

## Formation of Ru–M/Sibunit Catalysts for Ammonia Synthesis

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**Abstract**—The effects of the nature of ruthenium and alkaline promoter precursor compounds and support properties on the activity of Ru–(Cs, K)/Sibunit catalysts in the reaction of ammonia synthesis were studied. The formation of active centers in the catalysts was studied with the use of EXAFS, XPS, and electron microscopy. It was found that ruthenium and a portion of cesium occurred in metallic states in the reduced catalysts. The most active catalysts containing 4 wt % ruthenium at the atomic ratios  $[K] : [Ru] = 4.5$  and  $[Cs] : [Ru] = 2.5$  were obtained with the use of the  $[Ru(dipy)_3](OH)_2$  complex.

### INTRODUCTION

The synthesis of ammonium from nitrogen and hydrogen on a promoted iron catalyst (the Haber–Bosch process) is the main commercial method of nitrogen binding. However, this process is performed at comparatively high temperatures (620–820 K) and pressures (28.0–32.0 MPa) for both kinetic and thermodynamic reasons. Under these conditions, power and material inputs are high. To improve the efficiency of the process, catalysts of a new type are required, which can perform ammonia synthesis with high rates at reduced temperatures and pressures.

Catalysts based on ruthenium for the low-temperature synthesis of ammonia (620–740 K; 7.0–10.0 MPa) have been developed since the 1970s. Supported ruthenium catalysts modified with alkali and alkaline-earth metals exhibit the highest activity [1]. In this case, the best supports are carbon materials: activated carbons prepared from various raw materials (charcoal, coal, bone charcoal, lignin charcoal, etc.); graphite; and graphite-containing carbon, which has been widely used recently [2].

In 1992, British Petroleum and Kellog proposed to commercialize a new process for low-temperature ammonia synthesis with the use of a ruthenium catalyst modified with potassium oxide supported on porous graphite [3]. The laboratory of Professor Aika at the Tokyo Institute of Technology performs the basic research of ruthenium catalysts for ammonia synthesis [4–10]. These studies mainly include ammonia synthesis and nitrogen isotope exchange in the presence of modified ruthenium catalysts on various supports: activated carbon,  $Al_2O_3$ ,  $MgO$ , and lanthanide (cerium, lanthanum, and samarium) oxides. Alkali metal and barium compounds were used as modifiers. Physical techniques such as IR spectroscopy, XPS, and electron microscopy were occasionally used to study the catalysts. According to Aika *et al.* [6, 9] and Kowalczyk

*et al.* [11], the synthesis of ammonia occurs via the following steps:

- (1) the activation of nitrogen (dissociation on ruthenium) as a rate-limiting step;
- (2) the dissociation of hydrogen molecules on ruthenium and the consecutive addition of hydrogen atoms to adsorbed nitrogen with the final formation of a chemisorbed molecule of ammonia;
- (3) the desorption of ammonia and the liberation of the site for the next cycle.

According to the published data, the role of an alkaline promoter consists in electron-density transfer to ruthenium atoms because an excessive negative charge is required for the activation of the nitrogen molecule. Consequently, the support should not be an electron-density acceptor with respect to supported ruthenium crystallites or clusters. Of course, the above model is simplified because the genesis and properties of supported ruthenium catalysts for ammonia synthesis have not been adequately studied.

The graphite-like material Sibunit [12] was first used by Yunusov *et al.* [13], who prepared catalysts by supporting the potassium salts of ruthenium carbonylhydrides; these catalysts were active in the synthesis of  $NH_3$  without adding an electron promoter.

With the use of Sibunit, a procedure was developed for preparing Ru–Cs(K)/Sibunit catalysts, which were designed for performing reactions at moderate pressures and temperatures of 570–670 K [14].

The aim of this work was to study the dependence of the properties of these catalysts on the specific surface area ( $S_{sp}$ ) of the support and on the nature of ruthenium and alkaline promoter precursor compounds and to

determine the physicochemical characteristics of the catalyst components after various steps of preparation.

