

PHOTO-FENTON CATALYSIS FOR WET PEROXIDE OXIDATION OF PHENOL ON Fe-ZSM-5 CATALYST

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Catalytic wet peroxide oxidation of phenol over Fe-ZSM-5 commercial catalyst was carried out at room temperature, in a glass batch reactor, under constant air flow and halogen lamp light. At lower concentrations (0.5–2.0 mg phenol/100 cm³ water) phenol conversion of 100% was achieved. However, at higher phenol concentration (5.0 mg phenol/100 cm³ water) retardation of the catalytic activity was observed, similarly to our earlier results obtained with AlFe-pillared clay catalysts. A practical advantage of Fe-ZSM-5 catalyst compared to AlFe-pillared clay catalyst is its easy separation from the reaction solution.

INTRODUCTION

The removal of different organic compounds by homogeneous photo-Fenton reaction (system Fe²⁺, Fe³⁺, O₂, H₂O₂) has been known for over a century. In this reaction the generated OH[•] radicals decompose organic compounds to soluble end products. The standard redox potential of OH[•] radical is 2.8 V, which is high enough to enable the decomposition reactions of organic compounds¹. However, the iron ions remain in water solution after catalytic reaction. The mentioned disadvantage of this homogeneous catalytic system can be overcome with use of appropriate heterogeneous catalyst, like AlFe-pillared clay catalysts^{2–4} or Fe-ZSM-5 catalysts.^{5, 6} The Fe-ZSM-5 catalyst shows a quite different behavior compared with the homogeneous iron solutions. For example, in the presence of the P₂O₇⁴⁻ anions, the rate of the H₂O₂ decomposition increased by several times in the Fe-ZSM-5 suspension, while it is totally reduced in a homogeneous iron solution.⁶ The most part of zeolite iron ions in the framework positions exhibited no complexation by P₂O₇⁴⁻ anions as in the case of homogeneous solutions. Most part of the iron in the Fe-ZSM-5 suspension was stable even during the catalyst repeated use. No doubt that the high activity of the Fe-ZSM-5 catalyst in the H₂O₂ decomposition and organic oxidation results from the heterogeneous catalysis over the iron containing centers of the zeolite.⁶

In our previous papers^{3, 4} we reported our experiments with AlFe-pillared clay catalyst applied for wet peroxide oxidation of phenol. These catalysts oxidize phenol in water solutions at lower phenol concentration successfully (0.5 mg phenol/100 cm³ water), independently of the iron content in pillared clay catalyst. However, the removal of AlFe-pillared clay catalyst from the water solution is rather difficult. The fine AlFe-pillared clay particles suspended in reaction solution can not be removed by simple filtration, and therefore, they were removed by centrifugation. To avoid the mentioned problem, in this work, commercial Fe-ZSM-5 catalyst was applied. ZSM-5 zeolites are very stable in water solutions and their removal is simple. After the reaction the stable zeolite particles spontaneously settle on the bottom of the used reactor.

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RESULTS

For catalytic wet peroxide oxidation of phenol in water solution Fe-ZSM-5 catalyst (commercial name: FE-SH-27) was used. The producer of the selected catalyst is ALSI-PENTA Zeolithe GmbH, Schwandorf, Germany. From the product information sheet we received the following data,⁷ Table 1:

Table 1
Physical and chemical properties of the FE-SH-27 and of the SM-27 (H-ZSM-%) catalyst⁷

Designation	Unit	Value, FE-SH-27	Value, SM-27
Crystal structure		PENTASIL (MFI)	PENTASIL (MFI)
Size of the pore openings	nm	0.53 x 0.56 and 0.51 x 0.55	0.53 x 0.56 and 0.51 x 0.55
Average particle size	µm	< 10	< 20
Primary crystal length	µm	1-3	1-3
SiO ₂ /Al ₂ O ₃ molar ratio		23	23
Na ₂ O	%	0.02	<0.02
Fe ₂ O ₃	%	8	<0.05
H ₂ O	%	> 1	> 30-40

The Fe-ZSM-5 catalyst was obtained by solid-state ion exchange of a commercial ZSM-5 zeolite in the ammonium form. One of the possible ways of Fe-ZSM-5 catalyst synthesis is described in paper.⁸ The molar Fe/Al ratio in sample applied in our investigations was 0.75, according to the results obtained with XRF equipment.

