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Phenol oxidation with hydrogen peroxide using Cu/ZSM5 and Cu/Y5 catalysts

Karolina Maduna Valkaj, Ozren Wittine, Karmen Margeta, Teresa Granato[2], Andrea Katović[1], Stanka Zrnčević[2]

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, 10000 Zagreb, Croatia
[1] Universita della Calabria, Dip. Ingegneria Chimica e dei Materiali, Rende, Italia
[2] Corresponding author: e-mail: szrnce@fkit.hr

In this work, catalytic activity and stability of Cu/Y5 and Cu/ZSM5 zeolites in phenol oxidation with hydrogen peroxide were examined. The catalyst samples were prepared by the ion exchange method of the protonic form of commercial zeolites. The catalysts were characterized by the powder X-ray diffraction (XRD), AAS, while the adsorption techniques were used to measure the specific surface area.
The thermal programmed desorption of NH3 (NH3-TPD) was used for measuring the total number of acid sites formed on the surface of zeolites.
Catalytic performance of the prepared samples was monitored in terms of phenol, hydrogen peroxide and total organic carbon (TOC) conversion, by-product distribution and a degree of copper leached into the aqueous solution.
It was found that the activity of Cu/Y5 catalyst was generally higher than that of Cu/ZSM5 and that unlike Cu/ZSM5, Cu/Y5 catalyzed phenol oxidation more completely.

Keywords: waste water treatment; phenol oxidation; hydrogen peroxide; catalysts; Cu/ZSM5; Cu/Y5.

INTRODUCTION

Disposal of wastewater streams containing highly toxic organic pollutants generated by many industrial processes has become a growing concern in recent years. Among numerous classes of pollutants, phenols present a particular issue due to their being widely discharged into the environment and due to their toxicity to many living organisms. The effective removal of such pollutants, from the safety aspect is a challenging task given the increasingly stringent environmental laws and regulations. Biotreatment, adsorption and incineration have been traditionally applied for the purpose of their legal compliance[1]. However, toxic pollutants are lethal to the microorganisms employed in bioprocesses. On the other hand, incineration or adsorption merely transfer pollutants from a liquid to air or to a solid leaving, combustion by-products or a contaminated adsorbent for further disposal. Therefore, there is a clear need in testing and setting up the emerging alternative technologies that can deal with highly concentrated and/or toxic non-biodegradable organic water pollutants. Wet air oxidation (WAO) is an attractive method for the treatment of waste streams that are too diluted to be incinerated and too toxic to be treated biologically. The use of catalysts makes the process more attractive by achieving high conversion at a considerably lower temperature (353–473 K) and pressure (1–10 MPa). An alternative process that allows oxidation at the ambient or close-to-the-ambient conditions, thus limiting the investment costs, involves hydrogen peroxide as an oxidant in the so-called catalytic wet peroxide oxidation (CWPO). Hydrogen peroxide does not form any harmful by-products, and is a non-toxic and ecological reactant. Although, it is a relatively costly reactant, the peroxide oxidation compares very favorably to the processes that use gaseous oxygen. The lack of gas-liquid boundary removes mass transfer limitation and the hydrogen peroxide acts as a free radical initiator, providing hydroxyl radicals that promote phenol degradation.

Although the homogeneous catalyst applied in CWPO processes demonstrates a high efficiency, their recovery from the treated effluent is rather difficult and requires an additional process to remove the homogeneous catalyst in the reactor. This drawback can be overcome by using easily recoverable and reusable heterogeneous catalysts. Transition metals, mainly iron and copper, are used as active phases. Many materials containing mainly iron and copper as the precursors supported/intercalated on/in oxides[2,3], mesoporous molecular sieves[4–7], zeolites[8–16], pillared clays[17–21], carbon[22,23], and resins[24–27] are proposed as catalysts for the removal of organic compounds. These catalysts exhibit the advantages of a heterogeneously catalyzed process. Unlike a homogeneous catalyst they have relatively higher oxidation efficiency and lower sensitivity to pH under equal reaction conditions. However, during oxidation most of them suffer from deactivation caused by the leaching of a metal cation in contact with a hot acidic medium used in heterogeneous catalytic oxidation[13,14,16,23,27–29]. Therefore, the preparation of efficient and durable catalysts is still a challenge to the development of an advantageous catalyst for the oxidation for phenolic wastes.

Taking into account that the phenol is one of the most prevalent forms of toxic and poorly biodegradable chemical pollutants from industrial activities it is chosen as the model pollutant. The aim of the work is to use the copper-containing ZSM5 and Y5 zeolites in the CWPO of phenol in a batch reactor. The results will be analyzed in terms of phenol and TOC conversion as well as the hydrogen peroxide consumption. The efficient use of the oxidant will be assessed. Identification of the intermediate species will be carried out. Special attention will be paid towards evaluation of the catalyst stability in terms of copper leaching into the reaction mixture.

EXPERIMENTAL

Catalyst synthesis

The catalysts were prepared from the protonic forms of commercial ZSM5 (Leuna Werke), and Y5 (Süd Chemie) zeolites with different SiO_2/Al_2O_3 ratio. They were in the powder form. Ion exchange with copper acetate solution was carried out at 298 K over 24 hours and then the samples were dried 10 hours at the room temperature[14].

