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An XPS Study of the Promotion of Ru–Cs/Sibunit Catalysts for Ammonia Synthesis

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Abstract—The nature of surface cesium compounds in cesium-modified ruthenium–Sibunit catalysts for ammonia synthesis was studied by X-ray photoelectron spectroscopy (XPS). It was found that, on the reduction of promoted catalysts, cesium was incorporated into the micropores of Sibunit to form quasi-intercalation cesium–carbon bonds. In this case, the chemical state of cesium was close to its state in cesium suboxides. The subsequent interaction with atmospheric oxygen resulted in the oxidation of cesium, which occurred as cesium peroxide and cesium superoxide in the oxidized samples. Ruthenium occurred in a metallic state in the reduced samples. The activity of a Ru–Cs^+/C(1) sample was higher than that of inactive Ru–Cs^+/C(2). This is a consequence of the higher surface concentration of ruthenium, which is most likely due to an increase in the dispersity of metal particles, as well as of the higher probability of the interaction between the promoter and the active component due to a symbatic increase in the surface concentrations of both ruthenium and cesium.

INTRODUCTION

The catalytic synthesis of ammonia from nitrogen and hydrogen on a promoted iron catalyst (the Haber–Bosch process) is the main commercial method of nitrogen fixation. This process performed at lower temperatures (250–350°C) provides an opportunity to lower the pressure at which the required equilibrium yield of ammonia (20%) is reached to 30–50 atm. Thereby, the power consumption can be significantly decreased, as compared with commonly used process conditions: temperatures of 400–550°C and pressures of 280–320 atm [1]. To solve this problem and to increase the efficiency of ammonia synthesis under milder conditions, new catalysts are required that synthesize ammonia from nitrogen and hydrogen at high rates and lowered temperatures.

Studies performed in this area have indicated that ruthenium catalysts supported on various carbon materials promoted with alkali and/or alkaline earth metal compounds are among the most promising catalysts [2]. It was found that the efficiency of promotion in terms of the low-temperature activity of samples in the reaction of ammonia synthesis decreased in the order Cs > Rb > K > Na [3]. At the same time, the nature of promotion remains unclear. The nature of surface compounds, the reasons for an increase in the catalytic activity with increasing number of an alkaline promoter in the periodic table, etc., are still under discussion. It is clear that the processes of promotion should be studied using modern physical techniques in order to make progress in this area.

The aim of this work was to examine the nature of surface cesium compounds in cesium-modified ruthenium–Sibunit catalysts for ammonia synthesis. Cesium was chosen as a promoting additive because the activity of cesium-promoted samples is higher than that of samples with other alkali promoters. X-ray photoelectron spectroscopy (XPS), which is sensitive to the chemical (charge) states of test elements on sample surfaces (the depth of analysis is <3 nm), was used as the main investigation technique.

EXPERIMENTAL

In this work, two Ru–Cs^+/C samples with dramatically different activities in the reaction of low-temperature ammonia synthesis were studied. The graphite-like material Sibunit [4] with a specific surface area of 320 m^2/g was used as a carbon support (C). The active sample (Ru–Cs^+/C(1)) was prepared by the impregnation of Sibunit with an aqueous solution of a carbamide complex of ruthenium followed by reduction in a flow

Published data on E_b of $Cs3d_{5/2}$ and O1*s* for cesium compounds [7–11]

Cs compounds	E_b ($Cs3d_{5/2}$), eV	E_b (O1*s*), eV
Cs	726.1	–
$Cs_{2+x}O$	725.5	531.0
Cs_2O	725.0	528.2
Cs_2O_2	724.5	530.6
Cs_2O_4	724.2	532.9
CsOH	724.1	–
$CsNO_3$	724.4	532.5

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of hydrogen at $T = 400°C$ for 4 h. Next, the Ru/C sample was impregnated with an aqueous cesium nitrate solution and, after drying at 100°C, calcined in an atmosphere of argon at 300°C for 2 h. At the final stage, the sample was additionally reduced in hydrogen at 300°C. A special feature of the procedure used for preparing the inactive sample ($Ru–Cs^+/C(2)$) was that, unlike the active sample, the supported ruthenium complex was only dried at 100°C, rather than reduced after the first stage. Immediately afterwards, the sample was impregnated with a cesium nitrate solution and reduced in a flow of hydrogen at 400°C for 4 h. The concentrations of Cs and Ru in the samples were the same and were equal to 13.6 and 4.0 wt %, respectively. The reference sample, a sample of promoted Sibunit (Cs^+/C) with a cesium concentration of 13.6 wt %, was also prepared in accordance with the above procedure. The preparation procedure and the catalytic activities of $Ru–Cs^+/C$ samples were considered in more detail elsewhere [5].