## EXPERIMENTAL

**Starting substances.** Commercial  $\text{RuCl}_3\text{OH}$  (reagent grade),  $[\text{Ru}(\text{dipy})_3](\text{OH})_2$ , and  $[\text{Ru}(\text{dipy})_3]\text{Cl}_2$  (where dipy is dipyrityl) were used as starting ruthenium compounds. Alkaline promoters were introduced from solutions of  $\text{MOH}$ ,  $\text{MNO}_3$ , and  $\text{M}_2\text{CO}_3$  (where M is K or Cs) of analytical grade.

The  $[\text{Ru}(\text{dipy})_3]\text{Cl}_2$  complex was synthesized from  $\text{RuCl}_3\text{OH}$  in accordance with a published procedure [15] with the only difference being that hydroxylamine sulfate was used as a reducing agent.

The  $[\text{Ru}(\text{dipy})_3](\text{OH})_2$  complex was prepared by passing a solution of  $[\text{Ru}(\text{dipy})_3]\text{Cl}_2$  through a column with an AB-18 anion-exchange resin in the  $\text{OH}^-$  form.

Commercial samples of the graphite-like material Sibunit [12] with  $S_{\text{sp}}$  of 90, 215, and 320  $\text{m}^2/\text{g}$  were used for preparing the catalysts.

**Preparation of catalysts.** The preparation of the catalysts was a multistage process:

(1) the impregnation of Sibunit with various  $S_{\text{sp}}$  with the aqueous solutions of the ruthenium complexes with subsequent drying in air at 373 K for 1 to 2 h;

(2) the reduction of the sample in a flow of hydrogen at 673 K for 4 to 5 h;

(3) the supporting of a promoter compound on Ru/Sibunit by impregnation with the solutions of potassium or cesium hydroxide or salts with subsequent drying at 373 K for 1 to 2 h;

(4) the treatment in a flow of argon at 473–673 K for 2–4 h;

(5) the treatment in a flow of hydrogen at 473–673 K for 2–4 h.

The resulting catalyst was kept in a sealed ampule in an atmosphere of argon, which was specially purified to remove oxygen (in a number of cases, stages 4 and 5 were performed as described elsewhere [15, 16]). As an example, the synthesis of a particular catalyst is described below.

**4% Ru–13.6% Cs/Sibunit sample.** This sample was prepared as follows: The support was washed with water to remove dust and dried at 100°C. The prepared support (25 g) was placed in a solution of a dipyrityl complex of ruthenium (80 ml) with a concentration of 12.5 mg/ml and evaporated in a water bath with stirring. The air-dry sample was heated in air at 100°C (1 h) and then reduced with hydrogen at 450°C (4 h) followed by cooling in a flow of hydrogen or an inert gas.

Cesium nitrate (4.98 g) was dissolved in 70 ml of water. The resulting solution was added to the pellets of 4% Ru/Sibunit and evaporated in a water bath to an air-dry state with stirring at regular intervals. Next, the sample was kept in a drying oven at 100°C (1 h), treated sequentially with argon at 350°C (2 h) and with hydro-

gen at 350°C (2 h), cooled in a flow of hydrogen, and sealed in an ampule in a flow of argon.

**Catalyst activity.** The activity of the catalysts was determined in a flow two-reactor unit at 593 and 623 K, gas mixture ( $\text{H}_2/\text{N}_2 = 3 : 1$ ) pressures of 0.6 and 3.0 MPa and flow space velocities of  $(1.2\text{--}15.0) \times 10^3 \text{ h}^{-1}$ . The weight of a sample loaded in a reactor was 1.4 g. The catalyst activity was characterized by the amount of released ammonia (g) per gram of a catalyst under the standard conditions specified below.

**XPS spectra.** The XPS spectra were recorded on a VG ESCALAB HP electron spectrometer with the use of nonmonochromatized  $\text{AlK}_{\alpha}$  radiation ( $h\nu = 1486.6 \text{ eV}$ , 200 W). The scale of binding energies ( $E_b$ ) was precalibrated using the positions of the  $\text{Au}4f_{7/2}$  (84.0 eV) and  $\text{Cu}2p_{3/2}$  (932.6 eV) core-level peaks.