Catalyst characterization

Characterization of the samples was performed by a different conventional technique. Crystalline structures of all the prepared catalysts were checked by the X-ray diffraction analysis. The XRD patterns were obtained with Philips PW 1830 diffractometer using Ni-filtered CuKα radiation operating at 40 kV and 30 mA. The data were collected from 2θ ranging from 5° to 40° with resolution of 0.02°.

The surface morphology of the catalysts was examined using a FEG Quanta 200F FEI/Phillips scanning electron microscope (SEM).

Textural characterization of the catalyst samples was performed by means of nitrogen adsorption/desorption isotherms at 77 K using Micromeritics ASAP 2000. The catalysts were degassed under vacuum for 5 h at 623 K prior to N2 adsorption measurements. The total sorbed volumes, including adsorption in the micropores and mesopores and on the external surface, were calculated from the amount of nitrogen adsorbed at relative pressure p/p_0 of 0.96 before the onset of interparticle condensation.

Chemical composition of the catalysts was determined by atomic absorption spectrometry using Perkin Elmer AAS 3110 and ICP-MS analyzer.

Acidity measurement by temperature-programmed desorption of NH_3 was carried out using Micromeritics Pulse Chemisorb 2720 instrument. For NH3-TPD studies, the catalyst was activated in helium flow for 2 h at 673 K. Then the sample was cooled to 373 K before the adsorption of ammonia. Subsequently, 5% NH_3 with He was passed through the sample for 30 min to chemisorb ammonia. The excess physisorbed ammonia was flushed with helium at 393 K. Then the sample was heated at a rate of 10 K min^{-1} up to 873 K. The volume of gas desorbed was measured by a detector.

Catalytic evaluation

The catalytic tests were carried out in a stainless steel Parr reactor in a batch operation mode at the atmospheric pressure, the temperature values of 333, 343 and 353 K and the stirrer rotational speed of 200 rpm. Phenol degradation experiments involved an aqueous phenol solution (0.2 dm^3, 0.01 mol dm^{-3}). The solid catalyst (0.10 g dm^{-3}) was suspended in the solution under continuous stirring. When the reaction mixture was heated to a desired temperature hydrogen peroxide (0.10 mol dm^{-3}) was added to initiate the reaction. The pH was not adjusted during the reaction period, but pH was measured and recorded.During the reaction aliquots were withdrawn at the predetermined time intervals and filtered by means of 0.2 μm nylon membrane to analyze the reaction mixture. Decreases in phenol concentration, and decomposition of hydrogen peroxide were analytically monitored. Phenol and its conversion products were analyzed with HPLC chromatograph equipped with a Waters Spherisorb ODS2C column. The major detected products were: catechol, hydroquinone, maleic acid, oxalic acid and acetic acid. Hydrogen peroxide concentration was followed by a colorimetric method using a UV-1650PC Shimadzu spectrophotometer. Total organic carbon (TOC) was determined with a TOC-V CSN Shimadzu analyzer. Copper content in the filtered solution after reaction was determined by atomic absorption Perkin Elmer 2380.

RESULTS AND DISCUSSION

Characterization of the prepared catalysts

The physicochemical properties of the catalysts used in this study are listed in Table 1.

As it can be seen the BET surface area, the pore volume and acidity of ZSM5 were lower than those of Y5. The tests showed that the BET surface area of zeolites decreased with the copper loading. It had been expected that more pore cavities in the zeolite would be blocked by addition of metal ions, causing reduced accessibility of nitrogen as observed from the lower BET surface area. Table 1 shows the total number of acid sites formed on the surface of zeolites as determined from ammonia TPD. Acidity of the zeolite was related to its alumina content whereas increase in the overall acidity was expected with increased aluminium content in the zeolite[30]. It can be seen that the concentration of acid sites of zeolites matrix decreased with copper loading because the H+ ions which led to the acidity of the catalyst were replaced by metal ions.

In order to check the crystallinity of the samples before and after ion exchange with copper and the possible formation of copper oxides, the XRD patterns were recorded. As shown in Fig. 1 no significant difference was found between the diffractograms of the parent zeolites and the catalysts after ion exchange. Cu/ZSM5 and Cu/Y5 presented crystallinity between 95 and 100% in relation to the parent zeolite crystallinity, which indicated that catalyst lattice was practically unperturbed by exchange with copper.

The SEM micrographs of the Cu/ZSM5 and Cu/Y catalysts are shown in Fig. 2.

As shown, the morphology and the size of the crystallites depended on the SiO_2/Al_2O_3 ratios. The zeolite with lower

Table 1. Physicochemical properties of Cu-containing zeolites used in phenol oxidation

Sample	*SiO_2/Al_2O_3	Cu, wt. %	Acidity, mmol NH_3 g^{-1}	S_{BET}, m^2 g^{-1}	V_p, cm^3 g^{-1}	$\overline{r_p}$, nm	*Aperture size, nm
H-ZSM5	31		0.587	307.8	0.19	1.88	0.54x0.56
Cu/ZSM5	31	3.52	0.289	300.5	0.15	1.53	
H-Y5	5.2		2.101	595.21	0.38	1.94	0.74
Cu/Y5	5.2	3.54	0.699	579.6	0.36	1.91	

