by direct hydrothermal synthesis ($c_{HP} = 0.1\ mol\ dm^{-3}$, $c_{Ph} = 0.01\ mol\ dm^{-3}$, $w_{cat} = 0.1\ g\ dm^{-3}$, $Y_{Cu} = 2.53\ wt.\%$).

higher than activity of catalyst prepared by ion exchange method even the last one contain higher content of copper.

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

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

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

The kinetic parameters in Eqs. (1) and (2) were estimated using the Nelder–Mead method of nonlinear regression. The residual sum of squares calculated from the difference between the experimental and predicted concentrations was minimized in the regression. In nearly all cases, the reaction order with respect to phenol was almost similar or slightly lower than unity and therefore taken as 1. The results of the model analysis are shown as solid lines in Figs. 2–5. As can be seen, these kinetic models discriminated fits adequately the experimental data sinew only slight differences were found between the predicted results (curves) and the experimental ones (points).

The influence of the concentrations of catalytic active centers on the rate for phenol oxidation and hydrogen peroxide decomposition (when reactions are performed at different temperatures and on catalyst prepared by IE and DHS methods) are presented in Table 2.

It can be seen that the increasing temperature and loading of catalytic active material on catalyst support have a profound effect on rate constants for phenol oxidation and peroxide decomposition. Also, from the presented data it can be concluded that the activity of Cu/ZSM-5 catalyst prepared by direct hydrothermal synthesis (DHS) is higher than in the case when catalyst is prepared by ion exchange (IE) method, which is also confirmed by the E_a. Activation energy in phenol oxidation was from 66.20 to 95.77 kJ mol^{-1} what depend on catalysts preparation method. E_a values from the literature [19–22] varied from 55 to 175 kJ mol^{-1}. The lower ones were more characteristic of total oxidation of phenol to carbon dioxide, whereas the higher ones is probably resulted from polymerization to tars rather than from true oxidation. Our results, thus, fall within the range of total oxidation, as suggested by Pruden and Le [19]. The apparent activation energy for hydrogen peroxide decomposition was from 47.81 to 93.27 kJ mol^{-1} (depending on catalyst preparation method) what was comparable with the value reported by Perez-Benito [23].

The stability of DHS catalyst is also better than stability of IE catalyst because the leaching of active ingredient was lower.

Table 2
Effect of Cu loading on the rate constant in phenol removal and hydrogen peroxide decomposition at different temperatures

Y_{Cu} (wt.%)	k_{Ph} ($\times 10^3\ dm^3\ mol^{-1}\ min^{-1}$)						k_{HP} ($\times 10^3\ min^{-1}$)						E_a (kJ mol^{-1})	
	50 °C	55 °C	60 °C	65 °C	70 °C	80 °C	50 °C	55 °C	60 °C	65 °C	70 °C	80 °C	Ph	HP
Direct hydrothermal synthesis														
1.62	2.67	3.97	8.48	16.23	20.65	45.40	0.72	0.88	0.24	3.39	5.33	11.01	92.45	90.62
S.D. $\times 10^3$	4.5	4.3	5.5	11.0	9.5	7.5	4.5	4.3	5.5	11.0	9.5	7.5		
2.75	3.40	5.25	9.82	24.50	23.15	67.20	1.49	2.04	6.45	11.81	5.35	15.52	85.10	73.88
S.D. $\times 10^3$	5.7	4.5	5.0	15.3	11.0	15.0	5.7	4.5	5.0	15.3	1.1	1.5		
3.24	8.98	10.53	24.87	69.30	41.88	97.10	3.46	3.11	7.16	24.21	8.72	19.41	66.20	47.81
S.D. $\times 10^3$	5.7	10.6	5.0	11.1	11.0	15.0	5.7	10.6	5.0	11.1	11.0	15.0		
Ionic exchange method														
2.23	1.39	3.03	5.11	7.88	10.63	22.69	0.92	1.10	1.41	1.83	3.28	9.33	95.77	93.27
S.D. $\times 10^3$	32.0	4.3	6,8	8.8	4.9	7.0	32.0	4.3	6.8	8.8	4.9	7.0		
2.8	1.17	2.94	5.26	8.56	11.83	27.60	0.62	0.86	1.30	2.37	3.02	10.20	90.13	87.99
S.D. $\times 10^3$	3.8	3.0	3.1	5.9	6.9	7.7	3.8	3.0	3.1	5.9	6.9	7.7		
3.52	5.40	8.91	15.27	26.10	19.67	49.60	2.63	4.97	6.65	15.71	7.15	15.45	76.95	56.29
S.D. $\times 10^3$	3.8	6.6	7.7	10.1	6.7	9.3	3.8	6.6	7.7	10.1	6.7	9.3		

S.D.: standard deviation of measured and calculated values.