The morphology of the samples is given in the Figure 1. The morphology of the samples is similar to the sedimentary rocks. The average particle size of the samples is between 1-3 µm.

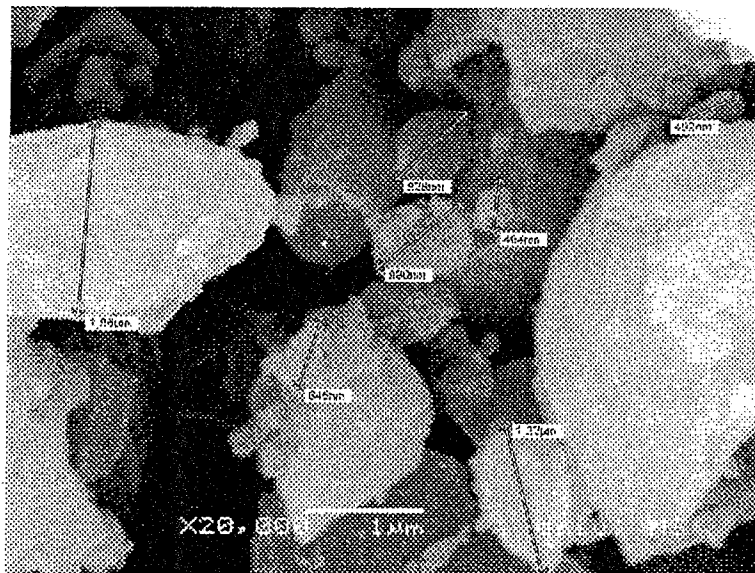


Fig. 1 – SEM picture of the Fe-ZSM-5 catalyst

The XRD pattern of the Fe-ZSM-5 zeolite sample is given in the Figure 2. In the diffraction pattern the reflexions at $2\theta = 33,15^\circ$ and $35,65^\circ$ originate from the iron compound hematite and the other peaks come from ZSM-5 zeolite.

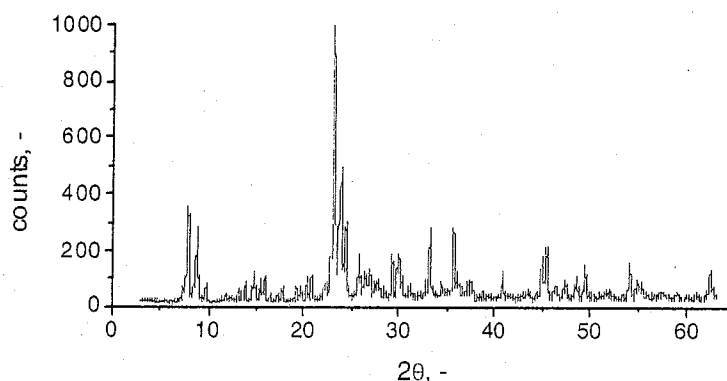


Fig. 2 – XRD pattern of the Fe-ZSM-5 catalyst

BET surface area determined with argon adsorption was $294 \text{ m}^2/\text{g}$, and with nitrogen adsorption we obtained $299 \text{ m}^2/\text{g}$. The micropore volume was calculated from the sorption capacity at a relative pressure of $p/p^0 = 0.02$ and proved via t-plot method. There was a good coincidence between argon, $120 \text{ cm}^3/\text{g}$ and nitrogen adsorption $123 \text{ cm}^3/\text{g}$. Langmuir surface area of iron zeolite is $392 \text{ m}^2/\text{g}$ with Ar and $399 \text{ m}^2/\text{g}$ with N_2 adsorption.

The surface acidity of the samples was estimated with the chemisorbed pyridine molecules. The pyridine molecules chemisorbed on Brønsted sites are characterized with bands at 1638 cm^{-1} and 1545 cm^{-1} , and the pyridine chemisorbed on Lewis sites is characterized with bands at 1452 and 1577 cm^{-1} .⁹ The ratio between Lewis and Brønsted acid sites can be estimated from the intensities of the bands at 1490 and 1450 cm^{-1} . Part of FTIR spectrogram is given in the Figure 3, where the Brønsted acid sites are presented with bands at 1632 cm^{-1} and 1554 cm^{-1} .