*Manufacture's data

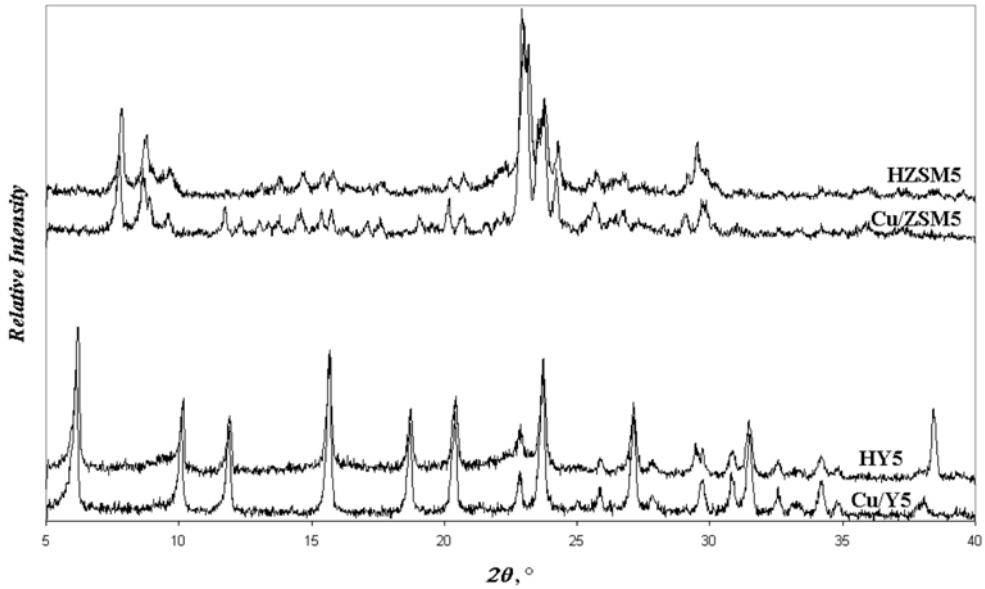

Figure 1. XRD patterns of ZSM5, Y5 and Cu-bearing zeolites

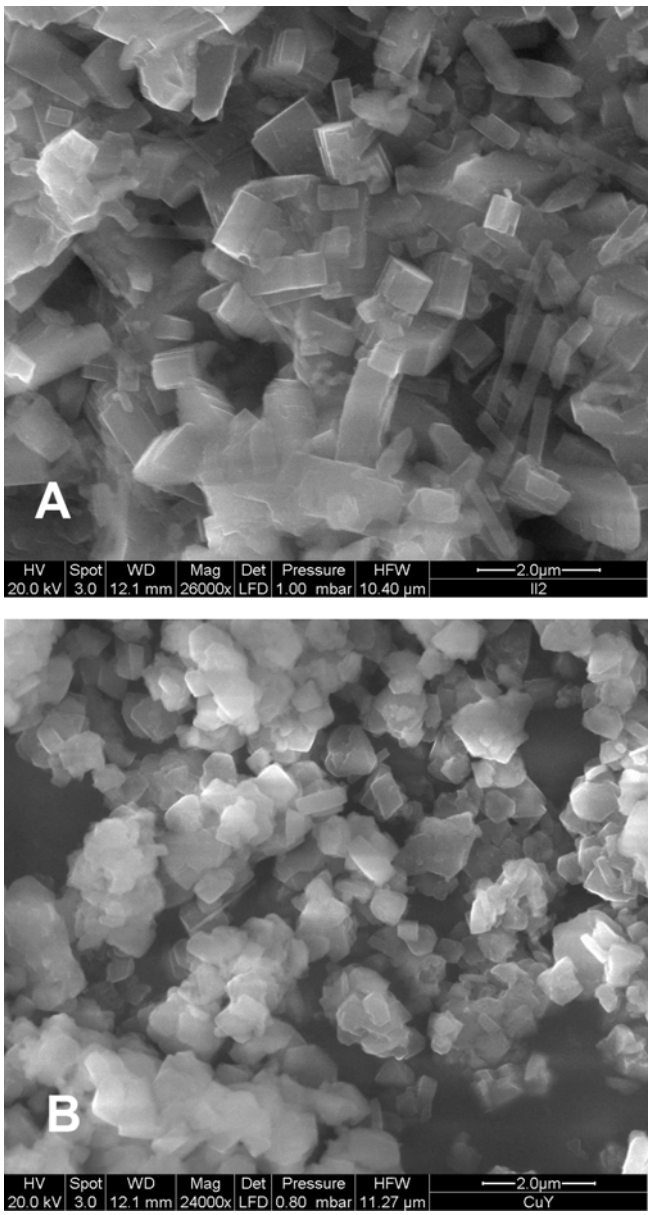

Figure 2. SEM micrographs of Cu/ZSM5 (A) and Cu/Y (B) catalysts having a SiO_2/Al_2O_3 ratio equal to: A) 31 and B) 5.2

SiO_2/Al_2O_3 ratio (Fig.2B) was constituted by agglomerates of small crystallites. However, with an increase of that ratio (Fig.2a), the crystals tended to be isolated or to geminate with morphology of hexagonally prisms as also observed by others authors[31].

Catalytic activity

A preliminary set of experiments were performed in order to compare the behavior of the Cu bearing zeolites and pure zeolites, and to discriminate the effect of adsorption and reaction. These experiments were carried out at 333 K, and other process parameters were as specified in Experimental Section (*Catalytic Evaluation*). Phenol conversion obtained after 180 min of the reaction are shown in Table 2.

