ISSN 1070-4272, Russian Journal of Applied Chemistry, 2007, Vol. 80, No. 2, pp. 193–200. © Pleiades Publishing, Ltd., 2007. Original Russian Text © S.V. Volkov, L.B. Khar'kova, Z.A. Fokina, O.G. Yanko, P.E. Strizhak, G.R. Kosmambetova, V.I. Gritsenko, A.M. Korduban, 2007, published in Zhurnal Prikladnoi Khimii, 2007, Vol. 80, No. 2, pp. 195–201.

> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

## New Cluster-Type Rhodium Selenochlorides in Oxidative Carbonylation of Methane

# S. V. Volkov, L. B. Khar'kova, Z. A. Fokina, O. G. Yanko, P. E. Strizhak, G. R. Kosmambetova, V. I. Gritsenko, and A. M. Korduban

Vernadskii Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

Kurdyumov Institute of Metal-Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine

Received March 30, 2006; in final form, October 2006

Abstract—New rhodium selenochlorides  $Rh_4Se_{16}Cl_{10}$  and  $Rh_4Se_{18}Cl_{10}$  whose structure is based on the cluster "cubane"  $[Rh_4(\mu_3-Se)_4]$  and products of their thermal transformations were obtained. The catalytic properties of the compounds on various carbon and silica supports in oxidative carbonylation of methane in the gas phase and their dependence on the catalyst preparation technique, type of support, and size of its nanopores were analyzed.

**DOI:** 10.1134/S107042720702005X

The ability to coordinate in the inner coordination sphere both organic and inorganic ligands creates a wide variety of complex compounds of rhodium, with the resulting opportunity to use these systems to develop catalytic systems with controllable functional properties. Possibly promising objects as catalysts for organic synthesis are chalcogenide and chalcohalide compounds of rhodium, synthesized in nonaqueous organic media without use of expensive templates [1, 2], and products of thermal destruction of these compounds. In systems of this kind, activation and conversion of reagents may occur not only at the central metal atoms, but also at chalcogenide sites. As a result, rhodium chalcohalides may be of particular interest for direct synthesis of complex substances from simple molecules. Single-stage synthesis of alcohols, aldehydes, acids, and esters from methane, carbon monoxide, and oxygen is a possible alternative to the multistage and energy-intensive processing of natural gas, which includes stages of steam reforming of methane into a mixture of H<sub>2</sub> and CO (3:1), high-temperature conversion of a mixture of  $H_2$  and CO (2:1) into methanol, and subsequent synthesis of aromatic oxygen-containing compounds from methanol [3].

The reaction of oxidative carbonylation of methane to give acetic acid was first performed in the liquid phase under elevated pressure [4], but carrying out the reaction in a heterogeneous catalytic system under atmospheric pressure is a simpler and more attractive method [5–8]. In this case, no aggressive and toxic solvents are used and liquid reaction products are easily removed from the reaction mixture.

In this study, catalysts prepared by deposition of new cluster-type rhodium selenochlorides onto silica and porous carbon materials in the reaction of oxidative carbonylation of methane to give oxygen-containing compounds were examined.

### EXPERIMENTAL

Rhodium selenochlorides were synthesized in the medium of Se<sub>2</sub>Cl<sub>2</sub>, with rhodium(III) chloride RhCl<sub>3</sub> · 4H<sub>2</sub>O used as a reaction form. In this medium, selenium can be present in various states and oxidation levels: as neutral molecules Se<sub>2</sub>Cl<sub>2</sub>, anions, Se<sup>2-</sup>, chain anions Se<sup>2-</sup><sub>n</sub> or molecules Se<sup>0</sup><sub>n</sub>, selenium dioxide SeO<sub>2</sub>, and selenyl dichloride SeOCl<sub>2</sub>. For this reason, the first stage of synthesis was performed at 80–90°C in the course of 120 h (RhCl<sub>3</sub> · 4H<sub>2</sub>O : Se<sub>2</sub>Cl<sub>2</sub> = 1 : 10) in an open reactor to enable release of the gaseous products, H<sub>2</sub>Se and HCl. In the second stage, the reactor was sealed and the heating was continued at 100°C in two different temperature modes:



