Fe-Cu aluminosilicate catalytic materials for oxidation of azo dyes

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Abstract. Fe-Cu aluminosilicate materials were obtained by replacing exchangeable cations of bentonite clay with polymer hydroxocations of iron and copper. The specific surface and porosity characteristics of the synthesized materials were determined using low-temperature nitrogen adsorption. It was established that modifying clay with iron and copper complex compounds and heating at 400 °C and 500 °C led to the formation of microporous materials with a specific surface area of 140-152 m²·g⁻¹. The catalytic properties of Fe-Cu aluminosilicate materials were studied in the oxidative degradation reaction of a diazo dye “direct pure blue” in aqueous solutions using hydrogen peroxide as oxidizing agent. It was shown that the materials were active catalysts for the dye oxidation and increased oxidation efficiency to 78-96% for 360 min at 40 °C. The results of the research allow to conclude that obtained Fe-Cu-aluminosilicate materials can be successfully used in the catalytic treatment of wastewater from organic dyes.

1. Introduction

Currently, environmental protection problems have become especially urgent due to the increasing global pollution of the hydrosphere by harmful waste products from human activities. One of the major sources of environmental pollution is the textile industry, which is characterized by large volumes of consumed water and a complex physico-chemical composition of wastewater. According to the chemical composition, the wastewater of textile enterprises is a multicomponent mixture of various compounds, including acids, salts of heavy metals, dyes of various classes, surfactants, chlorinated organic compounds, etc. [1]. Many of these substances adversely affect the ecology of natural water systems, slowing down the processes of self-purification and having a toxic effect on aquatic organisms [2-4]. Advanced oxidation processes (AOP) are among the most effective methods for the oxidative destruction of organic pollutants [5]. Such processes include Fenton and Fenton-like systems, the high oxidizing ability of which is caused by the generation of intermediate active particles such as OH radicals due to the reaction of H₂O₂ with iron ions [6]. It is economically feasible for industrial water treatment processes to use heterogeneous catalytic systems in which the transition metal compounds attached to a porous supports serve as catalysts. Clay minerals, which have a developed specific surface and functional groups capable of reacting with transition metal compounds, and are also characterized by environmental safety and low cost can be used as porous supports. Therefore, there has been considerable interest in the development of catalysts based on clay minerals [7-13]. Most of the published works are devoted to the synthesis and use of catalysts containing one transition metal. Catalysts containing two or more transition metals are less studied.
The aim of this work was to obtain Fe-Cu aluminosilicate catalysts on the basis of bentonite clay and complexes of iron and copper and to test their catalytic properties in the oxidative degradation of azo dye with aqueous hydrogen peroxide.

2. Materials and methods

2.1. Materials

FeCl₃·6H₂O, AlCl₃·6H₂O, CuCl₂·2H₂O, NaOH, 30% hydrogen peroxide were purchased from Chempack.

2.2. Synthesis of catalytic materials

A bentonite clay of the Mukhortalinsky deposit (Russia, Buryatia) the content of montmorillonite in which was about 90% was used to obtain the Fe-Cu aluminosilicate (Fe-Cu/AS) catalysts. The clay finely dispersed fraction consisted of oxides of the following elements (wt.%): SiO₂ - 65.50; Al₂O₃ - 13.50; Na₂O - 0.16; K₂O - 0.17; MgO - 1.36; CaO - 1.06; ZnO - 0.018; MnO - 0.002; Fe₂O₃ - 1.07; CuO - 0.002; H₂O - 17.16. The synthesis of the catalysts was carried out according to the intercalation method [14]. The intercalating solution I was prepared as follows: to the mixed water solution of iron chloride (0.1 M) and aluminum chloride (0.1 M) with a ratio Fe/Al = 1:10 mole/mole, heated to a temperature of 90 °C, 0.1 M sodium hydroxide solution was poured until a pH of 4.0 was reached with constant stirring. The solution was kept at 90 °C for 10 hours, then for 2 weeks at room temperature to form mixed Fe/Al polyhydroxocomplexes. Intercalating solution II was prepared similarly: to the mixed water solution of copper chloride (0.1 M) and aluminum chloride (0.1 M) with a ratio Cu/Al = 1:10 mole/mole 0.1 M sodium hydroxide solution was poured until a pH of 4.1 to form a mixed Cu/Al-polyhydroxycomplexes. Then, the intercalating solutions were simultaneously introduced dropwise into a 1% aqueous suspension of bentonite clay, which was previously treated with ultrasonic vibrations (3 min, 22 kHz). After 24 hours, the clay-containing solid phase was separated from the liquid phase by centrifugation and washed with distilled water, dried at 20°C, ground to a powder, then calcined for 2 hours at 400 °C (sample 1) and 500 °C (sample 2). Sample 3 was obtained analogously to sample 2, but without preliminary sonication of the clay. The surface area and porous structure characteristics of the materials were determined by nitrogen adsorption at 77 K on the ASAP-2400 Micromeritics unit [15]. The content of iron and copper in the materials was determined by atomic absorption analysis (AAS Solaar M6 spectrometer, Thermo Electron Corporation, UK) after treating with concentrated HCl. The iron content in samples 1 and 2 was 33.8 mg·g⁻¹, copper -1.5 mg·g⁻¹, in sample 3 - 30.7 mg·g⁻¹ and 1.1 mg·g⁻¹, respectively.