As can be seen the experiments carried out with the pure zeolites gave fairly similar results in the presence and absence of hydrogen peroxide as an oxidant. This suggests that the oxidation of phenol was almost negligible and that phenol removal took place essentially by adsorption. In the absence of hydrogen peroxide phenol oxidation on Cu-bearing catalyst was comparable to that observed with the pure support. Thus, again, practically only adsorption must have occurred. The addition of H_2O_2 greatly enhanced phenol conversion allowing the conclusion that phenol was being transformed through oxidation and that the Cu-bearing catalysts were active for that reaction.

Figs. 3 and 4 show the results obtained for phenol and hydrogen peroxide conversion as a function of the reaction time and temperature over the catalysts investigated. According to the expectation phenol oxidation and H_2O_2 decomposition increased markedly with an increase in the reaction temperature from 333 to 353 K.

Table 2. Phenol conversion over Y5 and ZSM5 zeolites, and Cu bearing zeolites with and without oxidant

	Y5	Y5 + H_2O_2	Cu/Y5	Cu/Y5 + H_2O_2
X_{Ph}, %	8.7	9.2	9.1	98.9
	ZSM5	ZSM5 + H_2O_2	Cu/ZSM5	Cu/ZSM5 + H_2O_2
X_{Ph}, %	6.2	7.4	7.2	66.4

It is well known that the oxidation rate and TOC removal are strongly dependent on the concentration of hydroxyl radicals. The radical concentration usually increases with the increasing reaction temperature in the CWPO proc-

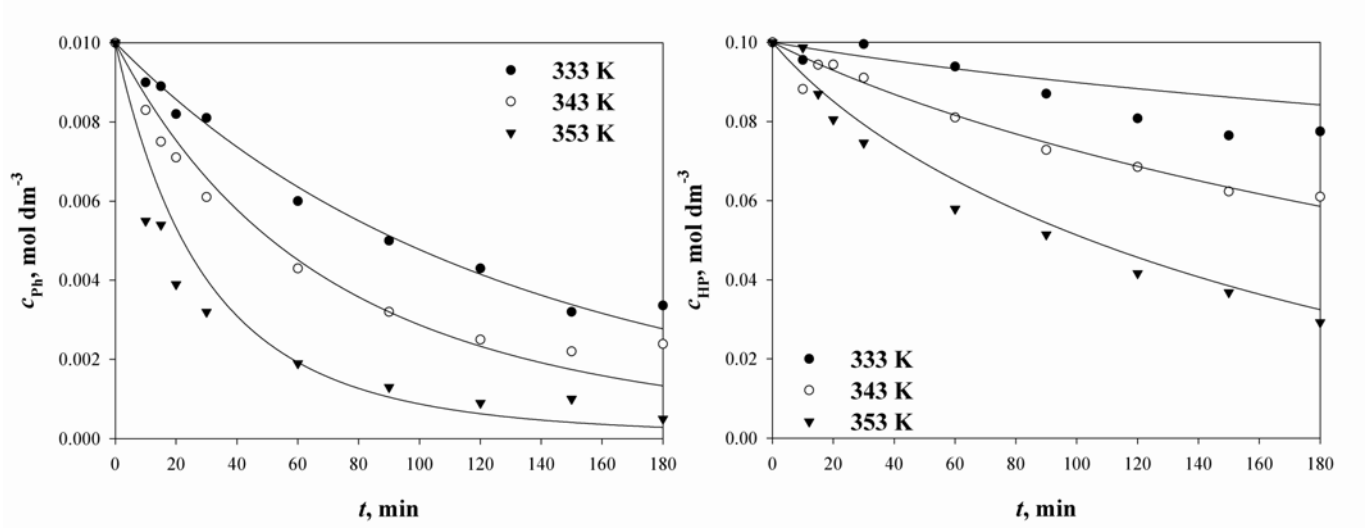

Figure 3. Phenol oxidation and hydrogen peroxide decomposition over Cu/ZSM5 catalyst as a function of temperature (c_{Ph}= 0.01 mol dm^{-3}, c_{HP}= 0.10 mol dm^{-3}, m_{cat} = 0.10 g dm^{-3})