**Fig. 1.** IR spectra: (a)  $Rh_4Se_{16}Cl_{10}$ ,  $Rh_4Se_{18}Cl_{10}$  and (b)  $Rh_3Se_3Cl$ ,  $Rh_3Se_5Cl$ ; (c) variation of the relative intensities of lines of the Raman spectrum of  $Rh_4Se_{18}Cl_{10}$  in the course of 2 h. (A) Absorption and (v) wave number.

with cyclic heating–cooling (60–80 h) and with continuous heating (180 h). The forming solid products,  $Rh_4Se_{16}Cl_{10}$  (1) and  $Rh_4Se_{18}Cl_{10}$  (2), were yielded by the following reactions

$$4RhCl_{3} \cdot 4H_{2}O + 12H_{2}O + 15Se_{2}Cl_{2} = Rh_{4}Se_{16}Cl_{10} + 32HCl + 6Se + 8SeO_{2},$$

 $\begin{aligned} 4 \text{RhCl}_3 \cdot 4 \text{H}_2 \text{O} &+ 12 \text{H}_2 \text{O} &+ 23 \text{Se}_2 \text{Cl}_2 &= \text{Rh}_4 \text{Se}_{18} \text{Cl}_{10} \\ &+ 32 \text{HCl} &+ 16 \text{Se} &+ 8 \text{SeOCl}_2 &+ 4 \text{SeO}_2. \end{aligned}$ 

The thermal decomposition products,  $Rh_3Se_3Cl$  and  $Rh_3Se_5Cl$ , were obtained in 40 h at 345 and 320°C in accordance with the reactions

$$3Rh_4Se_{16}Cl_{10} \xrightarrow{345^{\circ}C} 4Rh_3Se_3Cl + 13Se_2Cl_2 + 10Se,$$
  
$$3Rh_4Se_{18}Cl_{10} \xrightarrow{320^{\circ}C} 4Rh_3Se_5Cl + 13Se_2Cl_2 + 8Se.$$

Rhodium selenochlorides were studied using a set of mutually complementary physicochemical techniques: vibrational and X-ray photoelectron (XPS) spectroscopies; X-ray phase, thermal, and elemental chemical analyses. It was found that the complexes contain the structural fragments  $\mu$ -Se<sup>2-</sup>,  $\mu$ -Se<sup>2-</sup>,  $\mu_3$ -Se<sup>2-</sup>, Cl<sup>-</sup><sub>term</sub>, and Cl<sup>-</sup><sub>bridge</sub>, as well as coordinated Se<sub>2</sub>Cl<sub>2</sub> molecules.

A thermographic study was performed on an MOM Q-1500 instrument (Hungary) in the temperature range  $20-1000^{\circ}$ C (sample heating rate 5 deg min<sup>-1</sup>, sensitivity 250  $\mu$ V, sample weight 0.5–1 g) in special cuvettes under a constant lowered pressure, with gaseous decomposition products condensed in liquid nitrogen. To isolate solid thermolysis products, the starting compounds were kept at the temperatures of the effects recorded in the thermograms (345 and 320°C) for 40 h to constant weight of the solid residue.

For all the compounds formed both by direct synthesis and by thermal destruction, a chemical elemental analysis was made. The content of the metal was determined gravimetrically upon reduction of weighed portions of the compounds in a flow of hydrogen at 20–1000°C; that of chlorine, by argentometry in alkaline solutions through which gases evolved in reduction by hydrogen were passed; and that of selenium, from the difference.

IR spectra of the compounds suspended in Nujol were recorded on Nicolet Magna-IR 750 and Specord M-80 spectrometers,<sup>1</sup> and Raman spectra, on a DFS-24 spectrometer with a He–Ne laser excitation source (632.8 nm).

XPS spectra were measured with a modified ES-2402 electron spectrometer. An X-ray gun with a magnetic anode ( $E_{MgK_a} = 1253.6 \text{ eV}$ , P = 300 W) served as excitation source.

The catalytic properties of the samples were studied by passing a gas mixture with component ratio

<sup>&</sup>lt;sup>1</sup> The authors are grateful to B.V. Lokshin and Z.S. Klemenkova, staff members of INESS (Moscow), for assistance in IR spectral measurements.