2.3. Catalytic tests

The reaction of dye “direct pure blue” with water H₂O₂ was carried out in a reactor equipped with a thermostatic jacket and a magnetic stirrer ([dye] = 1·10⁻⁴ mol·L⁻¹, [H₂O₂] = 7·10⁻³ mol·L⁻¹, catalyst loading 3 g·L⁻¹, pH 4.6, 40 °C). The calculated volumes of dye and H₂O₂ solutions and a certain portion of the catalyst were poured into the reactor. 9 ml of distilled water was poured to 1 ml of the reaction mixture taken from the reactor and centrifuged to remove the catalyst. Then the absorption of the dye solution was measured using an Agilent 8453 UV – Vis spectrophotometer (Agilent Technologies, USA) at 616 nm (accuracy ± 5%). The dye concentration was determined by the calibration graph of the dependence of the optical density on the concentration of the standard dye solution. The dye oxidation efficiency (E) was calculated by the following expression: E (%) = ((C₀ - C)/C₀)·100%, where C₀ is the dye concentration at the beginning of the reaction, C is a current concentration of the dye.

3. Results and discussion

Isotherms of nitrogen adsorption on Fe-Cu/AS catalysts at 77 K are shown in Figure 1. The isotherms had a capillary-condensation hysteresis loop and were of type IV, which was characteristic of
mesoporous solids. A sharp rise in isotherms in the low-pressure region indicated the contribution of type I isotherm inherent in microporous sorbents [15].

Figure 1. Isotherms of low-temperature nitrogen adsorption on Fe-Cu/AS catalysts: 1 - sample 1; 2- sample 2.

The obtained samples of the Fe-Cu/AS catalyst had a mixed porous structure; both mesopores and micropores were characteristic of them. The texture characteristics of bentonite clay and catalysts are shown in table 1.

Table 1. The texture characteristics of the original clay and samples of Fe-Cu/AS catalyst.

|                | S, m²·g⁻¹ᵃ       | Vₚore, cm³·g⁻¹ᵇ   | Dₚore, Åᶜ   | Vₘicropore, cm³·g⁻¹ᵈ |
|----------------|------------------|-------------------|------------|----------------------|
| Bentonite clay | 98               | 0.235             | 96         | <0.001               |
| Sample 1       | 152              | 0.246             | 65         | 0.011                |
| Sample 2       | 147              | 0.186             | 51         | 0.006                |
| Sample 3       | 140              | 0.170             | 48         | 0.003                |

ᵃ S - specific surface area of catalyst, m²·g⁻¹
ᵇ Vₚore - pore volume, cm³·g⁻¹.
ᶜ Dₚore – pore diameter, Å.
ᵈ Vₘicropore – micropore volume, cm³·g⁻¹.