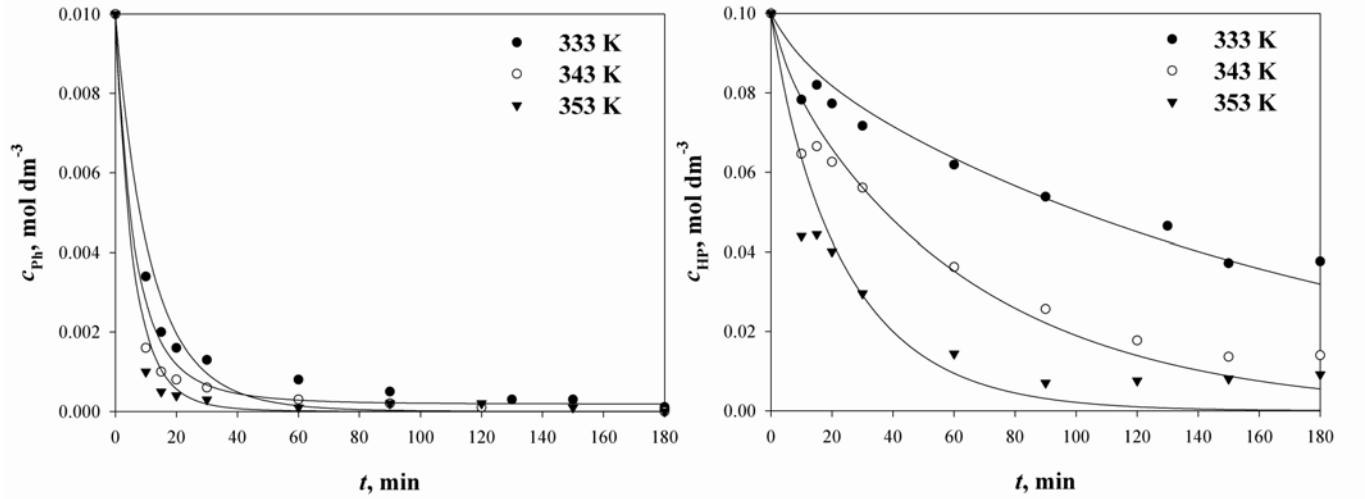

Figure 4. Phenol oxidation and hydrogen peroxide decomposition over Cu/Y5 catalyst as a function of temperature (c_{Ph}= 0.01 mol dm^{-3}, c_{HP}= 0.10 mol dm^{-3}, m_{cat} = 0.10 g dm^{-3})

esses. However, the higher reaction temperature may enhance thermal degradation rate of hydrogen peroxide. Therefore, the oxidation rate of organic compounds should be dependent on the competition between free radical formation and thermal degradation of H_2O_2. This means that phenol conversion might be related to the competition between the thermal decomposition of hydrogen peroxide and the free radical formation as also reported by Dubey at al. [32]. The results of the present study indicate that the rate of $OH^{\cdot}$ formation was higher than the rate of the thermal decomposition of hydrogen peroxide because the decrease in the phenol conversion was not monitored when reaction was carried out at higher temperature.

Also, as shown in Figs. 3 and 4, a Cu/Y5 catalyst oxidized phenol and decomposed H_2O_2 faster than Cu/ZSM5, although both of them possessed practically equal concentration of catalytic active centers. That could be attributed to the diffusion transport resistance of molecules in the pore of a Cu/ZSM5 catalyst, because a pore diameter of H-MFI zeolite was very close to the size of phenol and hydrogen peroxide molecule. Besides, as was mentioned in work of Čapek et al.[33], 60–80% of copper ions are located at the β-type of sites, represented by a six-membered ring positioned at the intersection of a straight and a sinusoidal channel with lower level of accessibility to reactants than other α-type Cu ions.

The molecular size of phenol and hydrogen peroxide calculated by periodic molecular mechanics optimization are listed in Table 3 [34].

Table 3. Molecular size of phenol and hydrogen peroxide*

Molecule	*a*, nm	*b*, nm	*c*, nm
Phenol	0.4792	0.4908	0.5090
Hydrogen peroxide	0.2476	0.2476	0.361

*Data taken from [33]

Comparison of the data from in Tables 1 and 3 shows that phenol and hydrogen peroxide would diffuse more easily in an H-Y5 zeolite pore than in an H-ZSN5 pore.

Another suggestion is that the different activity of the catalysts was caused by the different acidity of zeolites. It is well known that redox properties of transition metal cations, e.g. copper species promote generation of active hydroxyl radicals in the presence of hydrogen peroxide. In addition, it is assumed that the intrinsic acidity of a zeolite can influence the conversion of hydrogen peroxide, i.e. the highest formation rate of hydroxyl radicals[35]. Therefore, the better activity of a Cu/Y5 catalyst for phenol oxidation might have been the outcome of a higher concentration of

hydroxyl radicals generated over both sites, i.e. Cu^{2+} and H^+ sites. Although it is not fully correct to compare the activity of Cu ions exchanged in different zeolite structures, it is evident that the copper-bearing zeolite with large pores and higher acid strength acted as an effective catalyst for phenol oxidation.

The catalytic results have also shown that under mild reaction conditions phenol was rapidly removed from the Cu/Y5 catalyst with just 75% of stoichiometric oxidant concentration required for the complete mineralization of phenol, according to the reaction

$$C_6H_5OH + 14\ H_2O_2 \rightarrow 17\ H_2O + 6\ CO_2 \quad (1)$$

Which is contrary to other studies reported in literature, where the oxidant was used in excess[15,36].

Table 4 shows the final values of phenol, TOC and hydrogen peroxide conversion and efficiency in the use of an oxidant defined as TOC removal to H_2O_2 conversion ratio after 180 min of phenol degradation for the runs shown in Figs. 3 and 4.

As it can be seen TOC reduction was enhanced by increase of the reaction temperature. But in all the cases it was significantly lower than phenol conversion which indicated that oxidation of phenol proceeded through formation of different intermediates. The final result was far from complete mineralization, namely oxidation to CO_2 and H_2O[24]. The maximum TOC reduction reached 62% after 3 h in the case of Cu/Y5 when the reaction was performed at highest temperature and was close to 34% for Cu/ZSM5, which meant that significant amounts of refractory oxygenated intermediates still remained in the liquid phase as the reaction proceeded.

The value of that parameter indicates that hydrogen peroxide was not effectively utilized to generate reactive hydroxyl radicals that can further attack the organic compounds.

