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Original Research Paper

Hydrothermal synthesis, characterization and sorption properties of Al/Fe oxide–oxyhydroxide composite powders

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ABSTRACT

The Al/Fe oxide–oxyhydroxide composite powders were synthesized by hydrothermal method using metal salt solutions and urea as precursors. The effect of the $[Al^{3+}]$:$[Fe^{3+}]$ ratio and CTAB on the phase composition, textural properties, morphology, and thermal effects of composites was investigated. The β-FeOOH/γ-AlOOH powders prepared by hydrothermal treatment of the solutions with $[Al^{3+}]$:$[Fe^{3+}]$ = 6:1 showed highest surface area among the as-prepared samples. The morphology of the products was preserved after calcination at 700 °C, while the specific surface area significantly increased. The adsorption characteristics of Cr(VI) on the Al/Fe oxide–oxyhydroxide composite powders were investigated. It was shown that the adsorption equilibrium was attained within a short contact time (5–20 min). Adsorption isotherms of all samples were described by the Langmuir and Freundlich equations. Samples calcined at 700 °C showed higher adsorption capacity as compared to uncalcined samples. The α-Fe_2O_3/γ-Al_2O_3 composite powder has a greater sorption capacity as compared to these of pure γ-Al_2O_3 and α-Fe_2O_3.

1. Introduction

In recent years, preparation and investigation of particles with different morphology have attracted considerable interest due to the close relationship between size, shape of particles and performance of the product. Hydrothermal (solvothermal) method is the most widely used for synthesis of particles with various morphologies [1–3].

Aluminum and iron (III) oxides, and their hydrated species are widespread compounds and they are widely applied in different fields. Thus, boehmite (γ-AlOOH) is a promising material as catalyst support and adsorbent, and it can be used in optical and electronic devices, and ceramics. In addition, γ-AlOOH has proven itself as a highly sensitive material for thermoluminescence dosimetry [4]. The dependence of the γ-AlOOH morphology on surfactant addition, pH of the medium [5], nature of the anions [6] and temperature are well understood.

The gas sensing [7–9], magnetic [10], photocatalytic [11] and other properties of iron oxides with various morphologies as well as their use as an anode material for high-performance lithium ion batteries [12] have been studied extensively.

It is known that the "alumina–iron oxide" system exhibits catalytic properties, for example, in the reactions of oxidation and decomposition of various organic contaminants and dyes [13], Fischer–Tropsch process (hydrocarbon synthesis from CO and H_2O) [14,15] and hydrogen peroxide decomposition [16]. Furthermore, this mixed oxide system is also used as a catalyst for carbon nanotubes preparation [17]. Adsorption activity is an important characteristic of systems based on aluminum and iron oxides and their hydrated species. Thus, Chubar et al. [18] have prepared mixed hydrous oxides $ZrO_2{\cdot}xH_2O$, $Fe_2O_3{\cdot}Al_2O_3{\cdot}xH_2O$ and $Fe_2O_3{\cdot}2Al_2O_3{\cdot}xH_2O$ by sol–gel and hydrothermal methods and examined the effects of various factors on the sorption kinetics of phosphate ions. Mahapatra et al. [19] have prepared composite oxide with the molar ratio Al:Fe (1:1) by hydrothermal method and conducted the study of sorption of Congo red on uncalcined and calcined at 500 and 1000 °C samples. It has been shown that γ-Al_2O_3 obtained at 500 °C is a very good adsorbent for the 100% removal of Congo red.

It is known that compounds of hexavalent chromium (Cr(VI)) are life-threatening even at low concentrations because of the ability to penetrate through the cell membrane and react with the

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intracellular material [20]. Furthermore, Cr(VI) can induce cutaneous allergy and has a strong carcinogenic effect [21]. Respiratory problems, hemolysis, acute renal failure, weakened immune system, alteration of genetic material, lung cancer and pulmonary fibrosis are other toxic effects of chromium [22].

There are a number of works devoted to Cr(VI) sorption on the surface of aluminum and iron oxyhydroxides [21,23,24]. Nevertheless, there are a limited number of studies dealing with hydrothermal synthesis and properties of the mixed oxides of aluminum and iron, in which the functional characteristics of the synthesis products are mainly investigated, but the study of morphology is omitted.

In this paper, the effect of the $[Al^{3+}]$:$[Fe^{3+}]$ ratio and CTAB on the phase composition, textural characteristics, morphology, thermal effects, and Cr(VI) adsorption properties of the products of hydrothermal synthesis was investigated.

2. Experimental

2.1. Sample preparation

The procedure employed for preparing Al/Fe oxide–oxyhydroxide composite powders is described as follows. Firstly, $AlCl_3{\cdot}6H_2O$ (95.0–101.0%, Panreac), $FeCl_3{\cdot}6H_2O$ (97.0–102.0%, Panreac) with certain molar ratio (Table 1) and stoichiometric amount of urea (98.5%, Panreac) were dissolved in 60 ml of distilled water under magnetic stirring.