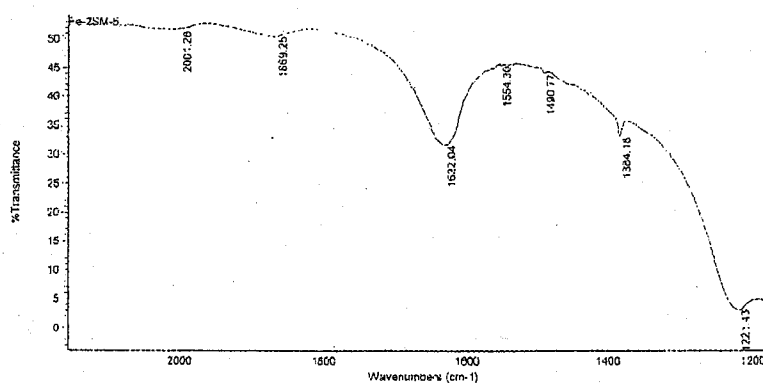


Fig. 3 – Brønsted acid sites on the Fe-ZSM-5 catalyst surface

State of iron in the samples was characterized by Mössbauer spectroscopy Figure 4. The spectrum is composed from the magnetic sextet of hematite ($\alpha\text{-Fe}_2\text{O}_3$, with a magnetic hyperfine field of 51.4 Tesla) and a central, inner small doublet characteristic of ionic species of Fe^{3+} (isomer shift: 0.34 mm/s , quadrupole splitting: 0.83 mm/s). The latest gives only 11 % contribution to the area of the spectrum.

The presence of magnetic splitting shows that the size of hematite particles is larger than c.a. 5 nm.

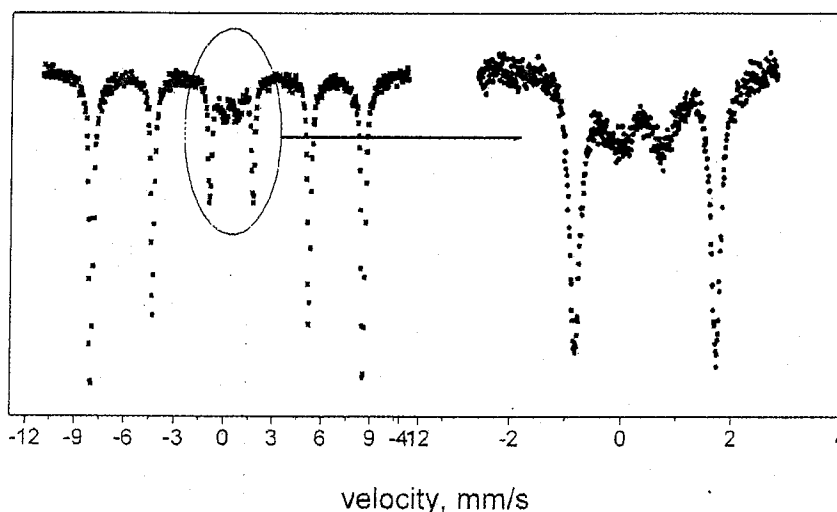


Fig. 4 – Mössbauer spectra of the Fe-ZSM-5 catalyst

The phenol conversion activity of Fe-ZSM-5 catalyst is shown in Figure 5. The phenol conversion at lower phenol content 0.5-2.0 mg/100 cm³ is 100 %. These results were obtained after 1 hour of the catalytic reaction. At higher phenol content the catalyst activity is continuously decreasing. The conversion at 3.0; 4.0 and 5.0 mg/100 cm³ phenol content in water solution is 97%; 90% and 46%, respectively.