It is well known that Fenton-like reactions are based on the $HO^{\cdot}$ production by catalytic decomposition of hydrogen peroxide. They are responsible for fast non-selective degradation and mineralisation of the organic matter[37]. The pathway of the reactions occurring in the presence of hydrogen peroxide can be described as follows:

$$Cu^{2+} + H_2O_2 \leftrightarrow Cu(OOH)^+ + H^+ \quad (2)$$

$$Cu(OOH)^+ \rightarrow Cu^+ + HO_2^{\cdot} \quad (3)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO^- + HO^{\cdot} \quad (4)$$

$$Cu^{2+} + HO_2^{\cdot} \rightarrow Cu^+ + H^+ + O_2 \quad (5)$$

$$RH + OH^{\cdot} \rightarrow H_2O + R^{\cdot} \rightarrow \text{further oxidation} \quad (6)$$

However, hydrogen peroxide can also be decomposed to other less active radical species as the results of parallel reactions, which inhibit the oxidant power of hydrogen peroxide (reaction (7)).

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2 \quad (7)$$

Generally, $HO_2^{\cdot}$ radicals do not play an important role in the mineralisation process as they have low reactivity compared to HO radicals[15].

It is clear from Table 4 that over the prolonged reaction times there was a significant decrease in the efficiency of an oxidant for the total oxidation of the organic compound, especially when the catalyst`s activity was higher. That fact had to be attributed to increased concentration of the low-weight carboxylic acids into a liquid phase as the reaction proceeded. These by-products were much less reactive with hydroxyl radicals, which reduced the efficiency of hydrogen peroxide. Low pH values found after 180 min of the reaction confirmed the presence of low-molecular-weight carboxylic acids as intermediates of phenol oxidation as well as generation of H^+ due to the production of hydroxyl radicals in the typical Fenton-like reaction scheme (reactions (2)–(6)).

The obtained higher catalytic performance of copper-ion-exchanged Y-type zeolite is supported by its better use of an oxidant. This fact shows that the nature of copper particles and textural properties of the Y zeolite matrix, seem to be responsible for a more efficient use of the oxidant and the resulting higher degradation rate of TOC.

It is well known that the catalytic wet peroxide oxidation of phenol is a very complex process, including a set of the parallel and series reactions, and involving many types of intermediates and final products[20,38,39]. They comprise aromatic compounds, mainly benzoquinone, hydroquinone and catechol, carboxylic acids (acetic, maleic, oxalic and fumaric acids) and other oxygenated compounds such as aldehydes and ketones.

Fig. 5 show the time-evaluation curves of intermediates identified when phenol oxidation was carried out over Cu/Y5 and Cu/ZSM5 catalysts. The figure shows that phenol yielded intermediate ring compounds as hydroquinone, catechol, p-benzoquinone and acids such as maleic, acetic, formic and oxalic. Fumaric acid was also identified only in traces. However, some important differences can be pointed out among these two catalysts. First, as already mentioned, the activity of Cu/Y5 catalyst was generally higher than that of Cu/ZSM5. The concentrations of hydroquinone and catechol, the most toxic species in the oxidation route of phenol, become negligible after 3 h, only when the Cu/Y5 was used. Secondly, Cu/Y5 catalyzed phenol oxidation more completely than Cu/ZSM5. The main carboxylic acids in the case of Cu/ZSM5 were maleic and acetic acid, and in the case of Cu/Y5 these were acetic and oxalic acid. Among the organic acids, oxalic acid deserved particular attention because it had been reported as the main responsible for metal leaching from Me-based catalysts and showed refrac-

Table 4. Effect of temperature on conversion after 180 min of a reaction

Sample	T, K	X_{Ph}, %	X_{TOC}, %	X_{HP}, %	pH	[a]Oxidant efficiency	
						60 min	180 min
Cu/ZSM5	333	66.4	9.0	22.5	3.6	0.61	0.40
	343	76.2	16.8	39.1	3.1	0.69	0.43
	353	95.0	33.9	70.7	2.7	0.72	0.48
Cu/Y5	333	98.9	38.3	62.2	2.5	1.29	0.61
	343	100	52.7	85.4	2.4	1.32	0.62
	353	100	62.1	90.8	2.4	1.54	0.68

[a]Defined as the ratio between the TOC and oxidant conversions [13]

