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Fe Containing ZSM-5 Zeolite as Catalyst for Wet Peroxide Oxidation of Orange II*

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Abstract

This study presents the catalytic performances of iron containing ZSM-5 zeolites, prepared by ion exchange or hydrothermal synthesis, in catalytic Fenton-like oxidation of Orange II in aqueous solution. The catalyst, ZSM-5 zeolite with Si/Al ratio of 42 loaded with iron by ion exchange, showed the highest activity. The decolorization of 99.7 percent, degradation of 87.0 percent and COD removal of 81.2 percent were achieved over this catalyst at an initial pH of 3.5. Incorporation of iron into ZSM-5 structure increased its catalytic activity. The hydrothermally prepared FeZSM-5 catalyst was more stable against leaching at low pH value due to the iron being in the framework.

KEYWORDS: ZSM-5 zeolite, wet peroxide oxidation, Orange II, Fenton-like oxidation

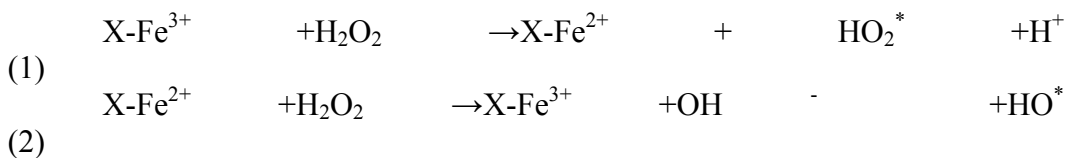
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1. INTRODUCTION

Azo type of dyes, characterized by having an azo group consisting of two nitrogen atoms (-N=N-) as the chromophore in the molecular, are the largest group of dyes and constitute more than a half of the global dye production. Apart from the aesthetic problems created when these colored effluents reach the natural water currents, they strongly absorb sunlight, thus preventing the photosynthetic activity of aquatic life and threatening the whole ecosystem. The conventional treatment methods such as coagulation, activated carbon adsorption and biotreatment processes were insufficient to treat azo dye waste water. These methods generally transfer waste components from one phase to another, thus causing secondary loading of environment. In this direction, Advanced Oxidation Processes (AOPs), based on the generation of highly reactive hydroxyl radicals as primary oxidant, appear as the good alternatives for dye abatement. Among them, the Fenton-like reactions are very promising because of high reaction yields and low treatment cost (Arslan et al., 2000; Neamtu et al., 2004; Netpradit et al., 2004; Dolphen et al., 2007; Liu et al., 2007; Nunez et al., 2007; Ramirez et al., 2007; Stolyarova et al., 2007; Sun et al., 2007; Garcia-Montana et al., 2008).

As known well, in homogeneous Fenton's process, it is needed to have up to 50-80 ppm of Fe ions in solution which is well above the European Union directives that allow only 2 ppm of Fe ions in tested water to dump directly into environment. On the other hand, the removal of the sludge-containing Fe ions is not cheap and needs large amount of chemicals. These drawbacks are overcome by developing heterogeneous catalysts prepared by incorporating Fe ions or iron oxides into porous supports. Saponite clay (Ramirez et al., 2007), SBA-15 (Bremmer et al., 2009), Y zeolite (Neamtu et al., 2004) and ZSM-5 zeolite (Stolyarova et al., 2007) have been used as support for the iron phases. Among them zeolites have a particular interest. Because their recovery from water and regeneration are not too difficult.

In heterogeneous Fenton's oxidation, Fe^{3+} reduction step with generation of HO_2^* radicals which are less reactive than OH^* radicals is followed by Fe^{3+} regeneration step with following of the HO^* radicals:



where X represents the surface of the catalyst (Ramirez et al., 2007).

The efficiency of Fe-containing zeolites in the Fenton reaction depends on the structural topology, surface chemistry and preparation method. The studies in literature indicate that FeZSM-5 zeolite can be successfully used in Fenton-like oxidation of Rhodamine 6G and methyl orange dissolved in water (Stolyarova et al., 2007; Dükkancı et al., 2010a; Dükkancı et al., 2010b). But it can not be effectively applied to all dyes.

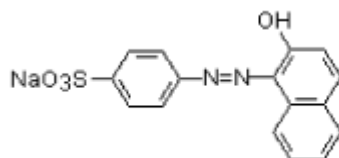
The aim of this study is to investigate the usability of Fe containing ZSM-5 zeolites in Fenton-like oxidation of Orange II which is used in coloring foods and drugs and as intermediates for making photosensitive dyes and drugs.

2. EXPERIMENTAL

2.1 Materials

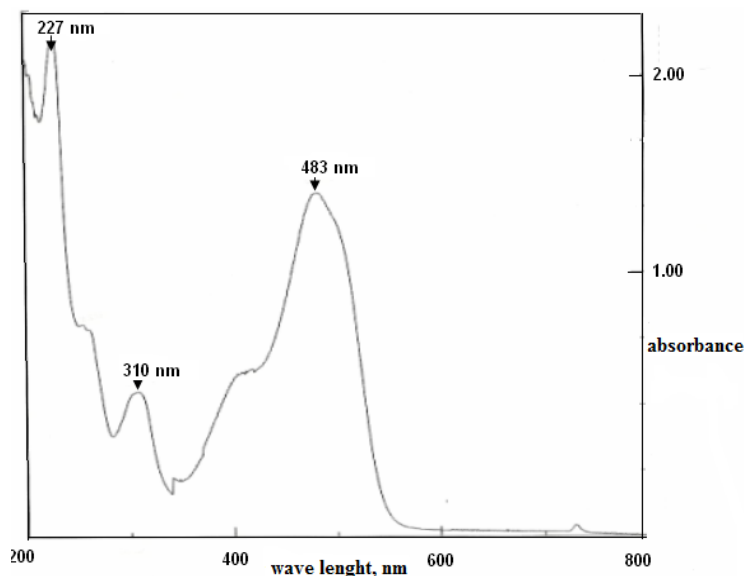
In the preparation of FeZSM-5 zeolite catalyst by ion exchange, ZSM-5 with Si/Al = 22 (VAW/Germany) and ZSM-5 with Si/Al = 42 (SüdChemie) were used as parent zeolites.