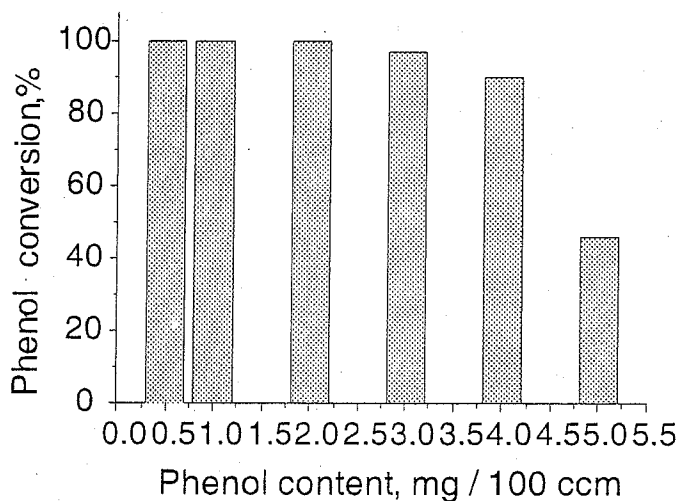


Fig. 5 – Dependence of phenol conversion on phenol content

DISCUSSION

The obtained results concerning the physico-chemical properties of the applied Fe-ZSM-5 catalyst for phenol removal from water solutions are in accordance with the data listed in Table 1 (Product Information from AISI-PENTA Zeolithe GmbH, Schwandorf, Germany). BET surface area does not offer the proper information about textural properties in the case of zeolites. BET theory does not work for the materials like zeolites. However, it is often used for comparison to other materials. The surface acidity of the samples is estimated over 0.4 mmol/g according to the data cited in paper.⁶ The concentration of acid centers is equal to 0.06 mmol/g for aluminosilicate, containing 0.1 wt. % Al₂O₃, and 0.2-0.4 mmol/g for the sample, containing 1.5 wt.% Al₂O₃.⁶ The used Fe-ZSM-5 catalyst contains over 1.5 wt. % Al₂O₃.

It is difficult to correlate any iron species with the catalyst activity. The iron coordination in different zeolites is different, also in pillared interlayered clays. All these catalysts have significant activity in phenol (or other organic compounds) degradation reactions.^{4-6, 10, 11}

The Mössbauer spectra of AlFe-PILC catalyst applied for phenol degradation⁴ is given in paper.¹¹ The Mössbauer data of iron species in AlFe-PILC catalyst are significantly differing comparing to the Mössbauer spectra of Fe-ZSM-5 catalyst. However, the two catalysts have similar activities. The Fe-ZSM-5 catalyst activity may probably be ascribed to the iron ions present in high dispersion in ionic form. The most part of iron in Fe-ZSM-5 catalyst exists in a stable form, does not leach from the catalyst and is active in the organics oxidation by hydrogen peroxide during repeated use of the catalyst.⁶ The percentage loss of the catalyst activity is much higher than the percentage loss of iron content during the catalyst use.⁶ The leached iron content, according to our results obtained by atomic absorption spectroscopy, was ≤ 0.3 ppm in the solution after the catalytic reaction. This results as well our results that the catalyst activity dramatically decrease with the phenol content in starting solutions support the idea about retardation of catalyst activity with the intermediates of phenol degradation products. Experimental proof was obtained with thermal analysis methods, investigating the fresh and used catalyst. DTA and TGA curves of the fresh and in phenol removal reaction used catalyst, at phenol content $5.0 \text{ mg}/100 \text{ cm}^3$, are shown in Figure 6. On the DTA curve of the used catalyst at 330°C appear a small exotherm peak as the consequence of the burning process of adsorbed phenol molecules and intermediary products.

