

HIERARCHICAL FeZSM-5 ZEOLITE FOR FENTON OXIDATIVE DEGRADATION OF WATER POLLUTANTS

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ABSTRACT

Fe-exchanged microporous and hierarchical ZSM-5 zeolites were investigated for the application in Fenton oxidative degradation of three water pollutant molecules, methyl violet, salicylic acid and diclofenac sodium. Hierarchical forms of ZSM-5 were prepared via alkaline treatment using NaOH prior to ion exchange. Samples were characterized using low temperature nitrogen adsorption and X ray diffraction; while diffuse reflectance UV-Vis spectroscopy was used to evaluate the nature of the Fe species. The efficiency of wet ion exchange as a procedure for iron incorporation was found to be higher for hierarchical zeolites. In addition, significantly less iron oxide species were found in them, compared to the purely microporous samples. Hierarchical FeZSM-5 samples exhibited superior catalytic activity in Fenton degradation processes; this was especially pronounced at lower initial concentrations of hydrogen peroxide.

Keywords: hierarchical FeZSM-5, ion exchange, Fenton oxidative degradation.

INTRODUCTION

Fenton processes are known to be effective and inexpensive methods for water and wastewater purification from toxic or non-biodegradable organic pollutants. Active oxidative species in Fenton reactions are generated in redox cycles in which Fe ions and hydrogen peroxide take part as reactants [1]. Fenton processes can be homogeneously or heterogeneously catalyzed. In this work, a series of iron exchanged microporous and hierarchical ZSM-5 zeolites were tested as Fenton catalysts. Hierarchical zeolites are a class of zeolitic materials which possess more than one level of porosity, typically micropores and mesopores. Due to the existence of mesopores in the structure, they often exhibit superior catalytic properties when compared to purely microporous zeolites [2]. The goal of this investigation was to evaluate the ion exchange process in hierarchical ZSM-5 zeolites and to probe their catalytic activity in Fenton degradation of water pollutants. Three pollutant molecules were chosen as substrates: methyl violet (MV), a widely used dye, and two pharmaceutically active substances, diclofenac sodium (DFC) and salicylic acid (SA).

EXPERIMENTAL

Hierarchical form of zeolite ZSM-5 (Zeolyst, SiO₂/Al₂O₃ = 50) was obtained via well established alkaline treatment (0.2 M NaOH) [3]. Ammonia forms of parent and modified ZSM-5 samples (ZP and ZM) were subjected to wet ion exchange using Fe(III)oxalate (room temperature, 24h, 3g zeolite per 50 ml). Four different concentrations of iron oxalate were used:

0.002 M, 0.005 M, 0.01 M and 0.02 M. Ion exchanged samples were thoroughly washed with deionized water, dried at 120 °C and calcined in air at 500 °C for 5h. Zeolitic samples were denoted as FeZP-*x* and FeZM-*x*, where P and M stand for parent and modified, respectively, and *x* is the concentration of iron oxalate used. All samples were characterized using N₂ adsorption at 78 K (Micromeritics 2010, pre-treatment at 400 °C, 4 hours), X ray diffraction (Bruker D5005, Cu K α , 2° to 80° (2 θ), 0.02° s⁻¹) and diffuse reflectance UV-Vis spectroscopy (Agilent Cary 5000 UV-Vis-NIR). Fenton degradation was carried out in closed flasks, at room temperature, with constant stirring, in the presence of H₂O₂. Samples were withdrawn from the reaction mixtures at 0.5 h, 1 h, 2 h, 3 h i 4.5 h, liquid phase was separated by centrifugation (Minispin from Eppendorf, 13400 rpm, during 2 minutes), and residual pollutant concentrations were measured using UV-Vis spectroscopy (Shimadzu UV-1650PC).