CH<sub>4</sub>: CO : O<sub>2</sub> = 10 : 4 : 1 through a quartz reactor with an inner diameter of 10 mm. The catalyst volume was 1.0 cm<sup>3</sup>. The experiments were performed under atmospheric pressure in the temperature range 400– 600°C at a volumetric flow rate of 6000 h<sup>-1</sup>. The specific surface area of the samples,  $S_{\text{BET}}$ , was found by the method of thermal desorption of nitrogen. The starting substances and gaseous reaction products (CH<sub>4</sub>, CO, O<sub>2</sub>, CO<sub>2</sub>) were analyzed with an LKhM-80 gas chromatograph equipped with a heat-conductivity detector. Liquid reaction products were frozen-out in a trap at a temperature of  $-70^{\circ}$ C and then analyzed on a Khrom-5 chromatograph with a flame-ionization detector and a column packed with Separon-BD sorbent.

The vibrational spectra of Rh<sub>4</sub>Se<sub>16</sub>Cl<sub>10</sub> and  $Rh_4Se_{18}Cl_{10}$  are identical. The spectra contain a complex set of frequencies repeated in the IR and Raman spectra (Figs. 1a, 1c). The broad band at 360-350 cm<sup>-1</sup> (IR), and the strong band at 350 cm<sup>-1</sup> (Raman) are associated with stretching vibrations of the Se-Cl bond in the  $Se_2Cl_2$  molecule. The frequencies 334, 315, 307 cm<sup>-1</sup> (IR)<sup>2</sup> and 331, 319, 310 cm<sup>-1</sup> (Raman) can be attributed to stretching vibrations of the Rh-Cl and Rh- $\mu_3$ -Se<sup>2-</sup> bonds. The weak bands at 274, 251, and 239  $cm^{-1}$  (IR) and the lines at 269, 255, and 240 cm<sup>-1</sup> (Raman) lie in the range of vibrations of the Se–Se bond in chain and annular  $Se_n$  molecules. From the whole set of frequencies of deformation vibrations, which lie below  $200 \text{ cm}^{-1}$ , the following frequencies can be distinguished: 146, 138 cm<sup>-1</sup> (IR) and 149, 138 cm<sup>-1</sup> (Raman). These frequencies correspond to deformation vibrations of the SeSeCl bonds in the individual  $\text{Se}_2\text{Cl}_2$  molecule (149 and 135 cm<sup>-1</sup>). Particular attention is attracted by the strong band at 215  $\text{cm}^{-1}$  (IR) and the line at 209  $\text{cm}^{-1}$  (Raman). The intensity of this line in the Raman spectrum sharply decreases under the action of laser light, whereas the intensities of the other lines remain unchanged (Fig. 1c). This frequency can be attributed to vibrations of the (Se–Se)<sup>0</sup> group coordinatively bound to rhodium. This group lies as a kind of dumbbell over faces of the cubane core. Relatively weakly bound  $\mu$ -Se<sub>2</sub> fragments can be split-off under the action of laser light, with the cubane structure preserved.

The IR spectra of the products of thermal decomposition,  $Rh_3Se_3Cl$  and  $Rh_3Se_5Cl$ , are identical (Fig. 1b), but strongly differ from the IR spectra of the starting rhodium selenochlorides,  $Rh_4Se_{16}Cl_{10}$  and  $Rh_4Se_{18}Cl_{10}$ , which points to profound changes in the original molecular structure. The doublet at 318 and 311 cm<sup>-1</sup> corresponds to vibrations of Rh–Cl and  $Rh_{-\mu_3}$ -Se<sup>2-</sup>. The broad absorption band peaked at 270 cm<sup>-1</sup> is associated with vibrations of the Rh–Se<sup>2-</sup>

**Table 1.** Rh $3d_{5/2}$  XPS spectra of rhodium selenochlorides

Se3d	<i>I</i> of component <i>a</i>	<i>I</i> of component <i>b</i>	<i>I</i> of component <i>c</i>		
FWHM = 1.5 eV	at $E_{\rm b}$ , eV				
	306.4 308.3		309.6		
$Rh_4Se_{16}Cl_{10}$	_	_	1.0		
$Rh_3Se_3Cl$ $Rh_5Se_3Cl$	_	1.0	_		
Rh <sub>3</sub> Se <sub>5</sub> Cl/F1	0.2	0.8	_		

and Se–Se bonds, which indicates that selenide bridges  $\mu$ -Se<sup>2-</sup> and "perselenide" fragments  $\mu$ -Se<sup>2-</sup> appear in the structure.