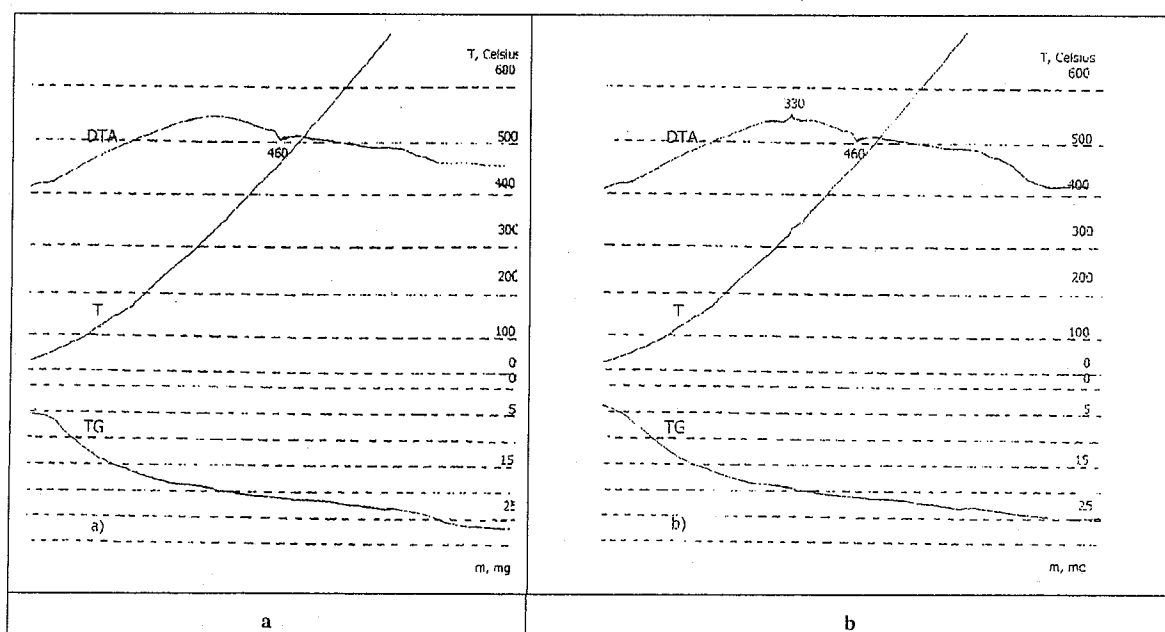


Fig. 6 – DTA and TGA curves of the fresh (a) and used (b) Fe-ZSM-5 catalyst

EXPERIMENTAL

Methods for catalyst characterization

The morphology of the gold coated sample was investigated with scanning electron microscopy JEOL JSM-6460LV. The crystal structure of the sample was studied with Siemens D500 X-ray diffractometer. XRD, ($\text{CuK}\alpha = 0.154 \text{ nm}$, 45 kV , 25 mA) in 2θ range 3° - 63° . The molar Fe/Al ratio in the applied sample was determined with X-ray fluorescence equipment, XRF, PW 2400 X-Ray Spectrometer, Philips, melted tablets with Li-meta borate. The textural properties were determined with low temperature nitrogen and argon adsorption at 77K in apparatus Micromeritics ASAP 2010. The acid base properties of the samples after pyridine adsorption were studied with Fourier transformed infrared spectrophotometer, Thermo Nicolet Nexus 670 FTIR applying KBr disc method.⁵⁷ ^{57}Fe Mössbauer spectra were recorded in an *in situ* cell at 77K and 300K . A $^{57}\text{Co}/\text{Cr}$ source was used in constant acceleration mode. The isomer shifts are relative to metallic $\alpha\text{-Fe}^0$. Spectra were computer-fitted and isomer shifts, quadrupole splittings, relative intensities etc. were deduced. Iron content after separation of the used catalyst from the reaction solution was determined by atomic adsorption spectrophotometer Unicam SP90A according to the procedure described elsewhere.¹² The thermal properties of the used and fresh sample were studied with Derivatograph, MOM 1000, from ambient temperature to 950°C with the heating rate of $5^\circ\text{C}/\text{min}$.

Catalyst activity measurements

Phenol oxidation was carried out at room temperature in a glass batch reactor at constant pH = 3.5-4.0. Phenol solution containing 0.5; 1.0; 2.0; 3.0; 4.0 and 5.0 mg phenol/100 cm³, alternatively, was placed into the reactor, together with 2.0 cm³ 0.1 M H₂O₂ and 0.5 g of well powdered Fe-ZSM-5 catalyst (commercial name: FE-SH-27). The reaction was carried out under vigorous stirring, constant airflow 30-35 cm³/min and halogen lamp light (CE 220/240V/50Hz-50W). Phenol conversions were determined after 1 hour of catalytic reaction by spectro-photometer (Specol, Carl Zeiss, Jena, GDR) as described elsewhere.¹³ The blank test measurement was carried out in absence of catalyst. The halogen lamp light has not shown measurable influence on the phenol conversion.

CONCLUSIONS

Comparing the received results with the results obtained in our previous investigations applying AlFe-pillared clays for phenol removal from water solutions^{3,4} we may conclude on a practical advantage by using Fe-ZSM-5 catalyst compared to AlFe-pillared clay catalyst, namely the easy separation from the reaction solution. In our previous investigations we had to apply centrifugation at rather high speed, about 3500 revolution/min for 5-6 minutes, for the separation of the used AlFe-pillared clay catalyst from the water solution. However, in the case of Fe-ZSM-5 zeolite, the separation of catalyst from the reaction suspension proceeds by spontaneous sedimentation of zeolite particles at the bottom of the used glass reactor. The activity of the catalyst can probably be ascribed to the stabilized ionic Fe³⁺ species.

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