Catalyst samples as pellets were placed within a specially made holder with low walls in air. The design of this holder allowed us to adjust the samples without rotation. After recording the photoelectron spectra, catalysts were reduced with a stoichiometric nitrogen–hydrogen mixture (2 h) at 653–673 K and a pressure of 1000 Pa immediately in the preparation chamber of the spectrometer.

An internal standard was used for the calibration of photoelectron lines; the Cls carbon line of the support (Sibunit) with  $E_b = 284.5 \text{ eV}$  was used as the internal standard. The relative concentrations of the elements on the surface of catalysts and the ratios between atomic concentrations were calculated from the integrated intensities of photoelectron lines taking into account the corresponding atomic sensitivity factors [17] with the use of the following equation:

$$n_x = \frac{I_x}{\sum_i \frac{I_i}{ASF_i}},$$

where  $n_x$  is the element concentration in the analysis zone (at. %), and  $ASF_i$  is the atomic sensitivity factors of the elements.

In addition to survey photoelectron spectra, the narrow spectral regions of  $\text{Ru}3d + \text{Cl}s$ ,  $\text{O}1s$ ,  $\text{Cs}3d$ , and  $\text{K}2p$  were recorded. The survey spectra were measured at an analyzer transmission energy of 50 eV, and individual spectral regions were measured at 20 eV.

The presence of ruthenium, an alkaline promoter (cesium or potassium), carbon, oxygen, and the admixture of chlorine ( $\text{Cl}2p$  line) was detected in all the samples; this is likely related to the sample preparation procedure. No other elements were detected (to within the sensitivity of XPS).

**Specific surface area.** The specific surface areas of supports and catalysts ( $S_{\text{sp}}$ ) were determined by the BET method from the single-point adsorption of nitrogen at 77 K.

**Table 1.** Effects of the specific surface area ( $S_{sp}$ ) of the support and the dispersity ( $D$ ) of ruthenium on the activity of 4%Ru–4%K/Sibunit catalysts

$S_{sp}$ , m <sup>2</sup> /g	Rate of NH <sub>3</sub> synthesis*, (g NH <sub>3</sub> ) (g Cat) <sup>−1</sup> h <sup>−1</sup>	$D$ , nm
320	0.18	1.5–2.0
215	0.12	4.5–5.5
90	0.022	10.0–15.0

Note: [Ru(dipy)<sub>3</sub>](OH)<sub>2</sub> and KOH are the precursors of Ru and K, respectively.

\* Under standard conditions: 623 K; 3.0 MPa; 2000 h<sup>−1</sup>; [H<sub>2</sub>] : [N<sub>2</sub>] = 3 : 1.

**Table 2.** Effect of the nature of the precursor compounds of ruthenium on the dispersity of ruthenium and on the activity of 4%Ru–4%K/Sibunit catalysts

Initial ruthenium compound	Rate of NH <sub>3</sub> synthesis*, (g NH <sub>3</sub> ) (g Cat) <sup>−1</sup> h <sup>−1</sup>	$D$ , nm
RuCl <sub>3</sub> OH	0	—
[Ru(dipy) <sub>3</sub> ]Cl <sub>2</sub>	0.13	5.0–6.0
[Ru(dipy) <sub>3</sub> ](OH) <sub>2</sub>	0.18	1.5–2.0

Note: KOH is the precursor of potassium.

\* Under standard conditions: 623 K; 3.0 MPa; 2000 h<sup>−1</sup>; [H<sub>2</sub>] : [N<sub>2</sub>] = 3 : 1.

**Dispersity (particle size).** The particle size of the supported ruthenium was evaluated with the use of a JEM-2010 electron microscope (Japan).

**EXAFS spectra.** The  $K$ -edge EXAFS spectra of ruthenium were measured at an electron energy of 2 KeV and a current of 80 mA at the VEPP-3 electron storage ring in the transmission mode. The spectrometer had a two-crystal Si(111) channel-cut monochromator and proportional chambers as detectors. The samples for spectroscopic measurements after treatments were transferred to gas-tight cells with beryllium windows away from air. The data were treated according to a standard procedure with the use of the VIPER program [18] for separating the oscillating part of the absorption coefficient and the EXCURV 92 program [19] for simulating structural data. The spectra were simulated in a wavenumber range of 3–14 Å<sup>−1</sup> for data represented as  $k^3\chi(k)$ .

