Cobalt-and copper-modified fly ash nanozeolites for environmental protection systems

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Abstract
In the present study, copper- (Cu-FAZ) and cobalt-modified (Co-FAZ) fly ash zeolites (FAZ) were prepared by an incipient wetness impregnation technique, and the loading of 6 wt. % copper or cobalt in the zeolite Na-X framework was achieved. Cu-FAZ and Co-FAZ were investigated by X-ray diffraction to clarify the state of Cu and Co into the FAZ matrix, while surface studies by nitrogen adsorption/desorption technique were carried out to study the effect of modification on the FAZ surface characteristics. Modified FAZ were investigated as heterogeneous Fenton-type catalysts for oxidative degradation of organic pollutants from waters.
Keywords: Fly ash zeolites, Modified fly ash zeolites, Fenton process, Degradation of organic pollutants

1. Introduction

Recently, Fenton-type catalytic oxidation based on highly reactive hydroxyl radicals released over Fe^{2+}/Fe^{3+}-catalytic centres has widely been studied as an advanced technique for effective degradation of organic pollutants from waters. Hydrogen peroxide is among the most preferable oxidants because it results in oxygen and water as the only end products of its decomposition (Centi et al.). Iron-exchanged zeolites are reported as possible Fenton's reaction catalysts for degradation of dyes (Soon and Hamied). Moreover, coal fly ash zeolites (FAZ) contain iron oxides transferred from the raw ash, which predetermines their catalytic activity. Catalytic efficiency of FAZ can be improved further by modifying them with second metal oxide nanoparticles. The simultaneous presence of Fe^{2+}/Fe^{3+} and $Cu^{2+}/Fe^{2+}/Fe^{3+}$ or $Co^{2+}/Fe^{2+}/Fe^{3+}$-centers in the modified FAZ will stipulate easier formation of oxidative radicals essential for the degradation of organic pollutants (Boycheva et al.). In this study, copper- (Cu-FAZ) and cobalt-modified (Co-FAZ) FAZ were prepared and investigated for their phase composition, surface properties and catalytic activity toward Fenton-based oxidation of methylene blue as model dye pollutant in waters.

2. Experimental

Coal fly ash (FA) was converted into zeolite Na-X by ultrasound assisted double stage fusion-hydrothermal synthesis. Solid mixtures of FA and sodium hydroxide in a weight ratio NaOH/FA=2.0 were fused in nickel crucibles at 550 °C for 1 h. The sintered samples were sonicated in distilled water for 15 min. As a second stage, the reactant liquors were hydrothermally activated at 90°C for 4 h. An incipient wetness impregnation technique was used for the preparation of Cu-FAZ and Co-FAZ. $Cu(NO_3)_2 3H_2O$ and $Co(NO_3)_2 6H_2O$ were dissolved in distilled water in an amount corresponding to 6 wt.% of Cu and Co loading, and were mixed with FAZ materials. The samples were dried at ambient temperature, and the precursor salts were decomposed in air at 500 °C for 2 h. The phase composition of the parent and modified FAZ was studied by X-ray powder diffraction using Brucker D2 Phaser diffractometer with CuKα-radiation. Nitrogen physisorption isotherms were measured at liquid nitrogen temperatures using a volumetric adsorption analyzer Tristar II 3020, Micromeritics. Samples were preliminary degassed at 260 °C for **4** h under helium flow. The catalytic performance of modified FAZ was tested toward methylene blue (MB) as a model contaminant by batch technique. Hydrogen peroxide was used as an oxidant added in over stoichiometic excess to 25 ml solution of MB with initial concentration of 20 mg/l. The oxidation tests were performed at 90 °C, fixed pH=2.0, and at different amount of catalyst. The optical absoption was measured at λ_{max}=665 nm using optical glass cuvettes with 10 mm in length.