The XPS spectra of all of the prepared samples were measured on a VG ESCALAB HP instrument using AlK_α characteristic radiation ($h\nu = 1486.6$ eV). The samples were rubbed into stainless steel gauze welded to a sample holder. The use of the gauze in place of a double-sided adhesive tape allowed us to heat samples directly in the spectrometer and to reduce them in hydrogen at $P = 1$ atm and $T = 350°C$. Before reduction, that is, immediately after loading into the spectrometer, the samples were also characterized by XPS. Henceforth, we will use the terms **oxidized** and **reduced** to denote samples characterized before and after reduction in the spectrometer chamber, respectively.

We analyzed both survey photoelectron spectra and narrow spectral regions characteristic of the main catalyst constituents: ruthenium and carbon ($Ru3d + C1s$), cesium ($Cs3d + CsMNN$), and oxygen ($O1s$). Impurity lines other than the lines of oxygen were not detected in the spectra. The survey spectra were recorded at an analyzer transmission energy of 50 eV, and particular spectral regions were recorded at 20 eV (to improve energy resolution). Before this study, the spectrometer was calibrated with reference to the binding energies of $Au4f_{7/2}$ (84.0 eV) and $Cu2p_{3/2}$ (932.6 eV) core levels. The good conductivity of the carrier allowed us to eliminate the manifestations of a charging effect. Therefore, all of the binding energies of core-level electrons of the test elements are presented in this work as determined from original spectra.

The relative concentrations of elements on the catalyst surfaces expressed as atomic concentration ratios were calculated from the integrated intensities of the corresponding photoelectron lines (I_X, I_C) corrected for atomic sensitivity factors [6] with the use of the following equation:

$$n_X = \frac{I_X}{ASF_X} \Big/ \frac{I_C}{ASF_C},$$

where n_X is the concentration of element X in the analysis zone (at %), and ASF_X and ASF_C are the atomic sensitivity factors of the element and carbon, respectively.

RESULTS AND DISCUSSION

At the first stage, we studied the interaction of the promoter with the pure support. Figure 1 shows the core spectra of $C1s$ and $Cs3d_{5/2}$ regions for a Cs^+/C sample and parent Sibunit. The spectra of the Cs^+/C sample were measured after its loading into the spectrometer and after the subsequent reduction. It can be seen that the $C1s$ spectrum of pure Sibunit is characterized by a binding energy of 284.4 eV. This value has repeatedly been reported in the literature on studies of various types of graphite carbon. The absence of peaks from the corresponding $Cs3d_{5/2}$ spectrum indicates that the cesium content of pure Sibunit is lower than the sensitivity of XPS (<0.1 at %).

The promotion of Sibunit with cesium (Cs^+/C sample) resulted in the appearance of an intense signal in the $Cs3d_{5/2}$ spectrum. In this case, the $C1s$ spectrum shifted by ~0.5 eV toward higher binding energies with respect to the initial spectrum of Sibunit (Fig. 1); this suggests a change in the chemical state of carbon atoms. Taking into account the depth of XPS analysis (~2–3 nm), we can state that the detected interaction is not restricted to a surface but extends in depth. It is believed that the promoter fills the micropores of the support at the sites of surface structural distortions. In the case of porous Sibunit, the number of these sites is sufficiently great to provide a shift of the entire $C1s$ spectrum (Fig. 1).

