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XPS Study of the Surface Composition of a Catalytic System: Iron Promoted by Potassium and Aluminum Oxides

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Abstract—The surface composition of a model catalyst for ammonia synthesis based on iron promoted with aluminum and potassium oxides was investigated by X-ray photoelectron spectroscopy. The surface was studied in oxidized, passivated, and reduced states. The redistribution of components on the surface is studied in the course of reduction in hydrogen and overheating at 700°C. It is shown that a 4–6-mn thick surface layer is enriched with promoters (K and Al) and impurities (Si), while the concentration of iron is low. Promotion by potassium and aluminum oxides makes the catalyst more resistant to overheating.

INTRODUCTION

Aluminum and potassium oxides are usual promoters of iron-based catalysts for ammonia synthesis [1]. Earlier, we studied the composition of the surface and the state of elements in model iron–potassium oxide [2] and iron–alumina [3] systems. It was shown that potassium (at an atomic potassium : oxygen ratio of 1 : 1) after reduction of samples by hydrogen is mainly accumulated on the iron surface, but alumina is distributed in the bulk and on the surface to form compounds with FeO. In addition, the surface composition changes from one sample to another over a wide range of concentrations. In this work, we continued our earlier studies and analyzed the composition of surface and near-surface layers of a model catalytic system based on iron promoted by aluminum and potassium oxides by XPS. The chemical composition and the preparation procedure of this system are close to those of the ammonia synthesis catalyst and model catalytic systems investigated in [1, 2].

A strong influence of promoters on each other is observed in doubly promoted model systems based on iron. The influence of potassium oxide on the size of α-iron crystallites was investigated by X-ray diffraction in doubly promoted systems containing 0–1.54 wt % K_2O and a constant concentration of Al_2O_3 (2.5 wt %) [4]. In the samples with a K_2O concentration higher than 0.58 wt % reduced at 500°C, a considerable growth of crystallite size was observed. This observation agrees with the fact that the surface area of the reduced catalyst containing more than 0.58 wt % K_2O decreases at a high reduction temperature [5]. The reason for crystallite growth was found by analyzing oxidized samples. Excess K_2O removes Al_2O_3 from magnetite and prevents a solid solution from forming [6]. Thus, K_2O affects the size of α-iron crystallites formed during the reduction of the doubly promoted catalyst [4].

Analysis of the surface of a reduced doubly promoted sample based on iron (0.85 wt % Al_2O_3 and 0.27 wt % K_2O) by Auger spectroscopy and selective chemisorption was previously carried out [7]. The concentration of Al_2O_3 on the surface measured by Auger spectroscopy is much lower than the value obtained from adsorption data. It was found that potassium and oxygen ions shield aluminum ions on the surface and the quantitative analysis of the surface by Auger spectroscopy underestimates the quantity of aluminum ions and the Al_2O_3 concentration.

Ammonia synthesis from nitrogen and hydrogen takes place on the surface of a promoted iron melt catalyst. Most likely, only catalyst components located in the near-surface layer of several monolayers directly affect the process. Therefore, an XPS study of the surface may provide interesting results because this method gives the most important information about the near-surface layers of solid-phase systems [8]. The investigation of the surface of samples in oxidized, passivated, and reduced states provides information on the redistribution of components in near-surface layers during reduction by hydrogen. In industrial plants, the catalyst for ammonia synthesis is subjected to temperatures that are much higher than working temperatures. Therefore, data on a change in the surface composition during catalyst overheating are important from scientific and practical points of view. The XPS study of the surface of catalytic systems treated at high temperatures in reducing media provided information on the surface composition and the charge state of elements on activated catalyst surface. It is necessary to take into account that the treatment of samples and further analysis of their composition by XPS were carried out in a spectrometer cell out of contact with an atmosphere. This makes the data more reliable.

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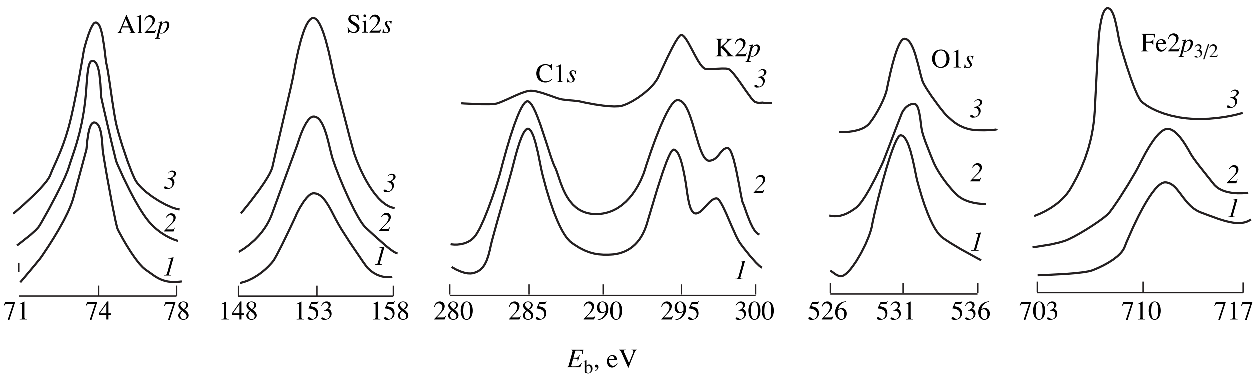