Orange II (OII) azo dye was supplied by Sigma-Aldrich and used as received without any purification. It is called as Acid Orange 7, C.I. 15510 where C.I. is the color index. The absorption spectra of OII is characterized by three main bands, one in the visible region ($\lambda_{\max} = 483 \text{ nm}$) which is responsible for the chromophoric components (for the color of dye arising from aromatic rings connected by azogroups) and the others in the UV region ($\lambda_{\max} = 227 \text{ nm}$ and $\lambda_{\max} = 310 \text{ nm}$) which represent the absorption of benzene-like and naphthalene-like structures in the molecule, respectively (Ramirez et al., 2007). Figure 1 presents the chemical structure of OII (a) and UV-vis absorption spectra of aqueous solution of OII (b). The H_2O_2 solution (35 % in wt) of analytical grade was obtained from Merck. Aqueous solutions containing 0.05 g/dm^3 azo dye were prepared with deionized water from a Millipore Direct Q purification unit.



(a)

Figure 1a. Chemical structure of OII



(b)

Figure 1b. UV-vis absorption spectra of aqueous solutions of OII

2.2 Catalyst Preparation

Ion exchange (IE) and hydrothermal synthesis (HT) methods were used for catalyst preparation. For ion exchange the method used by Schwidder et al. (2005) was applied with little modifications. For this purpose, 5 g of parent ZSM-5 zeolite (Si/Al=22 or Si/Al=42), 1.825 g of Fe powder (Riedel-de Haen AG) and 500 cm³ of deionized water were charged into a double-necked flask equipped with a gas - inlet tube and a magnetic stirrer. After the flask was flushed with nitrogen (in the study of Schwidder et al. (2005) argon was used) for 3 min, 4.14 cm³ of concentrated hydrochloric acid (in mass % of 37, J.T. Baker) was slowly added to the mixture. After the liquid was stirred under nitrogen atmosphere for 5 days it was removed, and the prepared ZSM-5 sample which was in reddish brown color was washed with deionized water. Washing was repeated until no Cl⁻ was detected in the washing water. Then catalyst was dried at room temperature and calcined. For calcination, catalyst was first heated to 423 K at a heating rate of 353 K/min and kept there for 15 min and then it was heated to 873 K at a rate of 323 K/min and kept at that temperature for 2h. The color of the sample did not change after calcination at 873 K. The catalysts were named as IE-FeZSM-5 (22) and IE-FeZSM-5 (42), respectively.

For the hydrothermal synthesis, the method given by Szostak et al. (1987) was applied. For this purpose, 4.16 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (> 99.99 %, Sigma) was dissolved in 50 g H_2O . The solution was acidified with 7.5 g of H_2SO_4 (94 – 98 %, Merck) and 100 g Na_2SiO_3 (97 %, Sigma) dissolved in 100 g H_2O was added to this fresh solution. Immediate formation of a pale yellow gel was observed. To the gel, 12 g tetrapropylammonium bromide (TPABr) (≥ 98 %, Fluka) in 25 g H_2O was added then its pH was dropped to 9.83 by addition of H_2SO_4 to solution. This gel was kept in an autoclave at 443 K for 3 days under autogeneous pressure. The resulting white solid was filtered, washed and dried at 373 K for 12 h. The calcination procedure given above was applied to this catalyst, too. The catalyst was called as HT-FeZSM-5.

2.3 Catalyst Characterization

The prepared catalysts were characterized by nitrogen adsorption, XRD, SEM, FTIR and ICP-AES measurements.

Powder X-ray diffraction patterns (XRD) of the solids were recorded in the range of $5\text{-}70^\circ$ by Philips X'Pert Pro with $\text{Cu-K}\alpha$ radiation to determine the crystalline structure of the the samples. Morphological properties were analyzed by scanning electron microscopy (Philips SFEG 30S SEM). Nitrogen adsorption isotherms at 77 K were measured using nitrogen adsorption (Micromeritics ASAP 2010) equipment after degassing the dried samples at 573 K for 24 h under $5 \mu\text{m}$ Hg vacuum. FTIR spectra were recorded in the $1700\text{-}400 \text{ cm}^{-1}$ with a Shimadzu FT-IR 8201 spectrometer using KBr pellet technique. A typical pellet containing 1 wt % of sample was prepared by mixing 2 mg sample with 200 mg KBr. Metal contents and Si/Al ratios of all the catalysts and parent zeolites were determined by Varian-96 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with fusion dissolution method.

2.4 Catalytic Activity Tests

The oxidative degradation of Orange II was performed under isothermal conditions (323 K) in a temperature-controlled shaded glass batch reactor equipped with a mechanic stirrer at about 280 rpm (Heidolph) and a pH electrode (Mettler Toledo). In a typical run, 0.15 dm^3 of aqueous dye solution (0.05 g/dm^3)

was placed into the reactor and the temperature was adjusted to 323 K. When the temperature reached to 323 K, pH of the solution was measured and 0.15 g of catalyst (1 g/dm^3) was introduced into the solution under continuous stirring. After stabilization of temperature at 323 K, pH of the solution was again measured and the solution was analyzed in order to determine whether the dye was adsorbed by the catalyst. Then a solution of 35 % H_2O_2 ($40 \text{ mmol}/0.15 \text{ dm}^3$ solution) was added into the dye solution and pH of the solution was again measured. This time was recorded as the starting time of the reaction. Reaction duration was taken to be 2h. For the experiments with initial pH of 3.5, pH was regulated by addition of H_2SO_4 into the dye solution. The samples taken periodically at every 15 min were diluted in 1:3.33 ratio. After centrifugation for 30 min to remove the catalyst, the samples were analyzed with UV spectrophotometer (Jasco 7800 UV/Vis) to determine the extent of decolorization and degradation degree of aqueous solution of OII as a function of time. The decrease in the intensity of the band at 483 nm was used as a measure of decolorization degree. The absorbance peak at 310 nm is due to the naphthalene ring of OII and the decrease of the intensity of this band was taken as a measure of degradation degree, which was attributed to the formation of intermediates resulting from the degradation of the azo dye which still contain benzoic and naphthalene type rings (Ramirez et al., 2007).

In addition to these measurements, the reduction in the chemical oxygen demand (COD) of the dye solution was determined by measuring initial and final (after oxidation for 2 hours) COD values of the aqueous dye solution with a Lavibond Checkit Direct COD Vario device after dilution of the samples in 1:4 ratio.

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

XRD patterns of synthesized catalysts and parent zeolites (ZSM-5 with Si/Al = 42 and 22) are given in Figure 2.