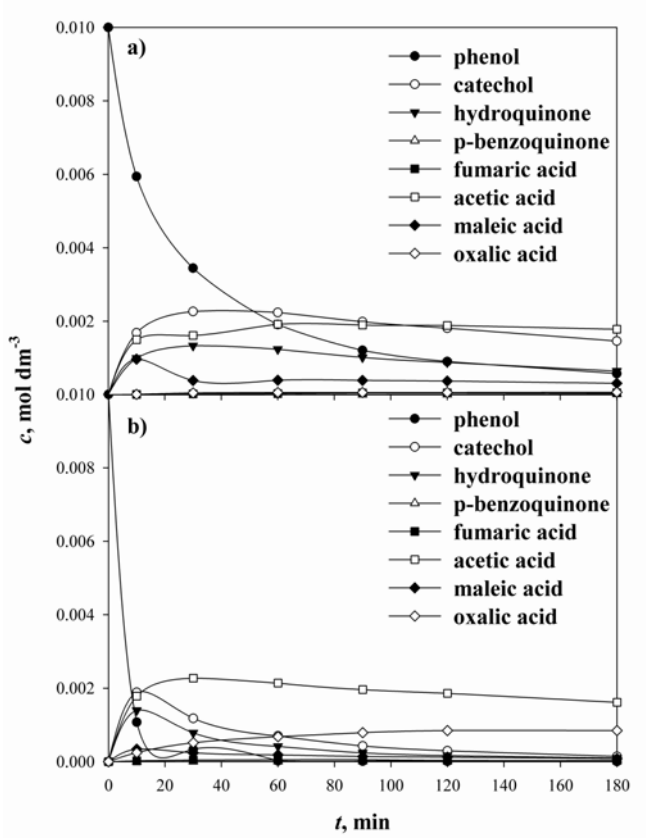

Figure 5. Time-evaluation curves of intermediates from CWPO of phenol a) Cu/ZSM5 and b) Cu/Y5 catalysts (T = 353 K, c_{Ph}= 0.01 mol dm^{-3}, cHP= 0.10 mol dm^{-3}, m_{cat} = 0.10 g dm^{-3})

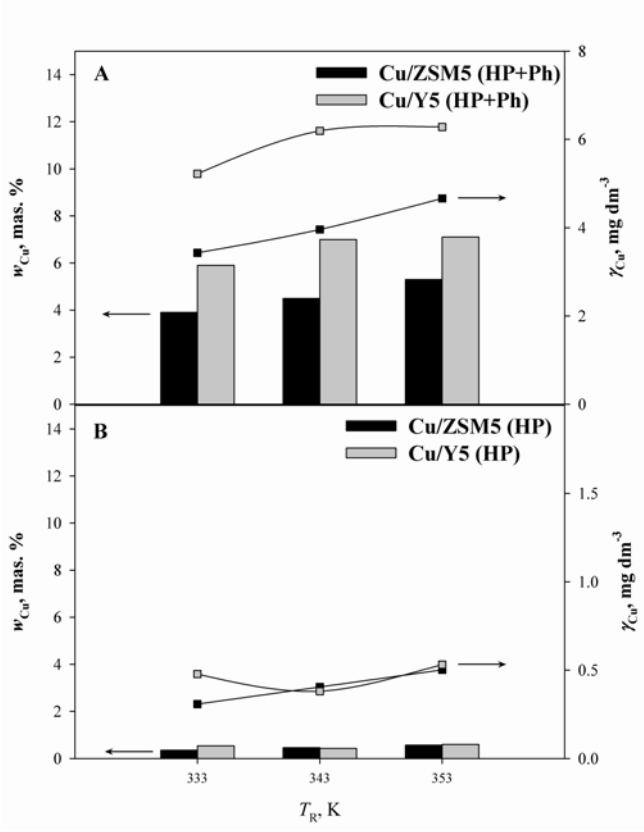

Figure 6. Effect of temperature on copper leaching: A) in the presence of phenol; B) in the absence of phenol. (t = 180 min, c_{Ph}= 0.01 mol dm^{-3}, c_{HP}= 0.10 mol dm^{-3}, m_{cat} = 2.5 g dm^{-3})

tory to oxidation by the CWPO process[22,29,40–42]. However, when the reaction was performed on Cu/ZSM5 catalyst (Fig. 4a) the concentration of oxalic acid was very low but that could not prevent leaching. It can be concluded that other intermediates of phenol oxidation were also responsible for copper leaching from the zeolite matrix[43]. Leaching could be attributed to catechol because it is well known that catechol is also a complexing agent as is oxalic acid[43]. Comparison of the final concentrations of these two complexing agents after 180 min of the reaction (Fig. 4) with the percentage of leached-off copper (Fig. 5 A) shows that oxalic acid is a stronger complexing agent than catechol.

Fig. 6 shows the effect of temperature on copper leaching when the reaction was carried out in the presence or absence of phenol.

After 3 h of the reaction the amount of leached Cu ranged from 3.9% (Cu/ZSM5) to 7.1% (Cu/Y5) whereas its loss was negligible when the aromatic compound had not been added to the aqueous solution. As expected, copper leaching increased with the increasing reaction temperature and catalyst`s activity. pH was another factor influencing the leach out Cu cations from zeolite structure into the solution[35,9]. The leaching of copper ions was enhanced at low pH values[36]. Since pH of Cu/Y5 suspension is lower than that of Cu/ZSM5 suspension (Table 3) the amount of leached copper during its use is expected to be higher in the Cu/Y5 sample.

In order to check if small amounts of leached copper were responsible for catalytic activity, after the first run the catalyst was filtered, then phenol and H_2O_2 were added to the solution in the same concentration as at the beginning of the experiment. The results are shown in Fig. 7.

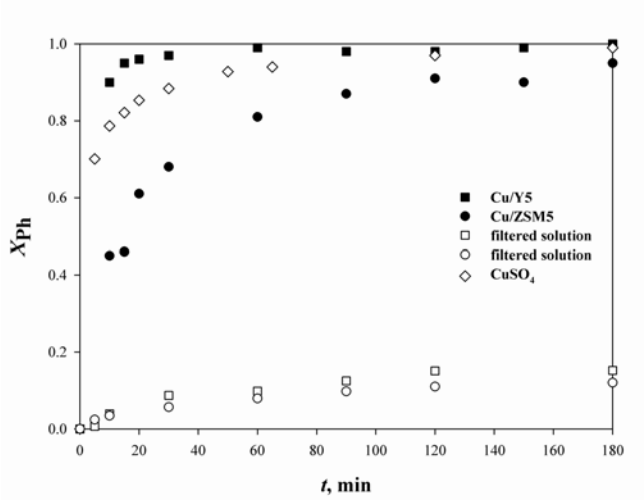

Figure 7. Phenol conversion as a function of time: fresh catalysts ■ Cu/Y5, ● Cu/ZSM5; after the filtration of the catalyst □ Cu/Y5, ○ Cu/ZSM5; ◊ $CuSO_4$ catalyst (T = 353 K, c_{Ph}= 0.01 mol dm^{-3}, c_{HP}= 0.10 mol dm^{-3}, m_{cat} = 0.10 g dm^{-3})