A growth in the surface area and an appearance of micropores were observed for the obtained catalyst samples as compared to bentonite clay, which indicated the intercalation of Fe/Al and Cu/Al polyhydroxocomplexes into the interlayer spaces of montmorillonite particles. It is known [12] that during the heat treatment of metal polyhydroxocomplexes located in the interlayer space of clay minerals they were dehydrated and dehydroxylated to form metal oxide particles acting as columnar supports, preventing the aluminosilicate clay layers from sticking under heating and contributing to the formation of micropores with slit-like morphology. This leads to the formation of a layered columnar structure characteristic of pillared clays [14]. Particles of oxides of transition metals serve as catalytic centers for redox reactions. Pretreatment of bentonite clay with ultrasonic vibrations contributed to better dispersion and separation of clay particles, which facilitated the entry of Fe/Al and Cu/Al polyhydroxocomplexes into their interlayer spaces, ultimately leading to the formation of more micropores and an increase in specific surface area. Sample 1 had the largest specific surface and highest porosity. An increase in the heating temperature to 500 °C led to a decrease in the specific surface and micropore volume.

Catalytic properties of Fe-Cu/AS samples were tested in the oxidation of the dye "direct pure blue" (the formula of which is shown in Figure 2) with H₂O₂ in aqueous solutions. It is widely used for dyeing cellulose, polyamide, cotton and silk fibers, leather, fur, wood and paper [16].
Oxidative degradation of the dye with H2O2 proceeds according to the equation [4]:

\[
C_{34}H_{24}N_6O_6S_4Na_4 + 69H_2O_2 = 34CO_2 + 2(NH_4)_2SO_4 + 2Na_2SO_4 + 2NH_4OH + 68H_2O
\]

During the dye oxidation, the intensity of the absorption band at 616 nm caused by the \( n \rightarrow \pi^* \) transition of electrons of azo groups [17] decreased and the dye solution became discolored due to the destruction of the dye molecule.

The results of kinetic experiments are shown in Figure 3 in the form of the dependence of the relative dye concentration \( \frac{C}{C_0} \) on the reaction time \( t \). A decrease in the dye concentration began immediately after the addition of H2O2 and a catalyst, whereas the rate of non-catalytic oxidation reaction was low. The efficiency of non-catalytic oxidation of the dye was less than 10% for 360 min at 40 °C. The dye oxidation efficiency under the influence of the catalysts was 78-96% under similar experimental conditions (Figure 4). The most active of the catalysts was sample 2, in the synthesis of which was used ultrasonic clay activation and heating was carried out at 500 °C.

The increase in the dye oxidation rate was caused by the catalytic decomposition of H2O2 under its interaction with iron and copper ions that were part of the catalyst with the generation of OH radicals, that had strong oxidizing properties and quickly oxidized the dye molecules as shown by scheme (1) [5, 10, 18]:

\[
\begin{align*}
\text{Fe}^{3+} + H_2O_2 & \rightarrow \text{Fe}^{2+} + HO_2^- + H^+, \\
\text{Fe}^{2+} + H_2O_2 & \rightarrow \text{Fe}^{3+} + OH^- + 'OH, \\
\text{RH} + 'OH & \rightarrow R^- + H_2O.
\end{align*}
\]

where RH is the organic molecule (dye).

In the interaction of H2O2 with Cu2+ ions, along with hydroxyl radicals, intermediate particles \([\text{Cu}^{II}O]\) are formed, which also quickly oxidize organic compounds [19-20], scheme (2):

\[
\begin{align*}
\text{Fe}^{3+} + H_2O_2 & \rightarrow \text{Fe}^{2+} + HO_2^- + H^+, \\
\text{Fe}^{2+} + H_2O_2 & \rightarrow \text{Fe}^{3+} + OH^- + 'OH, \\
\text{RH} + 'OH & \rightarrow R^- + H_2O.
\end{align*}
\]
\[
\begin{align*}
Cu^{2+} + H_2O_2 & \rightarrow Cu^+ + HO_2^- + H^+ , \\
Cu^+ + H_2O_2 & \rightarrow Cu^{2+} + OH^- + 'OH , \\
Cu^{2+} + H_2O_2 & \rightarrow [Cu^{III}O]^2+ + 'OH , \\
\left[ Cu^{III}O \right]^2+ + RH & \rightarrow Cu^+ + R^+ + OH^- .
\end{align*}
\]

4. Conclusion

Fe-Cu/AS materials were synthesized on the basis of bentonite clay and polyhydroxocomplexes of iron, copper and aluminum in two different ways. It was found that these materials were characterized by a high surface area compared to the original clay due to the formation of micropores. Fe-Cu/AS materials showed high catalytic activity in the oxidation of organic dyes and could be effectively used in wastewater treatment of textile enterprises.

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