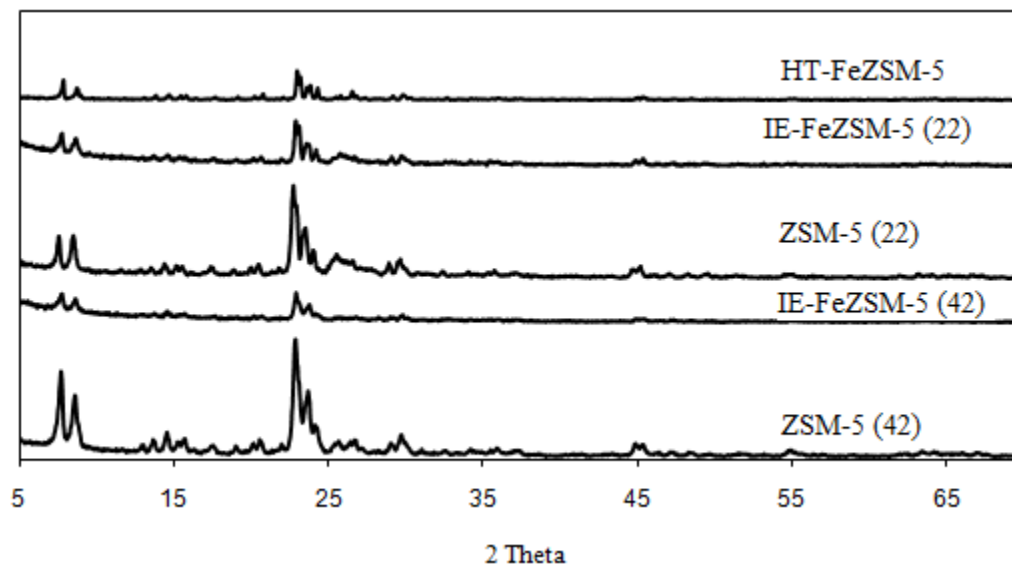


Figure 2. X-Ray Diffraction patterns of prepared catalysts and parent zeolites

All prepared samples exhibited the typical diffractograms ($2\theta = 7.9^\circ$ and 23.5°) of the ZSM-5 zeolites (MFI framework) given in literature (Klier et al., 1992; Nicolaidis 1999; Batista et al., 2001; Phu et al., 2001; Heinrich et al., 2002; Kuznetsova et al., 2004; Cheng et al., 2005; Mohamed et al. 2005; Stolyarova et al., 2007, Valkaj et al., 2007). The crystalline structure of the zeolite was not destroyed by the addition of iron by ion exchange. However, iron addition to the ZSM-5 structure caused a decrease in the characteristic peak intensities of ZSM-5 structure. This decrease can be attributed to the enhanced absorption of X-ray due to the iron cations, the reduction in crystal size of zeolite as a result of acid treatment and to the increase in the quantities of nonuniform zones connected with a partial dealumination process occurred during the preparation of FeZSM-5 catalysts (Batista et al. 2001; Schwidder et al., 2005; Mohamed et al., 2005; Ali 2007; Dükkançi et al., 2010a; Zhao et al., 2010).

Figure 3 presents the morphology of prepared catalysts and parent ZSM-5 zeolites used in ion exchange.

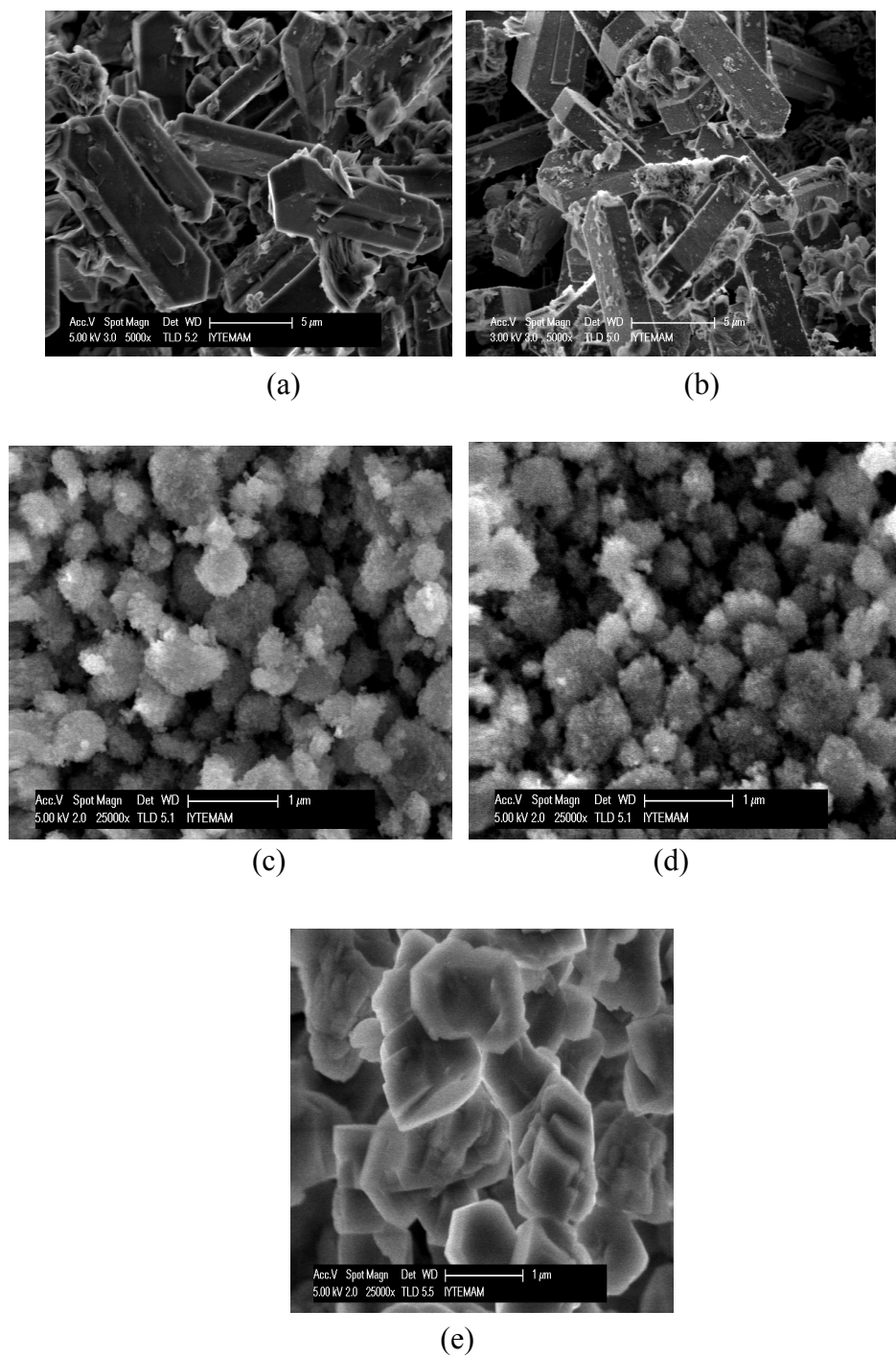


Figure 3. SEM images of prepared catalysts and parent zeolites
(a) ZSM-5 (22), (b) IE-FeZSM-5 (22), (c) ZSM-5 (42), (d) IE-FeZSM-5 (42),
(e) HT-FeZSM-5