Fig. 1. XPS spectra of Al2*p*, Si2*s*, K2*p*, O1*s*, and Fe2$p_{3/2}$ obtained with (*1*) oxidized, (*2*) passivated, and (*3*) reduced samples.

In this work, the XPS data on the surface and the near-surface layers of the model catalytic system consisting of iron promoted with aluminum and potassium oxides are presented.

EXPERIMENTAL

The samples for the analysis were prepared by the oxidative melting of carbonyl iron with Al_2O_3 and K_2CO_3 added. According to the data reported in [9], the catalytic system had the following chemical composition (wt %): Fe_2O_3 57.21, FeO 39.8, K_2O 0.76, Al_2O_3 2.23. The samples were prepared as follows. Several grains of melt prepared using the method described above (the grain size was 4–7 mm) were ground, then ~1 g of the sample consisting of particles with a size of 0.5–1 mm was additionally ground in an agate mortar. The final particle size was 5–20 μm. A thin layer of powder was deposited on a flat surface of a sample holder, and 1–2 drops of alcohol were added onto the sample. After the alcohol evaporated, the powder was fixed on the holder surface by adhesion. The weight of samples was 30–50 mg. The sample thus prepared for analyses contained $>10^5$ particles. These particles originated from different melt grains and, therefore, characterized a certain average chemical composition of the melt of model catalytic system. Using this method, we prepared three oxidized samples for analyses.

Minaev and co-workers [9] provided us with passivated samples tested for catalytic activity in ammonia synthesis in a laboratory high-pressure setup passivated with nitrogen containing 0.2% oxygen after catalytic tests [10]. After determining the surface composition of the passivated samples by XPS, the samples were reduced in the spectrometer cell. Reduction was carried out in an H_2 flow at 10^5 Pa, a space velocity of 10000 h^{-1}, and at a stepwise increase in temperature from 20 to 550°C for 3 h. The regime of sample reduction was close to that proposed in [9]. As it was shown, this regime leads to the reduction and activation of passivated samples if the catalyst samples are small (0.6–0.8 g) with a grain size smaller than 0.5 mm. Reduced samples were evacuated and placed into the cell for analysis without a contact with an atmosphere. Surface analysis was carried out in a vacuum of 10^{-7}–10^{-8} Pa by XPS method. The overheating of samples to 700°C was carried out in a special spectrometer cell in a hydrogen flow for 2 h. Then, the samples were evacuated and placed into the spectrometer chamber without a contact with atmosphere.

XPS spectra of the samples were recorded using an Escalab-5 spectrometer. For the quantitative analysis of the surface, Al$K_{\alpha_{1,2}}$-radiation ($h\nu$ = 1486.6 eV) was used. To determine the valence state of elements, Mg$K_{\alpha_{1,2}}$-radiation ($h\nu$ = 1253.6 eV) was applied. The elements on the surface were identified using spectra (0–1200 eV) recorded using by high-sensitivity scans. The spectrometer was calibrated using $4f_{7/2}$-electron lines of Au (84.0 eV) and $2p_{3/2}$-electron lines of Cu (932.6 eV). Sample did not acquire a charge during analysis. The quantitative analysis of the surface composition was carried out using the method described in [11]. The degree of sample reduction was determined using the program of spectrum simulation using the method described in [8] and by calculating the difference spectrum [12]. The results of experiments described in [13, 14] were also used.

Ion sputtering for the analysis of near-surface layers was performed by surface bombardment with Ar^+ ions with energies ranging from 0.5 to 10 keV. The maximal beam current was 200 μA, the diameter of the ion beam was 5–10 nm.

RESULTS AND DISCUSSION

Analysis of the samples in the initial oxidized state showed that, in addition to the main components (iron, alumina, and potassium oxide), silicon, oxygen, and carbon compounds are always present in a certain amount on the surface. They come with the material from which samples are prepared or admixed during melting adsorption in the contact with an atmosphere. Figure 1 presents the XPS spectra of lines Si2*p*, Al2*p*, C1*s*, K2*p*, O1*s*, and Fe2*p* obtained for the samples in oxidized, passivated, and reduced states.