## RESULTS AND DISCUSSION

We found that all three catalyst components—ruthenium, the promoter, and the support—play a large role in the formation of an active component of the Ru–M/Sibunit systems. First, we consider the effect of the  $S_{sp}$  of Sibunit on the properties of the catalysts because it was responsible for the support chosen for all the subsequent experiments.

### *Effect of the Specific Surface Area of a Support on the Dispersity of Ruthenium and on the Activity of Catalysts*

The activity of a Ru–K/Sibunit catalyst increased by one order of magnitude as the  $S_{sp}$  of Sibunit increased from 90 to 320 m<sup>2</sup>/g; this can be due to a symbatic decrease in the particle size of ruthenium from 10.0–15.0 to 1.5–2.0 nm, respectively (Table 1). All the results given below were obtained with the use of Sibunit with  $S_{sp}$  = 320 m<sup>2</sup>/g, which provided the highest catalytic activity.

### *Effect of the Nature of the Parent Compound of Ruthenium*

The initial ruthenium compounds had a noticeable effect on the activity of the resulting catalysts (Table 2). Samples that were inactive under the chosen synthesis conditions were obtained by the impregnation of the support with a solution of the RuCl<sub>3</sub>OH complex, which is characterized by the presence of inner-sphere chloride ions. Contrastingly, active catalysts were prepared with the use of the [Ru(dipy)<sub>3</sub>]Cl<sub>2</sub> complex, which contains Cl<sup>−</sup> ions in the outer sphere without the formation of Ru–Cl bonds. The activity of these catalysts increased upon the complete removal of chloride ions from the starting compound of ruthenium, as in [Ru(dipy)<sub>3</sub>](OH)<sub>2</sub>.

The negative effect of chloride ions on the rate of ammonia synthesis is well known [4]. In this work, we found that the catalyst is poisoned only by the chloride ions that are directly bound to the ruthenium atoms and are the most difficult to remove. A decrease in the catalyst activity was due to the stabilization of ruthenium in an oxidized state in the presence of chloride ions. A similar stability of platinum in alumina–platinum catalysts was observed by Smolikov *et al.* [20]. As noted above, surface ruthenium atoms should have an increased electron density for the addition and dissociation of the nitrogen molecule (a rate-limiting step of the reaction). Consequently, chloride ions should be removed from the nearest environment of Ru for the formation of an active center. Moreover, the metal particle size decreased in the absence of Cl<sup>−</sup> ions (Table 2). It is well known [21] that mobile chlorine-containing intermediates, which readily undergo agglomeration, are formed in the course of preparation of supported platinum catalysts from H<sub>2</sub>PtCl<sub>6</sub>. It is believed that in our case such a phenomenon also results in the formation of coarser ruthenium metal particles after impregnating the support with a solution of [Ru(dipy)<sub>3</sub>]Cl<sub>2</sub> than those prepared with the use of the OH form of a dipyridyl complex of ruthenium.

### *Effect of the Concentration and Nature of the Parent Alkaline Promoter Compound*

It is well known that the activity of ruthenium catalysts on supports other than Sibunit passes through a

maximum as the concentration of an alkali metal promoter is changed [7]. In our case, an analogous behavior was observed (Fig. 1).

As can be seen in Fig. 1a, the region of a maximum corresponds to the atomic ratio K/Ru = 4.5. Among Ru-Cs/Sibunit catalysts, samples with Cs/Ru = 2.5 were the most active catalysts (Fig. 1b). The extremal character of the dependence of the activity of the test systems on the concentration of the promoter [10, 22] can be explained by the fact that the number of ruthenium atoms with an increased electron density, which is of importance for the activation of the nitrogen molecule, increases with alkali metal concentration. It is likely that a decrease in the activity of catalysts with K/Ru > 4.5 and Cs/Ru > 2.5 is due to a considerable change in the texture parameters of the support under the action of alkali metals. A decrease in  $S_{sp}$  upon the supporting of catalyst components is most indicative (Table 3).