The crystallites of the catalyst synthesized by using parent ZSM-5 (22) were as coffin-like shape with a length of about 12 μm (Figure 3a and 3b) while the crystallites of the catalyst prepared by using parent ZSM-5 (42) were in spherical shape with a diameter of about 0.25 μm (Figure 3c and 3d). Incorporation of iron cations into the zeolite structure could not be clearly observed for IE-FeZSM-5 (42) sample, whereas introduction of iron into the zeolite framework (skeleton inside and/or outside) could be easily seen for IE-FeZSM-5 (22). On the other hand, HT-FeZSM-5 had crystallites in spherical form with about 1 μm in diameter (Figure 3e). The SEM images of HT-FeZSM-5 sample revealed that no secondary iron phase was present. This manifested that framework iron was present in the sample as evoked by XRD measurements.

FTIR spectra of the synthesized catalysts and parent ZSM-5 zeolites used in ion exchange method were displayed in Figure 4 in the range of 400-1700 cm^{-1} .

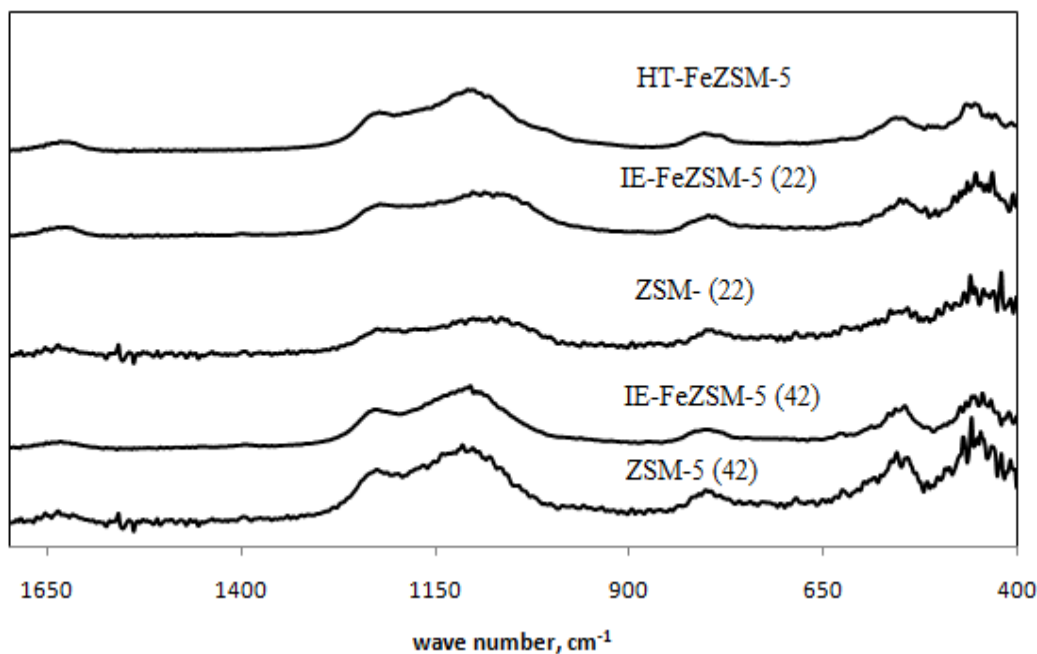


Figure 4. FTIR spectra of prepared catalysts and parent zeolites

The bands appeared at 445, 800, 1100, 1250 and 1650 cm^{-1} were assigned to different vibrations of tetrahedral and framework structure of ZSM-5 zeolite associated with minor changes due to the iron incorporation. The band at 550 cm^{-1} assigned to the five membered ring of the pentasil zeolite structure (Szostak et al., 1987; Phu et al., 2001; Cheng et al. 2005; Schwidder et al., 2005; Ali 2007).

Isotherms drawn by using nitrogen adsorption data were of type I with the exception of the isotherms of catalysts ZSM-5 (42) and IE-FeZSM-5 (42) (those are type II) according to IUPAC classification. Type I is typical for microporous materials while type II corresponds to multilayer formation, Figure 5.

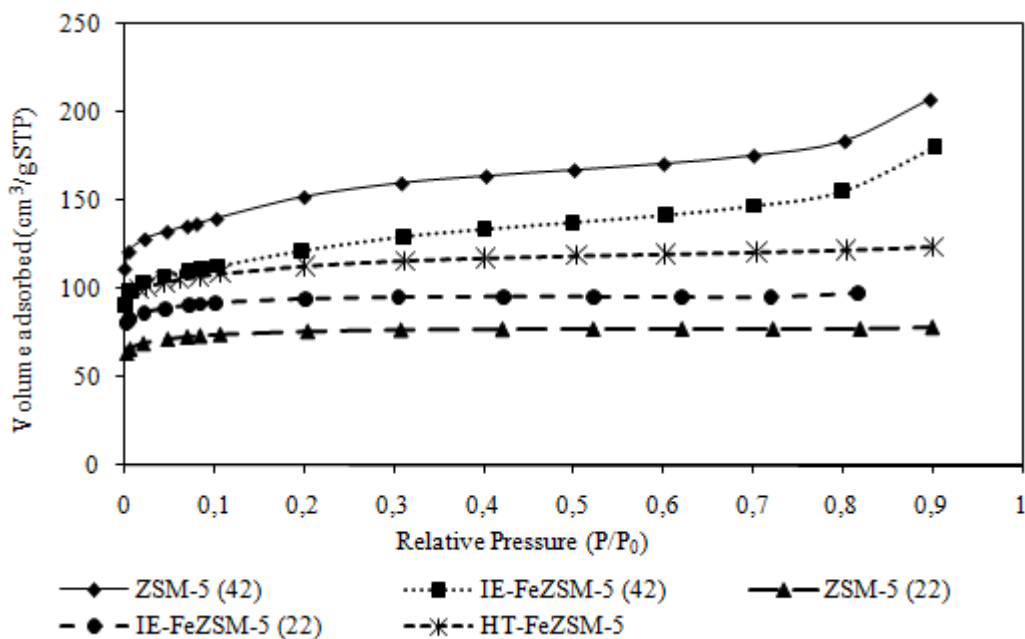


Figure 5. Nitrogen adsorption isotherms of prepared catalysts and parent zeolites

Table 1 presents the BET surface area (S_{BET}), macropore+mesopore surface area (S_{external}), total pore volume (V_p) and micropore volume (V_μ) of the catalysts prepared and of the parent zeolites used. The pore diameter was reported as the average pore diameter (d_{ave}) calculated by Horvath Kawazoe and BJH methods. Nitrogen adsorption results showed that mesopores were present in ZSM-5 structures used in the study.