3. Results and Discussions

X-ray experimental diffractograms of the parent and modified FAZ are plotted in Fig. 1. The main crystalline component observed is zeolite Na-X, while in addition low intensive reflexes of Co_3O_4 and CuO crystallites are observed on modified FAZ.

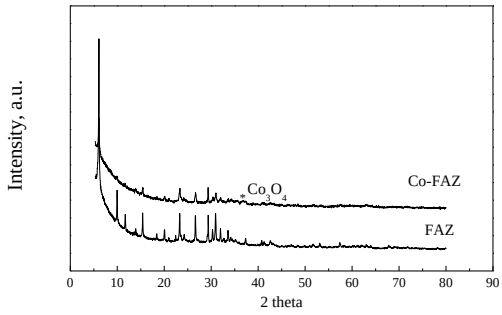

Figure 1. X-ray diffractograms of parent and modified FAZ.

Nitogen adsorption/desoprtion studies reveal a decrease of the specific surface area after the FAZ modification due to the partial pore blocking by metal oxide particles (Table 1).

Table 1. Surface properies of parent and modified FAZ.

Surface properties	**FAZ**	**Cu-FAZ**	**Co-FAZ**
S_{BET}, m^2/g	486	67	213
V_{micro}, cm^3/g	0.133	0.009	0.040
V_{meso}, cm^3/g	0.174	0.071	0.160
d_{meso}, Å	41.79	51.02	47.99
d_{micro}, Å	13.94	12.54	13.05

S_{BET}-specific surface; V_{micro},V_{meso}–volume described by micro and mesopores; d_{meso}, d_{micro}-average micro and mesopore sizes.

The efficiency of the heterogeneous oxidation (R,%) of MB over Cu-FAZ and Co-FAZ was evaluated by the following equation:

$$R= ((C_{MB,0} - C_{MB,\tau})/C_{MB,0})100, \% \quad (1)$$

Where: $C_{MB,0}$ and $C_{MB,\tau}$ are the initial and the current MB concentrations, mg/l.

Kinetic curves of the heterogeneous MB oxidation over the modified FAZ are presented in Fig. 2. The experimental results are described with a good approximation by the pseudo-first order kinetic model, applying the following linearized dynamic reaction equation:

$$-\ln(C_{MB,\tau}/C_{MB,0})=k\tau \quad (2)$$

where: k is the reaction rate constant, min^{-1};τ is the reaction time, min. The amount of modified FAZ has a significant impact on the kinetics of the oxidation process, as with a reduction in their amount the reaction is slowing down.

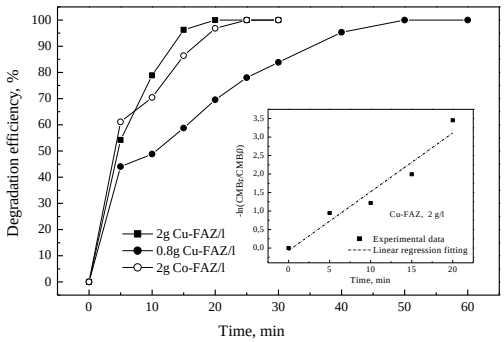

Figure 2. Kinetics of MB degradation over Cu-FAZ and Co-FAZ. Model liner fit in the intra set.

The obtained kinetic parameters and the correlation coefficients are listed in Table 2.

Table 2. Kintetic parameters of MB oxidation over modified FAZ

Sample	**Catalyst amount, g/l**	**Pseudo-first order**		
		k, min^{-1}	**$\tau_{1/2}^*$, min^{-1}**	**R^2**
Cu-FAZ	2.0	0.159	4.36	0.945
Cu-FAZ	0.8	0.069	10.05	0.951
Co-FAZ	2.0	0.213	3.25	0.954

*$\tau_{1/2}$ – the oxidation reaction half-life

4. Conclusions

The obtained results reveal fast oxidation of methylene blue over Cu- and Co-modified fly ash zeolites by Fenton-based process. The experimental kinetic curves are quantified with high accuracy by the pseudo-first order reaction dynamics.

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