It can be seen that the evaluated phenol conversion in the filtered solution was lower than in the heterogeneous system. In the absence of Cu/ZSM5 and Cu/Y5 catalysts (filtered solution) phenol conversion after 3 h was 12% and 15%, in contrast to the conversion of 95% and 100% in the presence of Cu/ZSM5 and Cu/Y5 catalysts. These data demonstrated that in the absence of solid catalysts (after filtration) catalytic activity was negligible. That meant that

the fraction of copper leached from the catalysts was not capable of destroying the organic pollutant.

Fig. 7 also shows another experiment with soluble copper species ($CuSO_4$) as a copper homogeneous catalyst, performed to compare its activity with the activity of the heterogeneous catalyst. The initial concentration of copper species in the aqueous solution was 3.53 ppm (equivalent to 0.1 g dm^{-3} of catalyst with 3.53% (w/w) copper load). Other reaction conditions were as those in the heterogeneous test. It can be seen that with equal copper load of the homogeneous $CuSO_4$ phenol conversion was inferior to the activity of the Cu/Y5 sample and superior to the activity of the Cu/ZSM5 catalyst. That fact confirmed the efficiency of the heterogeneous catalytic system.

Further research was focused on the stability and activity of the recovered Cu/ZSM5 and Cu/Y5 catalysts. After the first run, the catalyst was separated by filtration, washed with distilled water and dried over night at 378 K. It should be noted that filtration of the solid aimed at determining the amount of leached copper, was made in the hot solution in order to avoid possible problems of copper re-adsorption[40]. The catalysts were used in three consecutive experiments under identical conditions. As shown in Table 5, the catalyst`s activity expressed as XPh and XTOC obtained for the reused catalysts was similar to that obtained for the fresh catalyst although complete restoration was not achieved. On the other hand, a remarkable decrease in copper ions leached out to the aqueous solution was recorded. That indicated that the most unstable copper species (extra-framework species) leached and were lost during the first run, whereas leaching was almost negligible during further catalyst`s use. That meant that major part of copper existed in the framework position of the zeolite in a relatively stable form and was active in phenol oxidation by hydrogen peroxide during consecutive use of the catalyst.

Table 5. Activity and stability of reused Cu/ZSM5 and Cu/Y5 catalysts

Sample	X_{Ph}, %	X_{TOC}, %	Cu leached, %
$Cu/ZSM5_{fresh}$	95.0	33.9	3.9
$Cu/ZSM5_{reused\ (1^{st}\ run)}$	93.5	29.7	0.9
$Cu/ZSM5_{reused\ (2^{nd}\ run)}$	91.1	25.8	0.6
Cu/Y5	100.0	62.1	7.1
$Cu/Y5_{reused\ (1^{st}\ run)}$	99.1	59.12	2.2
$Cu/Y5_{reused\ (2^{nd}\ run)}$	97.3	55.9	1.9

It can be also concluded that hydrothermal stability of copper active species within the zeolite matrix is rather good and significantly higher than that obtained for other copper-containing catalysts operating under similar reaction conditions[27,45].

The results also indicate that the Cu/Y5 catalyst is a promising catalyst for phenol CWPO because mild reaction conditions (T=353 K, atmospheric pressure, initial H_2O_2 concentration below stoichiometric and the reaction time of 3 hour) allow complete elimination of phenol and other aromatic compounds with acceptable TOC conversion and without significant leaching of copper ions from the zeolite matrix, which maintains its activity during successive runs.

CONCLUSIONS

The present study reports the results obtained with phenol CWPO using Cu-bearing Y5 and ZSM5 zeolites as the catalysts.

It has been found that the activity and stability of a copper-containing catalyst depend on the environment of copper species and textural properties of support.

A promising catalyst in the reaction of phenol oxidation in a diluted aqueous solution with hydrogen peroxide is Cu/Y5 because mild reaction conditions (T=353 K, atmospheric pressure, initial H_2O_2 concentration below stoichiometric, and the reaction time of 3 hour) allow complete elimination of phenol and other aromatic compounds with acceptable TOC conversion and without significant leaching of copper ions from the zeolite matrix, which maintains its activity during successive runs.

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SYMBOLS USED

c_F	[mol dm^{-3}]	concentration of phenol
c_{HP}	[mol dm^{-3}]	concentration of hydrogen peroxide
m_{cat}	[g dm^{-3}]	catalyst weight
$\overline{r}_p$	[nm]	pore radius
S_{BET}	[m^2 g^{-1}]	surface area
t	[min]	reaction time
T	[K]	temperature
V_p	[cm^3 g\]	pore volume
X_F	[%]	conversion of phenol
X_{HP}	[%]	conversion of hydrogen peroxide
X_{TOC}	[%]	conversion of TOC

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