Table1. Some surface characteristics of prepared catalysts and parent zeolites

Catalyst	S _{BET} (m ² /g)	S _{external} (m ² /g)	V _p (cm ³ /g)	V _μ (cm ³ /g)	d _{ave} [*] (nm)	d _{ave} ^{**} (nm)	wt % Fe
ZSM-5 (22)	227.1	42.6	0.120	0.099	0.799	2.21	0.097
IE-FeZSM-5 (22)	283.7	53.9	0.151	0.123	0.800	2.28	2.630
ZSM-5 (42)	478.4	279.1	0.320	0.113	0.719	3.37	0.055
IE-FeZSM-5 (42)	386.5	206.6	0.279	0.098	0.717	3.66	6.510
HT-FeZSM-5	344.4	108.9	0.192	0.128	1.109	2.51	3.140

*By Horvath-Kawazoe

**By BJH

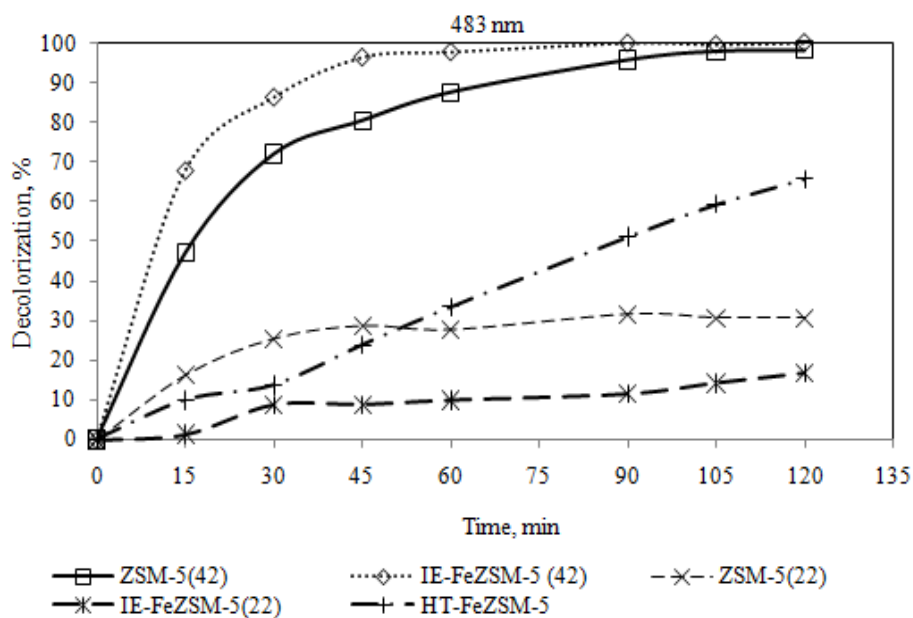
Average pore diameters found by BJH method are in a good accordance with those given in literature. Valkaj et al. (2007) reported the average pore diameter of Cu/ZSM-5 zeolites to be 2.01-2.75 nm and Zhao et al. (2010) to be 2.24 nm for ZSM-5 zeolite.

Iron loading to ZSM-5 zeolite by ion exchange leads to a reduction for IE-FeZSM-5 (42) catalyst and an increase for IE-FeZSM-5 (22) catalyst in surface area. These changes might be due to the formation of iron species inside the pores and blocking them and due to the changes in the pore size formed during the calcination step of the catalyst preparation. Table 1 presents the iron content of the catalysts, too. As seen, parent ZSM-5 (42) and ZSM-5 (22) zeolites include iron as impurity. 6.51 wt % iron was loaded into the zeolite prepared by ion exchange with ZSM-5 (42), while only 2.63 wt % iron could be loaded into zeolite ZSM-5 (22). Zeolite catalyst prepared by hydrothermal synthesis contained 3.14 wt % iron.

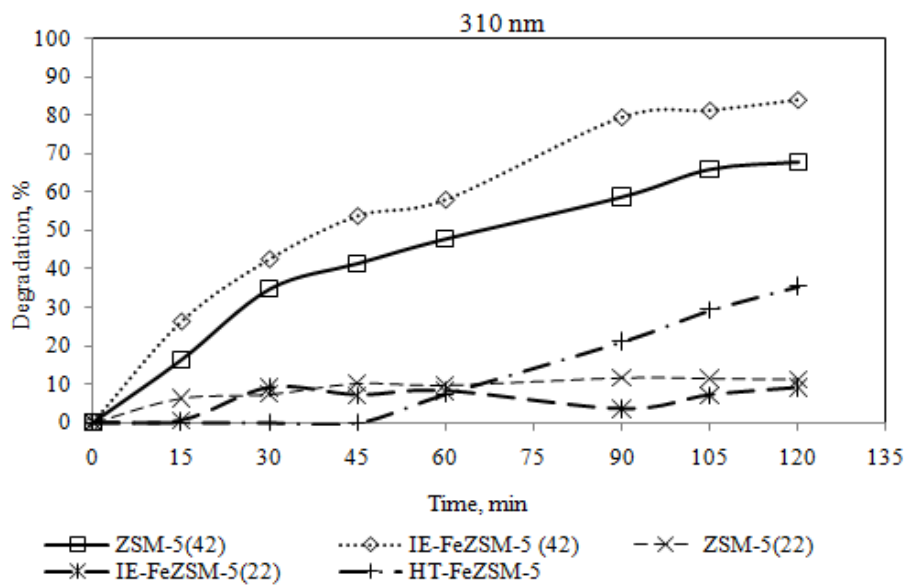
3.2 Catalytic Activity Tests

Catalytic Wet Peroxide Oxidation (CWPO) of Orange II was carried out under the conditions given in Section 2.4. No noticeable dye removal by adsorption took place over the catalysts tested in the blank runs without H₂O₂ at an initial dye pH of 7.0.