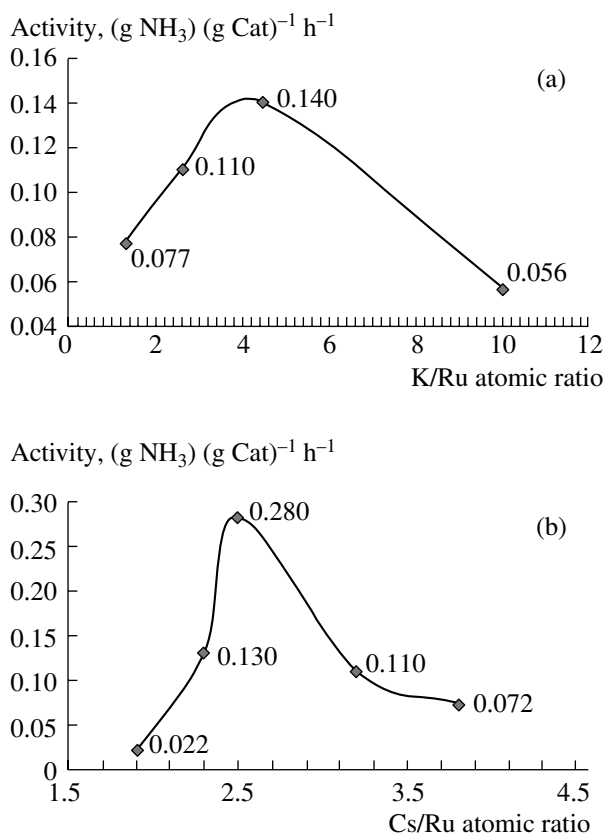
In this case,  $S_{sp}$  changed most significantly after the addition of alkaline promoters. Thus,  $S_{sp}$  decreased from 320 to 280 m<sup>2</sup>/g after supporting and reducing the [Ru(dipy)<sub>3</sub>]Cl<sub>2</sub> complex, whereas the subsequent supporting of KOH and further thermal treatments of the catalyst resulted in a decrease in  $S_{sp}$  to 70 m<sup>2</sup>/g. A considerable decrease in  $S_{sp}$  was also observed after supporting cesium. It is likely that a portion of the support pores and ruthenium particles were blocked as the concentration of the promoter was increased; this inhibited the interaction of reactants with active centers and resulted in a decrease in the activity.

It is well known that the activity of catalysts increased on going from potassium to cesium, which is a more electropositive promoter [23]. In our case, the rate of the reaction was increased twofold at the atomic ratio M/Ru = 2.5 and a ruthenium content of 4 wt %.

The nature of the parent alkaline promoter compound has a noticeable effect on the activity of the catalysts. The replacement of cesium hydroxide with cesium nitrate or partially with cesium carbonate resulted in a decrease in the rate of synthesis, and the catalyst impregnated with a solution of Cs<sub>2</sub>CO<sub>3</sub> was found to be inactive (Table 4).

We believe that the interaction of Ru with a cesium compound mainly occurs in the surface melt of the latter because it provides maximum contact between the reacting components. It is likely that a ruthenate-like compound is formed as a result of this, and that compound is converted after reduction into ruthenium-cesium aggregates, which are the active centers of catalysts for ammonia synthesis.

Under the experimental conditions (thermal treatment at 573–673 K), only cesium hydroxide could melt, which provided the production of the most active catalysts. It is likely that supported cesium nitrate occurs in a premelted state. The introduction of Cs<sub>2</sub>CO<sub>3</sub>, which does not form a melt, into an impregnation solution of CsOH removed a portion of the cesium



**Fig. 1.** Dependence of the activity of Ru-M/Sibunit catalysts on the M/Ru atomic ratio: (a) M = K ( $P = 30$  atm;  $T = 623$  K;  $w = 1300$  h<sup>-1</sup>; 4% Ru) and (b) M = Cs ( $P = 30$  atm;  $T = 623$  K;  $w = 3000$  h<sup>-1</sup>; 4% Ru).

from the introduction with ruthenium and noticeably decreased the catalyst activity. The catalyst was fully deactivated after impregnating with a solution of cesium carbonate.