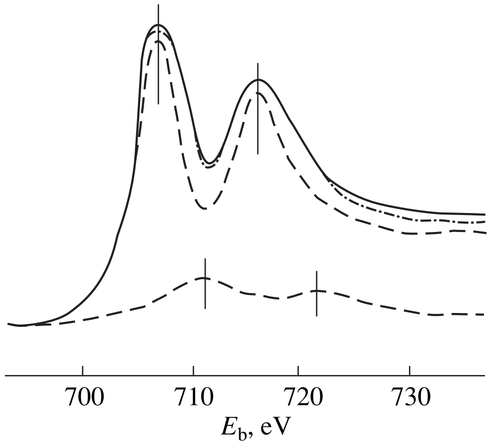

Fig. 2. XPS spectra of Fe2$p_{2/3}$ of the reduced sample: the solid line corresponds to the experimental spectrum, the dashed line is obtained by expanding the experimental spectrum into component lines, and the dash-and-dot line is the sum of the two dashed lines.

The shape and position of the Fe2$p_{3/2}$ line shows that iron on the surface of oxidized samples exists as Fe^{2+} and Fe^{3+}. The spectrum of the Fe2$p_{3/2}$ line is very broadened; therefore, the presence of nonstoichiometric iron oxides is not excluded. Using the shape and position of the K2p line ($E_b = 294.7 \pm 0.1$ eV), it is impossible to determine unambiguously the type of potassium compound, because the sensitivity of the K2p line to the nature of compounds is low [15]. A value of $E_b = 74 \pm 0.1$ eV was obtained for 2p electrons of aluminum. This value is typical of Al_2O_3 [16], but this range of binding energy is also typical of aluminum oxide included in minerals [17]. Silicon is likely present as SiO_2 ($E_b = 153.2 \pm 0.1$ eV).

Analysis of the shape and position of lines in the XPS spectra of elements in passivated samples showed that, in addition to Fe^{2+} and Fe^{3+}, there is also metallic iron in the analyzed layer (~5 nm). The value of binding energy and the shape of K2p, Al2p, and Si2s lines did not change after passivation.

Relative atomic concentrations of elements on the surface of the model Fe–K–Al–O system according to XPS data

Sample state	Relative concentration of elements, at. %				
	Fe	K	Al	Si	O
Oxidized sample	11.0	11.1	5.5	2.5	67.9
Passivated sample	11.4	4.5	13.0	1.0	69.0
Reduced sample	17.4	7.6	23.4	2.8	48.8
Sample reduced and overheated at 700°C for 2 h in H_2	16.3	2.7	28.4	2.2	50.4
Chemical composition in the bulk	41.9	0.5	1.5	–	56.1

The reduction of samples in hydrogen led to about 95% reduction of iron to metal in the layer under analysis. The rest of the iron probably exists in the form of oxide bound with aluminum oxide [3]. Figure 2 presents the result of expanding the XPS line Fe2$p_{3/2}$ obtained for this sample. The binding energy and the shape of K2p, Al2p, and Si2s lines did not change after reduction.

Figure 1 shows that the XPS spectrum of O1s line obtained for oxidized, passivated, and reduced samples is very broad and cannot be expanded into lines corresponding to oxide states of iron, potassium, aluminum, and silicon, as well as to adsorbed states of oxygen-containing compounds like H_2O, CO, CO_2, or others.

Quantitative analysis of the surface composition showed only small deviation of the relative atomic concentration of elements on the surface from one sample to another. The table presents the data averaged for three samples, as well as the chemical composition of the bulk. Carbon present on the surface of initial oxidized and passivated samples in the form of adsorbed hydrocarbons was considered as a surface contaminant and was not taken into account in the quantitative analysis of surface composition. Silicon dioxide found on the surface of the samples is also an impurity and in pour opinion should not affect considerably the results of the surface analysis because its relative concentration is rather low.

First, it is necessary to note that the bulk and surface compositions differ from each other. The surface is enriched with promoters and impurities. This leads to the reduction of iron concentration in the near-surface layer. According to the chemical composition, the K/Fe and Al/Fe ratios are of an order of 10^{-2}, whereas the concentration of potassium on the oxidized sample surface almost coincides with the iron concentration, and aluminum concentration is ~50% of iron concentration. Stoichiometric calculations for oxidized (and passivated) samples were not carried out because of the high concentration of adsorbed oxygen compounds on the surface.

The sample reduction carried out before the catalytic tests and further passivation led to the redistribution of components in the near-surface layer. That is, the aluminum concentration on the surface increased by more than a factor of two. This resulted in a decrease in the potassium concentration. Most likely, this is a consequence of an increase in the sample surface area during reduction by hydrogen [9]. This led to the redistribution of potassium compounds and, therefore, to a decrease in its concentration in the analyzed layer.