Color removal and degradation degrees were depicted in Figure 6 as a function of time at initial pH around 7.0 over the catalysts prepared. Each run was repeated twice. In the degradation and decolorization degree versus time plots in the presented paper, the standard deviation of the average of two independent runs changed in the range of ±0.01 to ±3.80.



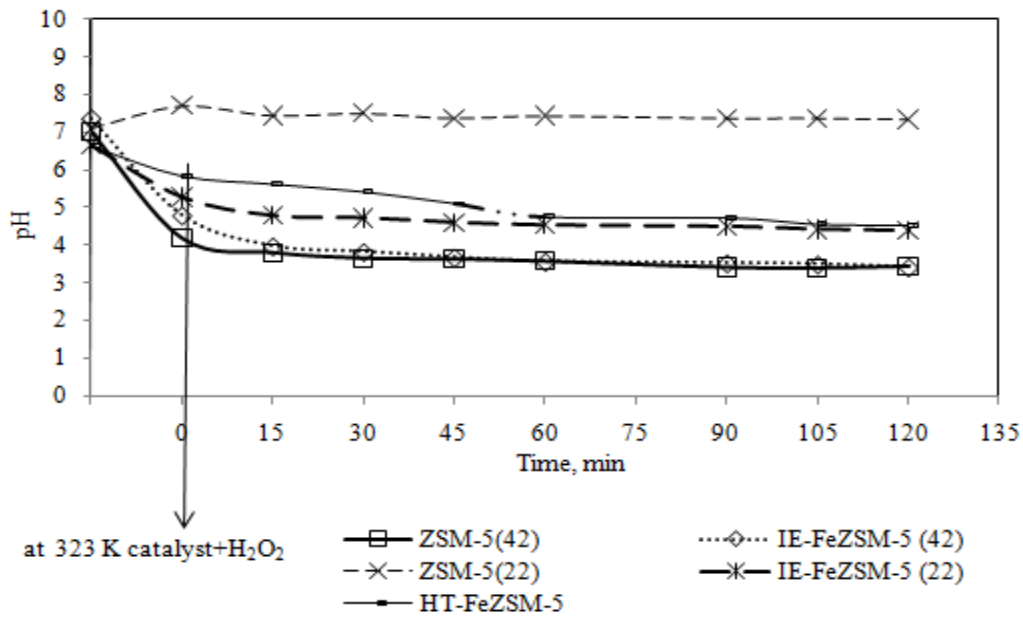
(a)



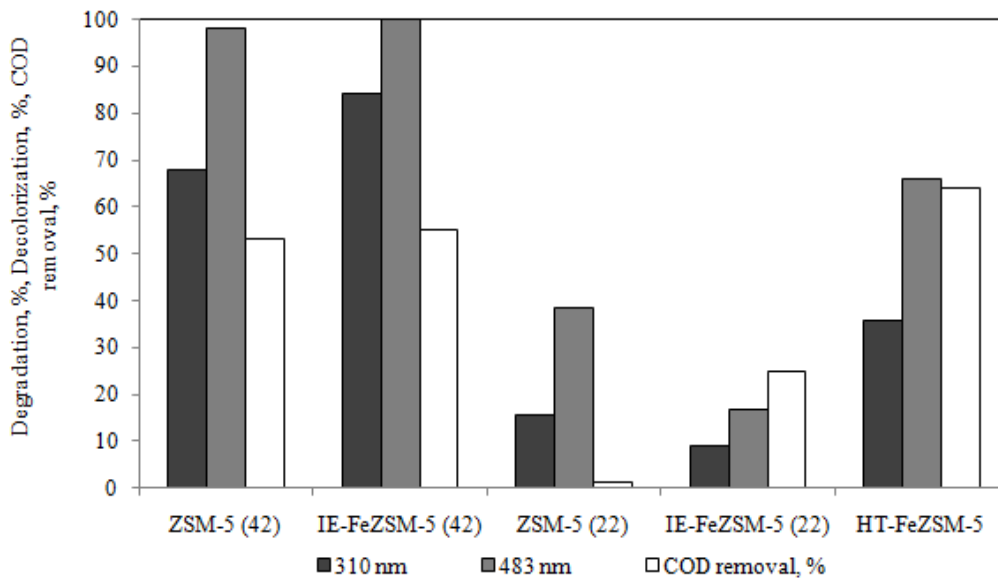
(b)

Figure 6. The influence of catalyst type on decomposition of OII as a function of time for initial pH around 7.0.

(a) Decolorization, % (b) Degradation %,



(c)



(d)

Figure 6, continued: (c) pH value, (d) COD removal, %

Parent ZSM-5 zeolites had already some iron (0.097 % in ZSM-5 (22) and 0.055 % in ZSM-5 (42)). A color removal of 98.2 % and degradation of 67.9 % were noticed after a reaction time of 2h when ZSM-5 (42) was used as catalyst. Incorporation of iron into the zeolite structure by ion exchange (IE-FeZSM-5 (42)) enhanced the degradation from 67.9 % to 84.0 % and the decolorization from 98.2 % to 99.99 %. On the other hand, IE-FeZSM-5 (42) catalyst had highest iron amount and the surface area among the catalysts tested. In addition it had the smaller particulate size which might lead to the activity observed. It was followed by HT-FeZSM-5, with color removal and degradation degrees of 65.8 % and 35.6 %, respectively. This catalyst had higher average pore diameter, surface area and iron content than those of the catalyst prepared with ZSM-5 (22), namely IE-FeZSM-5 (22). The latter catalyst and its parent zeolite showed lower activity in oxidation of OII. Loading iron to ZSM-5 (22) by ion exchange declined decolorization from 38.6 % to 16.7 % and degradation from 15.6 % to 9.1 %. This result may be attributed to the formation of iron oxide aggregates which are much less reactive than Fe^{2+} (Schwidder et al., 2005; Sjövall et al., 2006).

As the reaction proceeded, a sharp decrease in solution pH was observed with catalyst samples except ZSM-5 (22) which has the lowest activity in OII oxidation. The decrease in solution pH could be explained by the destruction of OII molecules into organic acids which led to a drop of pH. However, addition of ZSM-5 (22) and then H_2O_2 to the reacting mixture increased the pH of the solution from 7.1 to 7.7. This observation indicated that some Fe^{2+} species present in the parent zeolite structure (0.097 wt % iron) was oxidized to Fe^{3+} with the formation of OH^- ions which caused the increase of solution pH (equation 2). No significant change was observed in solution pH with time when ZSM-5 (22) was used as catalyst because of its low activity. ZSM-5 (22) had higher decolorization activity than IE-FeZSM-5 (22). This result may arise from the presence of Fe^{2+} rather than Fe^{3+} in ZSM-5 (22).