#### States of Ruthenium and Alkali Metals in the Catalysts

**(a) XPS study of the catalysts.** According to XPS data, a catalyst that was in contact with air (Table 5, sample A) contained RuO<sub>2</sub> (280.6 eV) and Cs<sub>2</sub>O (724.6 eV) (Fig. 2, spectrum 1).

**Table 3.** Changes in the  $S_{sp}$  of Sibunit upon supporting catalyst components

initial Sibunit	$S_{sp}$ , m <sup>2</sup> /g		
	Ru/Sibunit (4% Ru)	Ru-K/Sibunit (4% Ru, 4% K)	Ru-Cs/Sibunit (4% Ru, 13.6% Cs)
320	280	70	120
90	—	45	—

**Table 4.** Effect of cesium precursor compounds on the activity of 4%Ru–13.6%Cs/Sibunit catalysts

Cesium compound		Rate of NH <sub>3</sub> synthesis*, (g NH <sub>3</sub> ) × (g Cat) <sup>-1</sup> h <sup>-1</sup>
formula	melting temperature*, K	
CsOH	548	0.28
CsNO <sub>3</sub>	687	0.23
2/3 CsOH + 1/3 Cs <sub>2</sub> CO <sub>3</sub>	–	0.19
Cs <sub>2</sub> CO <sub>3</sub>	883 (decomp.)	0

Note: An ammonia complex is the precursor of Ru.

\* Data from [24].

\*\* Under standard conditions: 623 K; 3.0 MPa; 2000 h<sup>-1</sup>; [H<sub>2</sub>] : [N<sub>2</sub>] = 3 : 1.

**Table 5.** XPS data for Ru–Cs/Sibunit catalysts (4% Ru, 13.6% Cs)

Sample	Ru3d, eV	Cs3d, eV
Ru <sub>met</sub>	280.1 [25]	–
RuO <sub>2</sub>	280.7 [26]	–
Cs <sub>met</sub>	–	726.3 [27]
Cs <sub>2</sub> O	–	724.6 [28]
<b>A</b>	280.6	724.6
<b>B</b>	280.1	725.1
<b>C</b>	280.2	726.1
<b>D</b>	280.0	725.4

Note: **A** refers to an Ru–Cs/Sibunit sample that was in contact with air after preparation; **B**, **C**, and **D** refer to samples that were prepared and held in a stoichiometric nitrogen–hydrogen mixture.

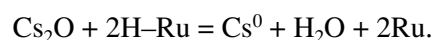
**Table 6.** Changes in the Gibbs energy in the interaction of oxides with atomic hydrogen

Oxide	$\Delta G_{600\text{ K}}^{\circ}$ , kJ/mol
Li <sub>2</sub> O	–193.1
Na <sub>2</sub> O	–311.3
K <sub>2</sub> O	–488.8
Rb <sub>2</sub> O	–511.4
Cs <sub>2</sub> O	–377.8
BeO	–94.1

Note: Data required for the calculations were taken from [30–32].

