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Titania-coated nanosilica–cobalt ferrite composites: Structure and photocatalytic activity

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ABSTRACT

In this study, a set of $CoFe_2O_4/SiO_2/TiO_2$ nanocomposites was synthesized. The total concentration of metals (Co + Fe) was varied from 3 to 9 mmol with respect to 1 g of SiO_2. Titania was formed in two concentrations — 2 and 4 mmol/g. The structure of the samples was analyzed by application of XRD, UV–vis spectroscopy, magnetometry, SEM, low-temperature nitrogen adsorption–desorption and Mössbauer spectroscopy. Photocatalytic degradation of an organic model compound – carbamazepine (CBZ) – was studied in the presence of the nanocomposites under ultraviolet irradiation ($\lambda = 254$ nm) in a batch reactor. Two types of media (distilled and tap water) were used. The X-ray diffraction patterns demonstrate the formation of $CoFe_2O_4$ and TiO_2 (anatase). The studied materials reveal a better activity than commercial sample of P25 (Evonik) during degradation of carbamazepine (CBZ). It has been found that the type of water medium affects the CBZ decomposition differently: there is residual CBZ observed in distilled water in 60 min of treatment. Contrastingly, in tap water the total decomposition of CBZ took place. This may be due to the occurrence of Fe^{3+} ions which stimulate the formation of active sites of chlorine dissolved in tap water.

1. Introduction

Cobalt ferrite and its based composites are of a great interest in various areas. They are used as adsorbents [1–3], catalysts [4,5], UV and visible light induced photocatalysts [6–13], anode materials [14], support for magnetic fluids, digital recorders and storage media due to their high room-temperature coercivity and intermediate magnetization [15,16]. Besides, there are lots of directions for biomedical applications, too [17–19]. $CoFe_2O_4$ is mechanically and chemically stable ferrimagnetic material [20], which cubic structure is related to the inverse spinel discovered by Bragg. Its magnetic properties depend both on particle size and shape, and ion distribution inside the structure [21–28]. Nowadays there are many ways of obtaining of cobalt ferrite and its composite materials — hydrothermal [14] and microwave–hydrothermal synthesis [20], sol–gel [29], hydrolysis using polyols (PEG and DEG) [27], co-precipitation from aqueous [30] and organic media [1,2], combustion using glycine [4], mechanical milling [31] and combinations of these techniques [5,32].

In this article we will concentrate on structural and photocatalytic properties of cobalt ferrite based nanocomposites. As it was reported previously, $CoFe_2O_4$-based photocatalysts belong to a variety of magnetically operated ones, which possess the very important advantage — they can be easily removed from reaction media by application of external magnetic field. This feature extends the limits of photocatalysts usage. Titania powder dispersed in water medium can be removed by its long term precipitation, centrifugal separation etc. It takes lots of time and/or energy wasting combined with usage of equipment sophisticated for applications under industrial conditions. Thus, the recovering procedure of nanosized objects from suspensions is of a great difficulty. It is worthy of note, that $CoFe_2O_4$ phase crystallizes at similar temperature as TiO_2 [6]. The second fact is caused by efficiency both of iron and cobalt oxides in provoking the degradation of water pollutants. $CoFe_2O_4$ itself can serve as quite a good photocatalyst for water treatment [33] because it is used to

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being considered as a semiconductor — the band gap value calculated by Jonker [34] is $E_g = 0.55$ eV, but it has been reported in [35] about $E_g = 1.42$ eV. Nowadays there's been a lot of scientific evidence that cobalt ions migrate from the octahedral to tetrahedral positions — not totally, but partially [36–39]. It would be a mistake to think that cobalt ferrite forms direct spinel structure — it is a typical inverse spinel-like ferrimagnetic.

As stated in [6,12,40–42], there is a general weakening of TiO_2 activity observed by direct layering of TiO_2 onto the surface of magnetic material. For instance, combining TiO_2 with ferromagnetic Fe_3O_4 or $CoFe_2O_4$ results in decreased activity of these composites vs. pure TiO_2 or commercial product P25. Such results, however, could conflict with the conclusions given in [10]. Surface charge can essentially control photocatalytic activity, and TiO_2-$CoFe_2O_4$ materials are more effective against atrazine degradation in comparison to TiO_2.

Nanosilica is chosen as intermediate to prevent the inactivating effect of magnetic matrix upon photoactivity of titania [40–42]. The second reason to use fumed SiO_2 stems from the fact that this stuff acts as a stabilizer of nanopatterned materials [43,44], which results in increase of specific surface area. This enhances the availability of surface active sites due to the rising degree of fineness that performs an interaction with ultraviolet or visible light. Other important functions of nanosilica in the "magnetic material@nanosilica@titania" systems – saving purity of TiO_2 phase [45], magnetic core stabilization [46] – are described in details.

Although TiO_2 is one of the most studied semiconductors used in various combinations [47–49], it was chosen to form novel composites described in this paper.

In our study we synthesized a set of bifunctional nanomaterials samples – $CoFe_2O_4$-based TiO_2 deposited onto fumed SiO_2 – and investigated their structural and photocatalytic properties at different concentrations of cobalt ferrite and titania.