Figure 6d presents COD removal after a reaction time of 2h. It was found that the highest COD removal was obtained by HT-FeZSM-5 catalyst as 64.0 %. This was followed by a removal degree of 55.0 % over IE-FeZSM-5 (42) and of 53.0 % over ZSM-5 (42) zeolite and of 24.8 % over IE-FeZSM-5 (22) while very little (1.1 %) COD removal was achieved over ZSM-5 (22) sample.

Figure 7 displays the catalytic behavior of the catalysts for initial pH of 3.5 which was regulated by addition of H_2SO_4 into the dye solution.

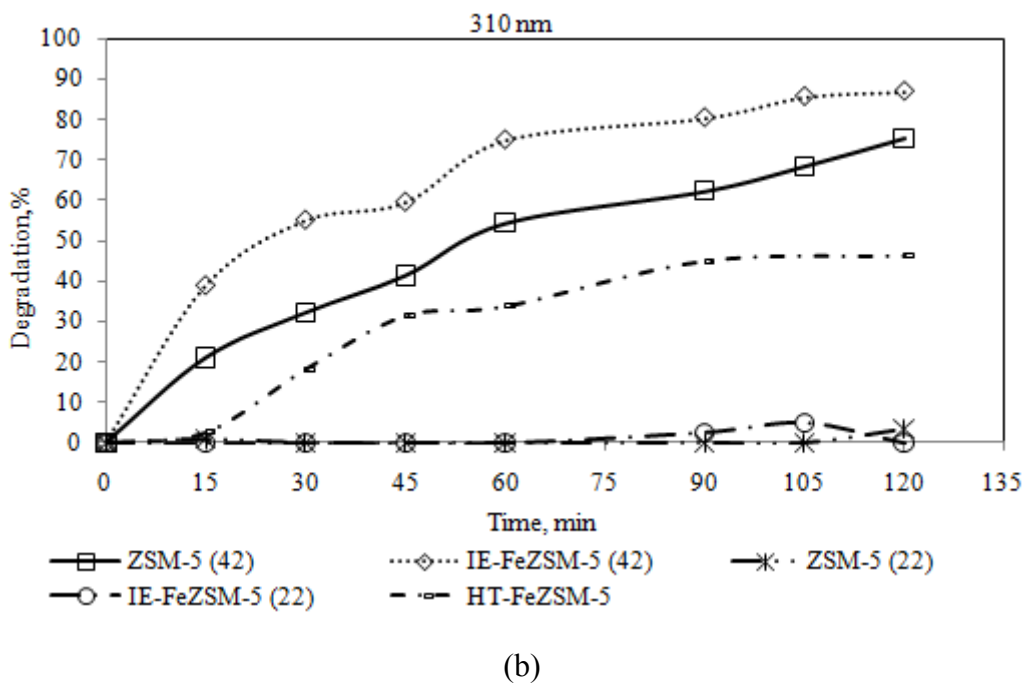
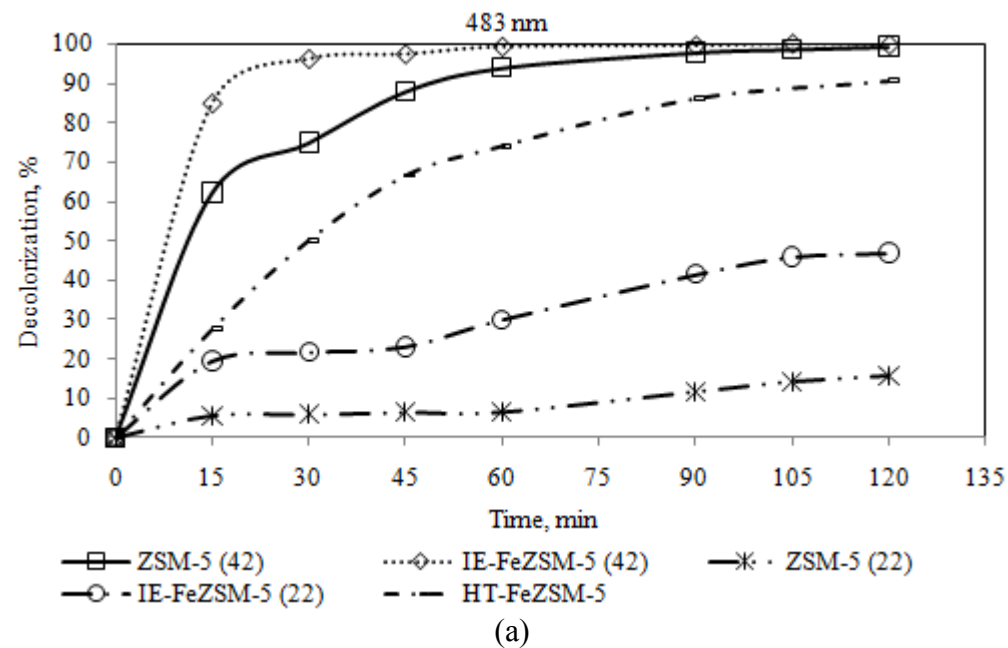
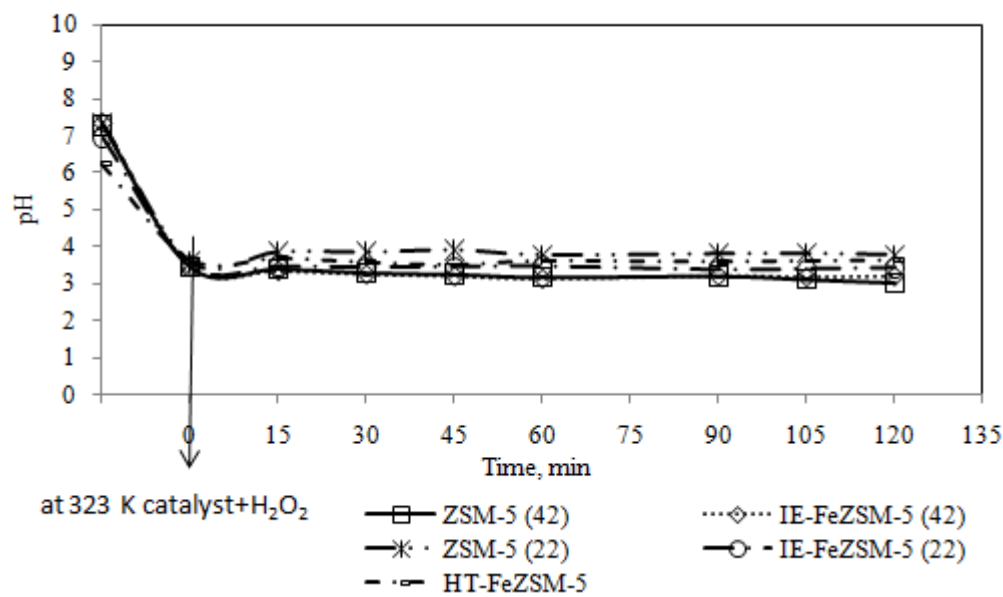
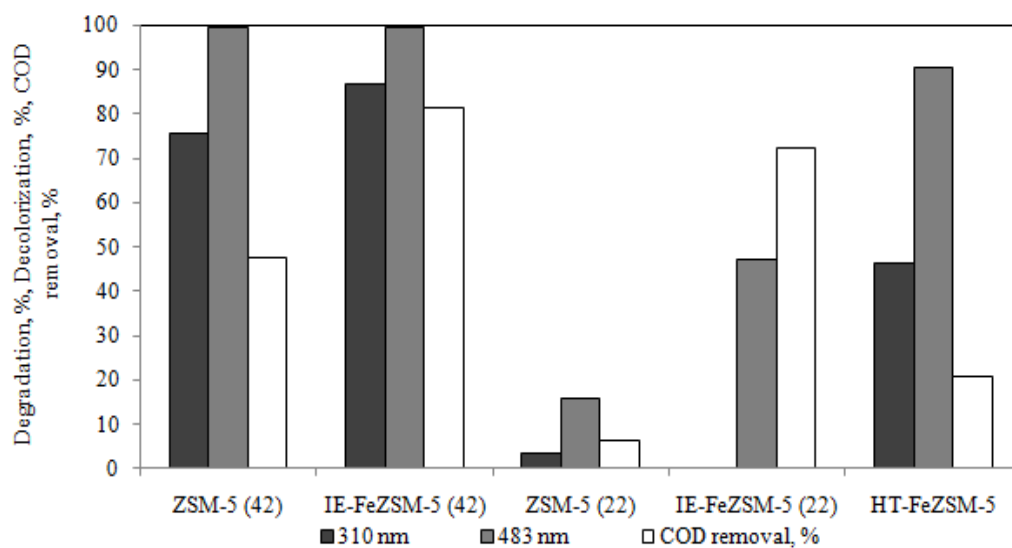