Subsequently, CTAB (99.0%, Acros) was added to B1–B5 solutions in the ratio of [CTAB]:[Al^{3+}, Fe^{3+}] = 1:6. The concentration of metal ions and pH value of the solutions were varied in the ranges of 0.16 ± 0.03 mol/L and 2.8 ± 0.5, respectively. The obtained solutions were transferred into steel autoclaves with platinum crucibles and treated at 160 °C for 24 h. After the reaction finish, the autoclave was naturally cooled down to room temperature. The solid products were collected by centrifugation (Ekros PE-6910 centrifuge, 3000 rpm, 30 min), washed with distilled water and dried at 50 °C in a ShS-0.25-45 drying chamber. As-prepared products were further calcined at 700 °C for 1 h with heating rate of 2 °C/min.

2.2. Adsorption experiments

Chromium solutions were prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$, 99.5%, Panreac) in double distilled water. Kinetic adsorption experiments were carried out as follows. 10 mL of $K_2Cr_2O_7$ solution (5 mg/L of Cr(VI)) was added to 20 mg of the adsorbent and the resulting suspensions were stirred at room temperature on a magnetic stirrer for 5–60 min. The adsorption isotherms of Cr(VI) ions on the Al/Fe oxide–oxyhydroxide composite powders were studied by the sample (20 mg) dispersion in 10.0 mL solutions containing the initial concentrations of Cr(VI) ions ranging from 2.5 to 15.0 mg/L. The resulting suspensions were stirred for 20 min. The pH values of the initial Cr(VI) solutions were 6.7 ± 0.2. After experiments, the suspensions were filtered through membrane filters with a 0.2 μm pore size. Cr(VI) concentration in the filtrate was determined by the 1,5-diphenylcarbazide method [25]. The NaF solution was used to mask the Fe^{3+} ions, because it binds Fe^{3+} into colorless and stable $[FeF_4]^-$ complex.

Table 1
Solutions used for carrying out the hydrothermal synthesis.

Composition of the starting mixture	Sample designation	$[Al^{3+}]$:$[Fe^{3+}]$ ratio
Aqueous solutions of $AlCl_3$, $FeCl_3$ and urea	A1	1:0
	A2	6:1
	A3	1:1
	A4	1:6
	A5	0:1
Aqueous solutions of $AlCl_3$, $FeCl_3$, urea and CTAB	B1	1:0
	B2	6:1
	B3	1:1
	B4	1:6
	B5	0:1

2.3. Characterization

XRD patterns of the samples were collected using a DRON-3 M diffractometer with Co K_α radiation tube (λ = 0.178892 nm). The reflex indexation, as well as the unit cells parameters calculation, were carried out using the PDWin 4.0 software complex. The particle morphology and size were investigated by electron microscopy using VEGA3 TESCAN scanning electron microscope (SEM) and Philips EM-420 transmission electron microscope (TEM) at the accelerating voltage of 100 kV. The high-resolution TEM (HRTEM) micrographs were recorded with a JEOL-2100F electron microscope at the accelerating voltage of 200 kV. Thermal analysis of the samples was performed on a NETZSCH STA 429 CD instrument. The heating was carried out with the rate of 20 °C/min in the temperature range from 40 to 1200 °C. The decomposition products were analyzed using a NETZSCH QMS 403 C quadrupole mass spectrometer. Nitrogen adsorption–desorption measurements were carried out at 77 K using Quantachrome Nova 1200e instrument. Chromium concentration in solutions was determined using a Shimadzu UV-1700 spectrophotometer at λ = 540 nm by the 1,5-diphenylcarbazide method [25]. Zeta potential values of suspensions were measured using a Malvern Zetasizer Nano ZS instrument.

3. Results and discussions

3.1. Characterization

3.1.1. XRD patterns

Fig. 1 represents the XRD patterns of the samples prepared by hydrothermal method without CTAB addition. As a result of hydrothermal treatment of $AlCl_3$–urea solution (A1), boehmite phase (γ-AlOOH, JCPDS No. 21-1307) was formed (Fig. 1, curve 1). The reflections attributed to γ-AlOOH are presented in the A2

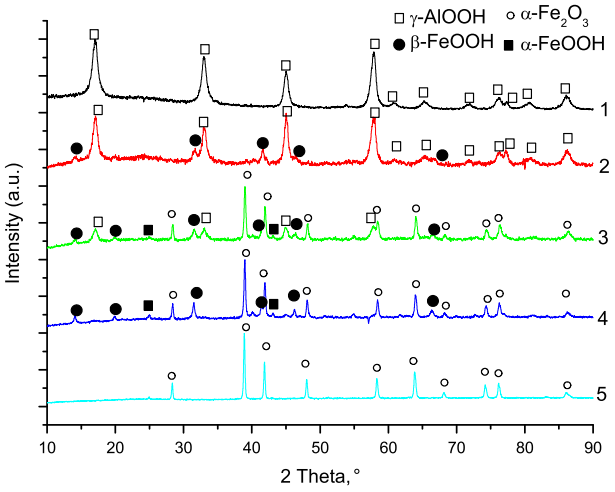

Fig. 1. XRD patterns of the as-prepared products: 1 – A1; 2 – A2; 3 – A3; 4 – A4; 5 – A5.