Note that the $C1s$ spectra of the reduced and oxidized samples were very similar, except for a slight broadening of the spectrum at higher values of E_b that appeared after the reduction of the sample in the spectrometer. In contrast, the $Cs3d_{5/2}$ spectra underwent considerable changes in the course of reduction. The spectrum of the oxidized sample was characterized by $E_b = 724.8$ eV, whereas the reduction of the sample in the spectrometer shifted the $Cs3d_{5/2}$ spectrum to $E_b = 725.3$ eV. In the general case, shifts to higher binding energies upon reduction are not typical of the majority of elements; however, some metals (silver, cadmium, cesium, and barium) are exceptions. Without considering in detail the reasons for these “inverse” shifts, note that an increase in the binding energy of cesium is indicative of the reduction of cesium. Indeed, as can be seen in the table, which summarizes published data [7–11] on the $Cs3d_{5/2}$ binding energies for a number of cesium compounds, the value of E_b in the $Cs3d_{5/2}$ spectrum of cesium metal is greater than that of the Cs^+ ion in ionic compounds, such as hydroxide, peroxide, and carbonate, by ~2 eV. A comparison of the experimentally measured $Cs3d_{5/2}$ binding energies with published data indicates that cesium suboxides most likely occurred in the reduced sample (see the table). The binding energy of 724.8 eV measured in the oxidized sample suggests that the formation of cesium peroxide or cesium superoxide occurred in contact with atmospheric oxygen (see the table).

We analyzed the $O1s$ spectra for the purpose of establishing a more correct assignment of the observed

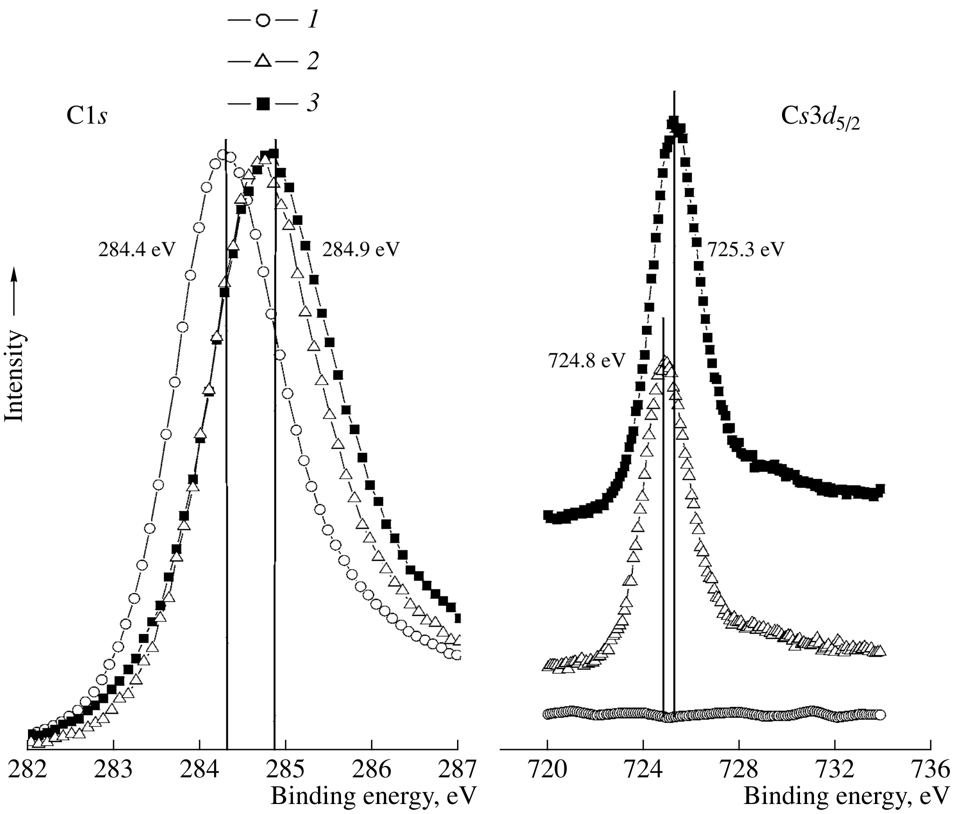

Fig. 1. Spectra of C1*s* and Cs3$d_{5/2}$ in (*1*) parent Sibunit and a Cs^+/C sample (*2*) before and (*3*) after reduction in the spectrometer.