A compound of ruthenium and cesium was formed in the course of calcination in argon; active centers containing catalyst components in a metallic state were formed during the subsequent reduction of this compound. In this case, the reduction of ruthenium with hydrogen is a thermodynamically allowed process, whereas alkali metal compounds in an oxidation state of +1 are not reduced with molecular hydrogen in accordance with classical thermodynamics. In the series of normal electrode potentials, alkali metals are at the left of a normal hydrogen electrode, whose potential is taken as zero, and exhibit high negative values [29] ( $E_0 = -2.92$  V for  $\text{K} \Rightarrow \text{K}^+ + \text{e}^-$ ;  $E_0 = -3.02$  V for  $\text{Cs} \Rightarrow \text{Cs}^+ + \text{e}^-$ ). Consequently, an alkaline cation  $\text{M}^+$  is not an oxidizing agent with respect to hydrogen. At the same time, according to XPS data, the prepared catalyst contained cesium metal (Table 5, sample C). This can be explained by the fact that the hydrogen atom or hydride ion is bound to the ruthenium atom rather than the hydrogen molecule enters into the reaction; ruthenium is capable of activating hydrogen with the cleavage of H–H bonds and the formation of surface Ru–H bonds. In this case, Cs<sub>2</sub>O is reduced with the participation of H atoms or even H<sup>–</sup> rather than molecular hydrogen. This is another reaction, which can be thermodynamically allowed. A calculation performed for the reaction of Cs<sub>2</sub>O reduction with the hydrogen atom ( $\text{Cs}_2\text{O} + 2\text{H} = \text{Cs}^0 + \text{H}_2\text{O}$ ) demonstrated that  $\Delta G$  for this reaction has a great negative value (Table 6), which corresponds to the practically irreversible occurrence of this reaction under the specified conditions.

The following reaction with the participation of hydrogen atoms associated with ruthenium should be considered more strictly:



Note that Aika *et al.* [33] explained the formation of cesium metal by the cesium oxide disproportionation  $2\text{Cs}_2\text{O} = \text{Cs}_2\text{O}_2 + 2\text{Cs}$ . However, this reaction scheme does not take into account the reducing atmosphere of ammonia synthesis, which atmosphere resulted in the formation of cesium metal (Fig. 2, spectrum 2) in our case (sample C). Samples **B** and **D** exhibited intermediate binding energies, which are likely related to the simultaneous presence of Cs metal and Cs<sup>+</sup> in Cs<sub>2</sub>O and in the Cs–O–Ru surface compound. The calculated ratios between the atomic concentrations of Ru and Cs in a near-surface layer of the catalyst provided support for the assumption on the blocking of a portion of the active metal by an alkaline promoter in support pores (Table 7).

The values of Ru/Cs in active samples **E** and **F** were much higher than the ratio for practically inactive sample **G**: 0.47–0.42 and 0.07, respectively. The argon etching of the surface of the catalysts resulted in the removal of a layer of 1 to 2 nm and in an outcrop of ruthenium at the surface, which manifested itself in an increase in the Ru/Cs ratio.

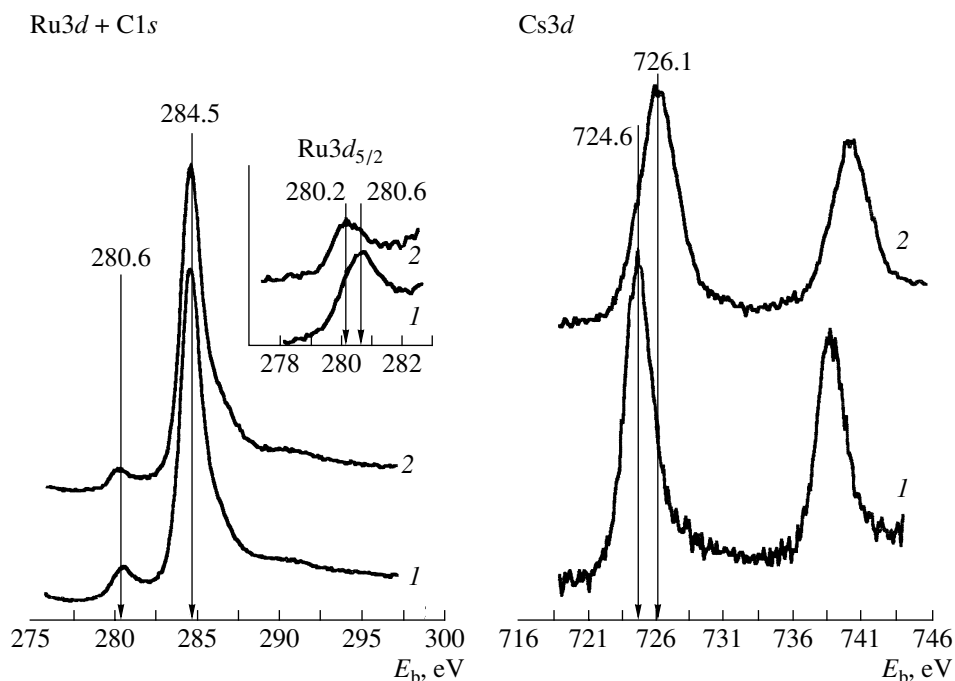


Fig. 2. Ru3d, C1s, and Cs3d XPS spectra of catalyst samples (1) A and (2) C.