It can be see from the table that the reduction of passivated sample by hydrogen led to the additional redistribution of components in the near-surface layer. The concentration of iron and promoters in the layer increases due to the desorption of oxygen-containing compounds from the surface. However, the ratios of

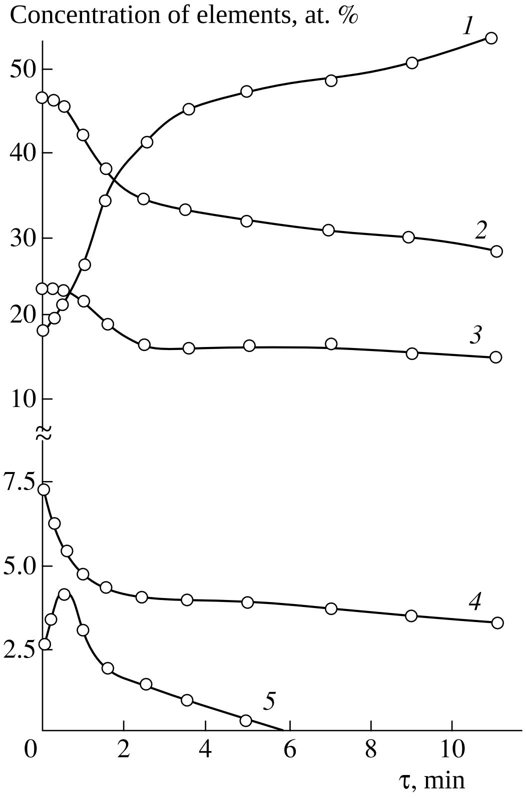

Fig. 3. The composition of the surface of the reduced sample as a function of the duration of etching with Ar^+ ions: (*1*) Fe, (*2*) O, (*3*) Al, (*4*) K, and (*5*) Si.

iron, potassium, and aluminum concentrations on the surface remain the same as for passivated samples.

It has been found earlier that the potassium-to-oxygen ratio on the surface of reduced iron is close to 1 : 1 [2]. The balance calculation of oxygen using data on elemental concentrations on the surface of the reduced sample gives the following value of the surface oxygen concentration (in at. %):

$$7.6(K_2O) + 23.4 \times 1.5(Al_2O_3) + 2.8 \times 2(SiO_2) = 48.3.$$

The difference from the experimental value of oxygen concentration is 0.5 at. %. Because iron is reduced to metal incompletely, this difference can be associated with a compound of iron with oxygen. This is rather probable in the presence of alumina.

It follows from the data presented in the table that the overheating of samples to 700°C also leads to the redistribution of components on the surface of the catalytic system. It is known that the overheating of catalysts for ammonia synthesis leads to their sintering and, as a result, to a decrease in their surface area [8]. Therefore, the results can be explained as follows. A decrease in the surface area should lead to an increase in the relative concentration of promoters on the surface. However, only the concentration of aluminum oxide increases, while the relative concentration of potassium compound on the surface decreases significantly. Most probably, this is explained by the desorption of potassium compounds from the surface in this case and by concentrating aluminum oxide on the remaining surface. Note that this catalytic system (judging from changes in surface composition) is more resistant to overheating than two catalytic systems investigated earlier, which contain only one promoter [2, 3].

Analysis of the near-surface layers in the model system was carried out using ion sputtering of the surface. The results are presented in Fig. 3. A considerable decrease in the potassium concentration during the first 30 s of ion etching of the catalyst surface is accompanied by an increase in the iron and silicon concentrations. This confirms that a potassium compound partially covers the surface of iron and silicon oxide by nearly a monolayer. Then, an intensive sputtering of aluminum and silicon oxides located on the surface of iron crystallites begins. At the same time, the sputtering of potassium compound continues. The latter process is probably related to the removal of aluminum and silicon oxides from the surface and accompanied by an increase in the iron concentration on the surface. After the removal of promoters and contaminants from the surface of iron crystallites (the thickness of this layer is 2–4 nm), the composition of the surface does not further change during etching.

CONCLUSION

Thus, we showed in this work that the composition of near-surface layers accessible to XPS analysis (4–6 nm thick) differs dramatically from the bulk composition. The surface is enriched in promoters and impurities, but the iron concentration on the surface is relatively low. The iron concentration on the surface is most dramatically affected by aluminum oxide. Under the experimental conditions, iron is reduced to metal by 94–98%, and the rest of it remained in the form of oxides. The promoting effect of aluminum and potassium oxides on iron makes the catalytic system more resistant to overheating compared to similar catalytic systems with only one of the promoters.

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