Cs3$d_{5/2}$ lines to particular cesium compounds. Previously, in a study of individual cesium oxides on the surface of silver [10], we found that the positions of O1*s* spectra are characteristic of each of these oxides: cesium oxide Cs_2O, cesium peroxide Cs_2O_2, and cesium superoxide Cs_2O_4 are characterized by E_b (Cs3$d_{5/2}$) of ~528, ~530.3, and ~533 eV, respectively. Cesium suboxide (the formation of $Cs_{11}O_3$ as the most stable compound was assumed) gave the O1*s* signal with a binding energy of ~531 eV. Moreover, the Cs/O atomic ratios were also close to stoichiometric values for corresponding oxides.

Figure 2 shows the O1*s* spectra of parent Sibunit and the Cs^+/C sample. Because the initial spectra were broadened (Fig. 2a), we analyzed difference spectra (Fig. 2b). The use of difference spectra allowed us to distinguish the states of oxygen bound to cesium from the states of oxygen on the surface of Sibunit. It can be seen that the spectrum of the reduced sample exhibited an additional O1*s* line with E_b = 531.0 eV (Fig. 2b, curves *2–1*), as compared with the spectrum of Sibunit. This supports our conclusion on the occurrence of a suboxide in the reduced sample. The Cs/O atomic ratio of ~3, which is close to the stoichiometric ratio for the bulk suboxide $Cs_{11}O_3$, is an additional argument for the attribution of the Cs3$d_{5/2}$ line with E_b = 725.3 eV to cesium suboxide. In the oxidized sample, this ratio became close to 1, which suggests the formation of cesium peroxide. Indeed, a corresponding signal with E_b = 530.5 eV appeared in the O1*s* difference spectrum (Fig. 2b, curves *3–2*). However, a weak signal with E_b = 532.5 eV was present, which indicates that a small amount of cesium superoxide can be formed.

However, it should be noted that, in the case under discussion, the above insertion of cesium ions at the sites of structural distortions in Sibunit makes the formation of a three-dimensional cesium suboxide phase improbable. It is most likely that the cesium–carbon bonds play the role of suboxide cesium–cesium bonds in our sample. Indeed, electron-density transfer from the carbon atom to the cesium ion can occur in the formation of quasi-intercalation bonds of this type [11]. In this case, a positive charge is accumulated at the carbon atom, whereas the charge at the cesium ion decreases. The observed shifts of photoelectron spectra (Fig. 1) are fully consistent with the proposed electron-transfer behavior. As noted above, a “positive” shift of the C1*s* spectrum is indicative of an electron-density deficiency at carbon atoms, whereas a “positive” shift of the Cs3$d_{5/2}$ spectrum upon the reduction of the sample is indicative of an increase in electron density at cesium ions. An analogous assumption on the formation of cesium–metal bonds was used previously for explaining the thermal stability of reduced cesium on the surface of silver single crystals [10]. In contact with atmospheric air, the high oxygen affinity of cesium results in