Figure 7. The influence of catalyst type on decomposition of OII as a function of time for initial pH around 3.5.

(a) Decolorization, % (b) Degradation %,



(c)



(d)

Figure 7, continued: (c) pH value, (d) COD removal, %

The change of solution pH from 7 to 3.5 did not affect the ordering of degradation and color removal efficiency. The catalyst prepared by ion exchange, IE-FeZSM-5 (42) was still the most active one. The initial color removal and degradation rates of OII increased significantly with decreasing pH. Low pH accelerated the oxidation (Neamtu et al., 2004). The degradation efficiency increased from 84.0 % to 87.0 % over IE-FeZSM-5 (42) catalyst and from 67.9 % to 75.4 % over ZSM-5 (42) zeolite while decolorization degree remained nearly constant after 2h oxidation. However, over ZSM-5 (22) a degradation degree of 3.3 % and no degradation over IE-FeZSM-5 (22) was observed. Incorporation of iron into the ZSM-5 structure enhanced COD removal in OII oxidation over all ion exchanged zeolites at pH of 3.5. It changed with iron addition from 47.4 % to 81.2 % on ZSM-5 (42) zeolite and from 6.3 % to 72.2 % on ZSM-5 (22) zeolite. However, low pH affected negatively the COD removal in OII oxidation with FeZSM-5 catalyst prepared hydrothermal synthesis (HT-FeZSM-5). COD removal decreased from 64.0 % to 20.7 % by lowering the initial pH of solution.

3.3 Catalyst Leaching Tests

Amount of iron loss from catalyst into the solution was determined by measuring the iron concentration in the solution after a reaction time of 2h with atomic absorption spectrophotometer (Varian 10 plus). Table 2 presents these results for two pH conditions studied.

Table 2. Iron leaching during the CWPO of Orange II after 2h

Catalyst	Iron leached, mg/L at pH=7 / at pH=3.5	Iron loss, % at pH=7 / at pH=3.5
ZSM-5 (42)	-	-
ZSM-5 (22)	-	-
IE-FeZSM-5 (42)	2.6 / 3.8	3.9 / 5.8
IE-FeZSM-5 (22)	2.4 / 3.1	8.9 / 11.8
HT-FeZSM-5	2.2 / 1.6	7.9 / 5.6

No iron leaching was obtained with parent ZSM-5. Leaching of extraframework iron species (ion exchange samples) was much larger than in the framework (HT-FeZSM-5). IE-FeZSM-5 (42) catalyst was the best one from the point of leaching test with the results of 3.9 % loss at a pH of 7 and 5.8 % at a pH of 3.5 among the ion exchanged catalysts. Iron leaching increased with decreasing value of pH with the exception over HT-FeZSM-5 catalyst. This catalyst seems to be stable under the acidic conditions.

The effect of temperature, the amounts of H_2O_2 and catalyst on catalytic wet peroxide oxidation of Orange II were investigated over IE-FeZSM-5 (42) catalyst at pH of 7. Stability of the catalyst and decolorization kinetics were also studied on that catalyst. Stability tests showed that IE-FeZSM-5 (42) has a long-term stability without destroying the zeolite structure during the runs. The obtained results will be presented in the next paper.

4. CONCLUSIONS

Different activities were observed over the catalysts studied. IE-FeZSM-5 (42) gave the best color removal, degradation degree and COD removal. The activity of the catalyst changed depending on the pH. Higher color removal and degradation were observed at low pH. Leaching of iron changed depending on the catalyst prepared. Ion exchanged zeolite gave high leaching at pH=3.5 compared to zeolite prepared by hydrothermal synthesis. Fe leaching for IE-FeZSM-5 (42) catalyst was a bit higher than European Union directives ($< 2 \text{ mg/dm}^3$). ZSM-5 catalyst with lower particulate size and higher surface area showed higher ion exchange capacity and activity.

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