RESULTS AND DISCUSSION

Analysis of the textural properties of Fe exchanged ZSM-5 zeolites (Table 1) revealed that the samples retained microporous and hierarchical structures of their respective parent zeolites (ZP and ZM). Details on ZP and ZM properties are described elsewhere [4]. Fe content, obtained by chemical analysis, was found to be significantly higher in hierarchical FeZSM-5 zeolites, compared to the purely microporous ones, exchanged under identical experimental conditions. Results presented in Table 1 show that it is necessary to use approximately doubled concentrations of Fe oxalate for microporous ZSM-5 in order to achieve similar Fe content as in hierarchical FeZSM-5. Furthermore, DR UV-Vis spectroscopy (Figure 1) revealed that less Fe oxide species [5] were formed in hierarchical FeZSM-5 samples during the ion exchange procedure, although the total Fe content is always higher, compared to the respective microporous samples. Even when microporous and hierarchical FeZSM-5 samples with similar Fe content (exchanged from different oxalate concentrations) are compared; large Fe oxides are much less favored in hierarchical zeolites. This result can be of importance, since it is considered that isolated Fe ions and small Fe_xO_y clusters are more catalytically active than large oxide species.

Table 1. Fe content and selected textural properties of FeZSM-5 zeolites.

	FeZP- 0.02	FeZM- 0.02	FeZP- 0.01	FeZM- 0.01	FeZP- 0.005	FeZM- 0.005	FeZP- 0.002	FeZM- 0.002
Fe (%) ^a	0.25	0.41	0.22	0.33	0.15	0.21	0.09	0.14
S _{meso} (m ² /g) ^b	92	167	86	161	79	144	73	144
S _{BET} (m ² /g) ^c	430	515	416	505	396	451	374	459

^aICP, ^bt-plot method, ^cBET method

Catalytic activity of hierarchical FeZSM-5 zeolites in Fenton processes was shown to be superior to that of their purely microporous analogues (Figure 2). This result was obtained for all three investigated pollutants, methyl violet, salicylic acid and diclofenac sodium.

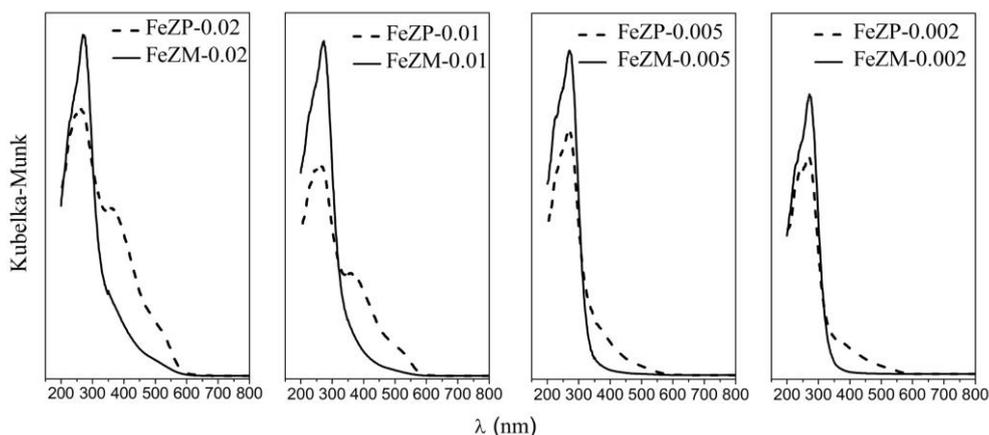


Figure 1. DR UV-Vis spectra of microporous and hierarchical FeZSM-5 zeolites.

The reduction of concentration of any of the substrate molecules was significantly larger for hierarchical samples even if the least active hierarchical and the most active microporous sample were compared, that is, regardless of Fe content. It may be inferred that the main reason behind these results is the facilitated diffusion of the reactants through the zeolitic structure in hierarchical samples, which can have great influence on the reaction rate. However, higher dispersity of Fe species is also likely to influence superior activity of modified FeZSM-5. Finally, the amount of iron present in a sample was found to correlate with catalytic activity of all investigated samples, but only when series of microporous and hierarchical zeolites were considered separately.