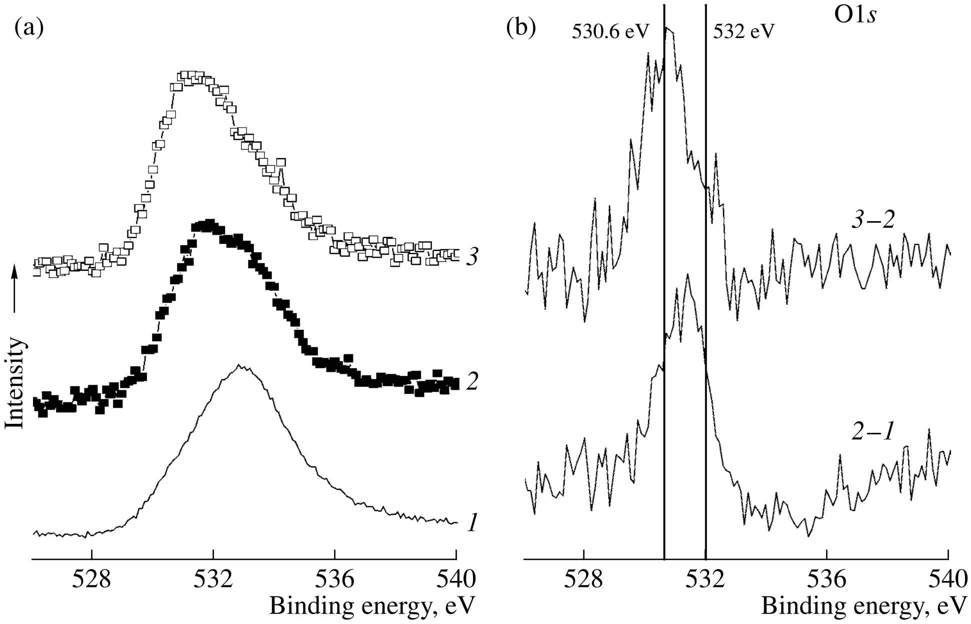

Fig. 2. (a) Initial and (b) difference spectra of O1*s* in (*1*) parent Sibunit and a Cs^+/C sample (*2*) before and (*3*) after reduction in the spectrometer.

the rupture of quasi-intercalation carbon–cesium bonds and in the formation of cesium–oxygen bonds. This explains the observed shift of the $Cs3d_{5/2}$ spectrum of the oxidized sample toward lower values of E_b (Fig. 1).

The introduction of ruthenium before supporting cesium affected the character of interactions between cesium and Sibunit. The C1*s* binding energies given below for all of the test samples indicate that the shift of the C1*s* spectrum upon promoting the samples with cesium reached a maximum in the case of the Cs^+/C sample (0.5 eV) and decreased in the case of Ru–Cs^+/C samples.

Samples	Sibunit	$CsNO_3/C$	Ru/C	Cs^+/C	Ru–Cs^+/C(1)	Ru–Cs^+/C(2)
E_b (C1*s*), eV	284.4	284.4	284.4	284.9	284.6	284.6

It is most likely that the introduction of ruthenium suppressed the interaction of the promoter with the support because a portion of cesium ions reacted with ruthenium. A conclusion on the occurrence of two cesium species in cesium-promoted Ru/C catalysts was drawn recently [12] based on data obtained by temperature-programmed desorption.

Unfortunately, the spectral resolution of our photoelectron spectrometer was insufficient for separating the signals of cesium that interacted with Sibunit from the signals of cesium bound to ruthenium. This statement is illustrated by the spectra of $Cs3d_{5/2}$ (Fig. 3a) and O1*s* (Fig. 3b) in the reduced Cs^+/C, Ru–Cs^+/C(1), and Ru–Cs^+/C(2) samples. It can be seen that all of the samples after reduction in hydrogen were characterized by close positions of the $Cs3d_{5/2}$ and O1*s* spectra. In this case, the measured binding energies of ~725.3 and ~531.0 eV, respectively, suggest the formation of quasi-intercalation cesium "suboxides."

Note that the $Cs3d_{5/2}$ spectra of all of the oxidized samples also exhibited close binding energies of 724.7 eV, which suggested the transfer of cesium to a more oxidized state in contact with atmospheric air. Because the oxidized samples could contain various cesium compounds (oxides, hydroxide, and carbonates) depending on the duration and conditions of storage in air, their spectra were not analyzed in more detail. Moreover, attention was focused on the reduced samples because the reduction of samples in a spectrometer can be considered as a model of the action of a reaction atmosphere (a mixture of hydrogen and nitrogen); it is well known that this reaction atmosphere exhibits a high reduction potential.

Figure 4 shows the $Ru3d_{5/2}$ spectra measured in the reduced Ru–Cs^+/C(1) and Ru–Cs^+/C(2) samples. For comparison, Fig. 4 also shows the spectrum of a bulk ruthenium sample as a polycrystal of ruthenium. Before spectroscopic measurements, the surface of this sample was cleaned by a sequence of etching with Ar^+ ion and vacuum heating. It can be seen that the positions of maximums in the $Ru3d_{5/2}$ spectra of all of the samples are similar (280.2 eV); this suggests that ruthenium occurred in a metallic state in the supported Ru–Cs^+/C samples after reduction. Unfortunately, the overlapping