4. Conclusions

The present work describes wet oxidation of aqueous solutions of phenol with hydrogen peroxide using heterogeneous Cu/ZSM-5 catalyst under mild conditions. The factors affecting oxidation of phenol and peroxide decomposition in the slurry reactor system as well as their kinetic characteristics is obtained. The rate of phenol oxidation and hydrogen peroxide decomposition increases with the increase of reaction temperature and concentration of catalytic active material on ZSM-5. 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.

From the obtained data can be concluded that the activity of Cu/ZSM-5 catalyst prepared by direct hydrothermal synthesis (DHS) is higher than the activity of catalyst prepared by ion exchange (IE) method which was confirmed by activation energy for phenol oxidation and hydrogen peroxide decomposition. The stability of DHS catalyst is also better than stability of IE catalyst because the leaching of active ingredient is lower.

Further studies are conducted towards determination of intermediate products and improvement of operating conditions by process optimization.

Acknowledgements

References

[1] S. Imamura, Ind. Eng. Chem. Res. 38 (1999) 1743.
[2] F. Luck, Catal. Today 27 (1996) 195.
[3] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Ind. Eng. Chem. Res. 34 (1995) 2.
[4] S. Hamoudi, F. Larachi, A. Sayari, J. Catal. 177 (1998) 247.
[5] O.J. Hao, K.K. Phull, J.M. Chen, Water Res. 28 (1994) 283.
[6] V.S. Mishra, J.B. Joshi, V.V. Mahajani, Ind. Chem. Eng. J. 35 (1993) 211.
[7] K.K. Phull, O.J. Hao, Ind. Eng. Chem. Res. 32 (1993) 1772.
[8] S.H. Lin, S.J. Ho, Appl. Catal. B: Environ. 9 (1996) 133.
[9] Q. Wu, X. Hu, P.L. Yue, X.S. Zhao, G.Q. Lu, Appl. Catal. B: Environ. 32 (2001) 151.
[10] F. Arena, R. Giovenco, T. Tore, A. Venuto, A. Parmaliana, Appl. Catal. B: Environ. 45 (2003) 51.
[11] A.F.J. Santiago, J.F. Sousa, R.C. Guedes, C.E.M. Jeronimo, M. Benachour, J. Hazard. Mater. B 138 (2006) 325.
[12] K. Fajerwerg, H. Debellefontaine, Appl. Catal. B: Environ. 10 (1996) 229.
[13] J. Barrault, M. Abdellaoui, C. Bouchoule, A. Majeste, J. Tatibouet, A. Papayannakos, Appl. Catal. B: Environ. 27 (2000) 225.
[14] G. Centi, S. Perathoner, T. Torre, M.G. Verduna, Catal. Today 55 (2000) 61.
[15] Z. Barjaktarović, S. Zrnčević, Kem. Ind. 51 (2002) 259.
[16] G. Ovejero, J.L. Sotelo, F. Martinez, L. Gordo, Water Sci. Technol. 44 (2001) 153.
[17] S. Zrnčević, Z. Gomzi, Ind. Eng. Chem. Res. 44 (2005).
[18] M.M.J. Treacy, J.B. Higgins, R. von Ballmos, Collection of Simulated XRD Powder Patterns for Zeolite, 3rd revised ed., 1990, p. 524.
[19] B.B. Pruden, H. Le, Can. J. Chem. Eng. 54 (1976) 319.
[20] H. Ota, S. Goto, H. Teshima, Ind. Eng. Chem. Fundam. 19 (1980) 180.
[21] R.S. Willms, A.M. Balinsky, D.D. Reible, D.M. Wetzel, D.P. Harison, I&EC Res. 26 (1987) 606.
[22] L. Jaulin, E. Chornet, Can. J. Chem. Eng. 65 (1987) 64.
[23] J.F. Perez-Benito, J. Inorg. Biochem. 98 (2004) 430.