2. Experimental

The synthesis of nanomaterials consisted of two stages and did not contradict to the logic of techniques described by other authors previously:

(i) obtaining of $CoFe_2O_4/SiO_2$ nanocomposites,
(ii) TiO_2 deposition onto silica-ferrite surface.

2.1. Materials

To synthesize the nanocomposites iron(III) acetylacetonate Fe(acac)$_3$ (Sigma Aldrich, 99.95%), cobalt(II) chloride $CoCl_2·6H_2O$ (Khimlaborreaktiv, p.a.) and fumed silica SiO_2 A-380 (produced at pilot plant at Chuiko Institute of Surface Chemistry, Kalush, Ukraine) were used. Titanium(IV) di-isopropoxide-bis-acetylacetonate Ti(i-PrO)$_2$(acac)$_2$ as a precursor of TiO_2 was exploited (Sigma Aldrich, 75 wt.% in isopropanol, IPS).

2.2. Preparation of $CoFe_2O_4/SiO_2$ nanocomposites

Cobalt ferrite was obtained at fumed nanosilica surface via liquid-phase synthesis. Fe(acac)$_3$ and $CoCl_2·6H_2O$ were dissolved in IPS. The joint solution was heated up and brought to boil to intensify dissolving of the precursors.

A-380 was introduced into the solution. Obtained dispersions were homogenized, IPS was evaporated, and then residue was dried at 85 °C. The dried products were comminuted and put into a melting pot. The samples were calcined at 600 °C in a muffle furnace. As a result, all the annealed samples turn black. The total concentrations of both metals (Co + Fe) comprised 3, 6 and 9 mmol/g of SiO_2 and correspond to the samples labeled as FeCo-3, FeCo-6 and FeCo-9 respectively.

The amounts of the used precursors and the symbols of the obtained samples are given in the Table 1. As a reference, pure cobalt ferrite ($CoFe_2O_4$) was synthesized under the same conditions to compare structural changes after combination with nanosilica.

Table 1
Amounts of the precursors for $CoFe_2O_4/SiO_2$ synthesis.

Sample	Components, g			Isopropanol
	Fe(acac)$_3$	$CoCl_2·6H_2O$	SiO_2	
FeCo-3	2.82	1.10	4.00	100
FeCo-6	5.64	2.19	4.01	100
FeCo-9	8.47	3.27	4.02	100
FeCo (reference)	2.83	1.09	–	20

2.3. Preparation of $CoFe_2O_4/SiO_2/TiO_2$ nanocomposites

The procedure of $CoFe_2O_4/SiO_2/TiO_2$ synthesis included sorption of Ti(i-PrO)$_2$(acac)$_2$ onto $CoFe_2O_4/SiO_2$ composites and its further hydrolysis.

Ti(i-PrO)$_2$(acac)$_2$ was adsorbed onto the cobalt ferrites samples. Before the adsorption, oxide samples were dried at 110 °C for 1 h, and then a solution of Ti(i-PrO)$_2$(acac)$_2$ in IPS was added and stirred. The suspension was dried at room temperature for 24 h and then at 80 °C for 3 h. After the samples had been dried, they were calcined at 600 °C in muffle furnace to form anatase.

Titanium precursor to $CoFe_2O_4/SiO_2$ weight ratio were kept at 1:1 to result $C_{TiO2} = 2$ mmol/g. After preparation, the samples were halved and TiO_2 was introduced to one half of each sample again at the same ratio. As a result, we have obtained $CoFe_2O_4/SiO_2/TiO_2$ nanocomposites in two concentrations of titania — 2 (labeled as FeCo-3-Ti1, FeCo-6-Ti1 and FeCo-9-Ti1, Table 2) and 4 (labeled as FeCo-3-Ti2, FeCo-6-Ti2 and FeCo-9-Ti2, Table 3) mmol/g. Two synthesized SiO_2-free $CoFe_2O_4/TiO_2$ samples (FeCo-Ti1 and FeCo-Ti2) were involved for studying phase composition and the presence of tetrahedral/octahedral surrounding of Co^{2+}.

Table 2
Synthesis of $CoFe_2O_4/SiO_2/TiO_2$ nanocomposites at $C_{TiO2} = 2$ mmol/g.

Sample	m ($CoFe_2O_4/SiO_2$), g	m (Ti(i-PrO)$_2$(acac)$_2$), g	C (TiO_2), mmol/g
FeCo-3-Ti1	1	1	2
FeCo-6-Ti1	1	0.99	2
FeCo-9-Ti1	1.7	1.7	2

Table 3
Synthesis of $CoFe_2O_4/SiO_2/TiO_2$ nanocomposites at $C_{TiO2} = 4$ mmol/g.

Sample	m (FeCo-n-Ti1), g $n = 3, 6, 9$	m (Ti(i-PrO)$_2$(acac)$_2$), g	C (TiO_2), mmol/g
FeCo-3-Ti2	0.42	0.42	4
FeCo-6-Ti2	0.42	0.42	4
FeCo-9-Ti2	0.52	0.52	4