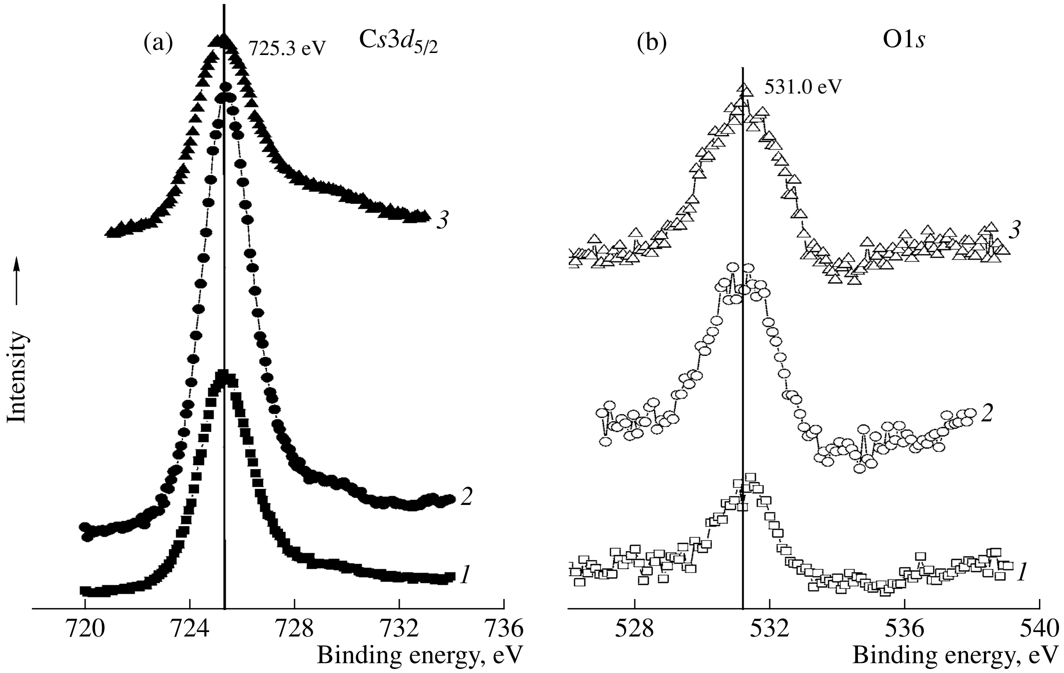

Fig. 3. (a) Initial spectra of $Cs3d_{5/2}$ and (b) difference spectra of O1*s* in reduced (*1*) Cs^+/C, (*2*) Ru–Cs^+/C(1), and (*3*) Ru–Cs^+/C(2) samples. The difference spectra were obtained by subtracting the spectrum of Sibunit from the spectra of initial samples.

of the $Ru3d_{3/2}$ spectral line with the main line of the support did not allow us to analyze in more detail nonuniformities in the chemical state of ruthenium.

The only difference between the test catalyst samples consists in the much higher intensities of both the $Cs3d_{5/2}$ (Fig. 3a) and $Ru3d_{5/2}$ (Fig. 4) spectra of the active Ru–Cs^+/C(1) sample, as compared with inactive Ru–Cs^+/C(2). A decrease in the intensity of an XPS signal reflects a decrease in the surface concentration of ruthenium in the Ru–Cs^+/C(2) sample; this can explain a decrease in the catalytic activity. However, the reasons for this phenomenon are unclear. Indeed, if this were due to the shielding of ruthenium particles with the promoter, a higher intensity of the signal of cesium in the inactive sample would be expected. However, an opposite trend was found in our case. It is evident that the experimental data available are insufficient for making a final conclusion on the nature of the observed differences. At the same time, the differences in sample preparation procedures (see Experimental) and similar intensities of the $Cs3d_{5/2}$ spectra of the inactive sample and promoted Sibunit allowed us to propose a reasonable explanation of the processes.

As noted previously, it is most likely that the interaction of the promoter with the support results in the insertion of cesium into the micropores of Sibunit with the formation of quasi-intercalation cesium–carbon bonds. The insertion of a bulky ion such as cesium into near-surface graphite layers occurs with the highest rate at structural distortions. A decrease in the specific surface area of the promoted support from 320 to 170 m^2/g, as determined by the BET method, is additional evidence for the blocking of micropores upon the promotion of Sibunit with cesium compounds.