**(b) EXAFS study of the catalysts.** The phase state of ruthenium was identified from EXAFS data based on the characteristics considered below. The Ru–Ru distances (~0.27, 0.38, and 0.43 nm) are characteristic of ruthenium metal, whereas the Ru–O and Ru–O–Ru distances are characteristic of RuO<sub>2</sub>. The Ru–O distances for the octahedral and tetrahedral environments of ruthenium are close to 0.2 and 0.17–0.18 nm, respectively. Thus, the type of oxygen environment of ruthenium can be determined from the Ru–O distance. The fraction of ruthenium in an oxidized state can be determined by comparing the measured coordination number of the Ru–O bond and the true coordination number (4 or 6). The formation of a ruthenium dioxide phase was detected by the appearance of a Ru–O–Ru distance

of ~0.31 nm. The absence of this distance is indicative of the formation of a mixed Ru–Cs oxide.

Table 8 summarized the data on the nearest interatomic distances for reference samples and catalysts. The results of EXAFS measurements are consistent with the above XPS data on the state of ruthenium in Ru–Cs catalysts. Only ruthenium metal was detected in a reduced catalyst. After keeping a sample of Ru/Sibunit in air in the course of supporting a promoter and drying, ~40% ruthenium was converted into RuO<sub>2</sub>. These results are indicative of the deep oxidation of supported ruthenium on contact of the sample with air because the EXAFS technique provides information on the entire volume of the catalyst. It is believed that the subsequent calcination in argon is favorable for the interaction of cesium oxide with RuO<sub>2</sub> to form the

Table 7. Ratio between the atomic concentrations of Ru and Cs in 4%Ru–13.6%Cs/Sibunit catalysts according to XPS data

Sample*	Rate of NH <sub>3</sub> synthesis*, (g NH <sub>3</sub> ) (g Cat) <sup>-1</sup> h <sup>-1</sup>	Ru/Cs ratio in the reduced catalyst	Ru/Cs ratio after argon etching
Ru–Cs/Sibunit (E)	0.052	0.47	0.82
Ru–Cs/Sibunit (F)	0.039	0.42	0.86
Ru–Cs/Sibunit (G)	0.00	0.07	—

Note: An ammonia complex is the precursor of Ru, and CsNO<sub>3</sub> is the precursor of Cs.

\* E and F refer to the samples that were initially calcined in argon and then reduced in hydrogen; G refers to the sample that was initially reduced in hydrogen and then calcined in argon.

\*\* At 593 K; 0.6 MPa; 1300 h<sup>-1</sup>; [H<sub>2</sub>] : [N<sub>2</sub>] = 3 : 1.

**Table 8.** EXAFS data for 4%Ru–13.6%Cs/Sibunit catalysts

Sample	Distance, nm
Ru <sub>met</sub>	0.265, 0.270, 0.379 (Ru–Ru)
RuO <sub>2</sub>	0.199 (Ru–O)
Prepared catalyst	0.270, 0.376 (Ru–Ru)
Sample after the stage of supporting CsNO <sub>3</sub> and drying in air	0.199 Ru–O (~40% RuO <sub>2</sub> )
	0.270 Ru–Ru ~(60% Ru)
	0.315 Ru–O–Ru

CsRu<sub>4</sub>O<sub>8</sub> ruthenate. The decomposition of this compound in a reducing atmosphere results in the formation of highly dispersed ruthenium metal particles modified with an alkaline component. These particles are the active centers of a catalyst for ammonia synthesis; however, there is no direct evidence for this assumption.

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