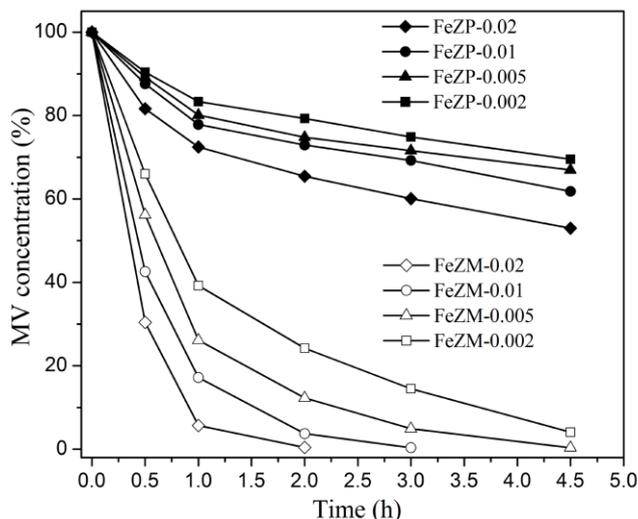


Figure 2. Degradation of methyl violet catalyzed by FeZSM-5 zeolites, $[MV]_0 = 0.0002$ M, $[H_2O_2]_0 = 0.04$ M.

Another important advantage of hierarchical FeZSM-5 samples used in this study was revealed in experiments in which the amount of hydrogen peroxide was varied. It was shown that, at lower initial H_2O_2 concentration, the differences in the catalytic activities between microporous and hierarchical samples were much more pronounced. These results are presented in Figure 3. From a practical and environmental point of view, this is an important finding, since achieving satisfactory degrees of pollutant degradation at low peroxide concentrations is always preferred in Fenton processes.

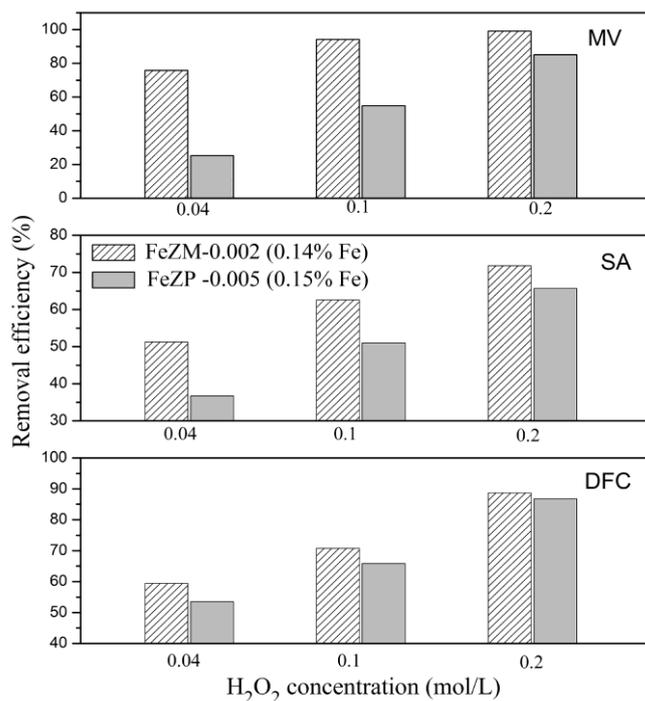


Figure 3. Influence of initial H₂O₂ concentration on the degradation efficiency, [MV]₀ = [SA]₀ = [DFC]₀ = 0.0002 M, t = 2h.

CONCLUSION

Introduction of iron via wet ion exchange in hierarchical ZSM-5 zeolite resulted in higher Fe content and higher degree of dispersity of Fe species, compared to purely microporous FeZSM-5. Catalytic Fenton activity of hierarchical samples was superior to that observed for microporous samples, especially at low initial concentrations of hydrogen peroxide.

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