If ruthenium is supported on Sibunit before the introduction of cesium, the vacant sites of structural distortions can act as the nucleation sites of ruthenium nanoparticles, thereby preventing their agglomeration upon reduction. In this case, the blocking of defect sites on the surface of Sibunit hinders the introduction of cesium. Consequently, the surface concentrations of both ruthenium and cesium should increase. This increase was observed in the active sample, whose

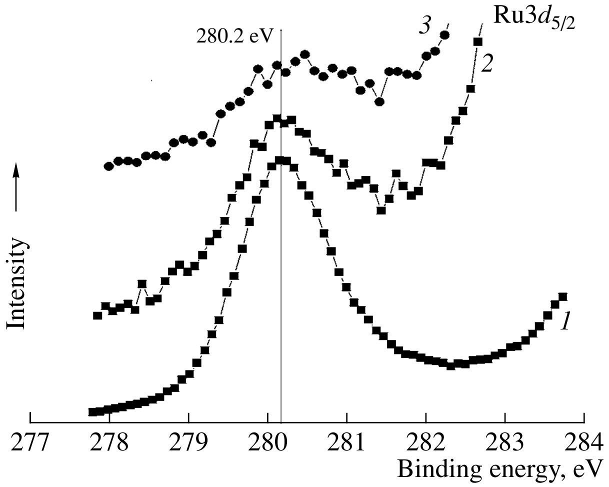

Fig. 4. Spectra of $Ru3d_{5/2}$ in reduced samples: (*1*) Ru (polycrystal), (*2*) Ru–Cs^+/C(1), and (*3*) Ru–Cs^+/C(2).

preparation procedure consisted in the successive supporting of ruthenium and cesium compounds with the intermediate reduction of the Ru/C sample before promotion (see Experimental).

It is likely that structural distortion sites remain vacant if Sibunit preimpregnated with ruthenium salts is only dried, rather than reduced, before impregnation with a cesium nitrate solution. In this case, ruthenium and cesium will compete for the structural distortion sites in the subsequent procedure of reduction. A consequence of this will be the insertion of a portion of cesium into the near-surface layers of Sibunit and a stronger agglomeration of ruthenium particles, which are not bound to a regular graphite surface so strongly as they are to defects. The lower dispersity of ruthenium and the near-surface arrangement of cesium decrease the photoelectron signals of both ruthenium and cesium; we found such a decrease in our measurements. Increased surface concentrations of ruthenium and cesium in the Ru–Cs^+/C(1) sample, as compared to those in the Ru–Cs^+/C(2) sample, also increase the probability of the interaction of the promoter and the active component. It has been hypothesized in the literature that this increases the activity of ruthenium in low-temperature ammonia synthesis. Note that this is consistent with a higher promoting ability of cesium, as compared with that of alkali metals arranged above in the periodic table. Indeed, a greater ionic size of cesium, as compared with those of potassium, rubidium, and, especially, sodium, largely prevents the penetration of cesium into near-surface layers at regular areas of graphite layers. The interaction of ruthenium and cesium can be more effective because the preparation procedure of the active sample implies the formation of ruthenium oxide on the surface of ruthenium metal particles in contact with atmospheric air. The subsequent impregnation of this sample with cesium nitrate primarily provides for the interaction of cesium ions with the oxidized surface of ruthenium to form cesium ruthenates. In the inactive sample, the intact carbamide environment of ruthenium (the stage of reduction was absent) is an impediment in the interaction of cesium ions with ruthenium. To test the above hypothesis on the surface processes that occur in the formation of the active centers of ruthenium catalysts for low-temperature ammonia synthesis, additional experiments should be performed, and we intend to do this in the future.

CONCLUSIONS

(1) The promotion of Sibunit with cesium nitrate with the subsequent reduction resulted in the insertion of cesium into support micropores with the formation of quasi-intercalation cesium–carbon bonds. In this case, the chemical state of cesium was close to the state in cesium suboxides, for example, in $Cs_{11}O_3$.

(2) The subsequent interaction with atmospheric oxygen resulted in the rupture of cesium–carbon bonds; the promoter occurred as cesium peroxide and cesium superoxide in the oxidized samples.

(3) Ruthenium occurred in a metallic state in the reduced samples. The higher activity of the Ru–Cs^+/C(1) sample, as compared with that of the inactive Ru–Cs^+/C(2), can be explained by the higher surface concentration of ruthenium, which was most likely due to an increase in the dispersity of metal particles. A symbatic increase in the surface concentration of cesium implies a higher probability of the interaction of the promoter and the active component.

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