The Rh3 $d_{5/2}$  XPS spectra of the compounds Rh<sub>4</sub>Se<sub>16</sub>Cl<sub>10</sub> and Rh<sub>4</sub>Se<sub>18</sub>Cl<sub>10</sub>, Rh<sub>3</sub>Se<sub>3</sub>Cl and Rh<sub>3</sub>Se<sub>5</sub>Cl, and of Rh<sub>3</sub>Se<sub>5</sub>Cl on a carbon support are presented in Table 1 and Fig. 2. The spectra were analyzed by decomposition into components by the Gauss–Newton method. The Rh3 $d_{5/2}$  XPS spectra of the compounds Rh<sub>4</sub>Se<sub>16</sub>Cl<sub>10</sub> and Rh<sub>4</sub>Se<sub>18</sub>Cl<sub>10</sub> (Fig. 2a) have a single component (c) with Rh3 $d_{5/2}$  $E_b$  = 309.6 eV, which indicates that rhodium is present in the oxidation state +3. The spectra of the thermal decomposition products Rh<sub>3</sub>Se<sub>3</sub>Cl and Rh<sub>3</sub>Se<sub>5</sub>Cl (Fig. 2b) contain a single component (b) with Rh3 $d_{5/2}$ 



**Fig. 2.**  $\text{Rh}_{3d_{5/2}}$  XPS spectra of rhodium selenochlorides: (a)  $\text{Rh}_4\text{Se}_{16}\text{Cl}_{10}$ ,  $\text{Rh}_4\text{Se}_{18}\text{Cl}_{10}$ ; (b)  $\text{Rh}_3\text{Se}_3\text{Cl}$ ,  $\text{Rh}_3\text{Se}_5\text{Cl}$ ; and (c)  $\text{Rh}_3\text{Se}_5\text{Cl}$  on a carbon support (fullerene black F1). (*I*) Intensity and (*E*) energy.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 80 No. 2 2007

$Cl 2p_{3/2}$ FWHM = 1.2 eV	I of a component at $E_{\rm b}$ , eV			
$Rh_4Se_{16}Cl_{10}$ $Rh_4Se_{16}Cl_{10}$	0.64/197.8	0.36/198.1		
$\frac{Rh_4Se_18E1_10}{Rh_3Se_3Cl}$ $\frac{Rh_3Se_5Cl}{Rh_3Se_5Cl}$	0.42/197.2	0.53/198.0	0.05/200.5	

**Table 2.**  $Cl_{2p_{3/2}}$  XPS spectra of rhodium selenochlorides

Table 3. Se3d XPS spectra of rhodium selenochlorides

Se3 <i>d</i> FWHM = 1.5 eV	$I$ of a component at $E_{\rm b}$ , eV			
Rh <sub>4</sub> Se <sub>16</sub> Cl <sub>10</sub>		0.24/55.9	0.53/56.5	0.23/57.0
$     Rh_4Se_{18}Cl_{10}      Rh_3Se_3Cl      Rh_3Se_5Cl $	0.38/54.6	0.62/55.3		

 $E_{\rm b}$  = 308.3 eV, which may be due both to a significant decrease in the number of chlorine atoms substituted by selenium and to a lowering of the oxidation state of rhodium.

The Cl2 $p_{3/2}$  spectra of the starting rhodium selenochlorides (Table 2) contain two components with  $Cl2p_{3/2} E_b$  197 and 198 eV, which can be attributed, according to published data [9], to a bridging chloride atom in the polymeric structure of rhodium selenochlorides. The Se3d spectra of rhodium selenochlorides (Table 3) have three components, which points to three different energy states of selenium in these molecules. To the  $\mu_3$ -Se<sup>2-</sup> group is attributed the peak at Se3d  $E_{\rm b}$  = 55.9 eV. This energy somewhat exceeds the corresponding value for selenides MSe with Se3d $E_{\rm b} = 53.3-54.5$  eV [9] and is caused by a decrease in the amount of negative charge on the selenium atom bonded to three, rather than one, metal atoms. The component Se3d  $E_{\rm b}$  = 56.5 eV is attributed to -Se-Se- chain fragments with zero charge and is larger than that in elementary selenium, in which Se3d  $E_{\rm b} = 55.5$  eV because of the complexation. The higher-lying line Se3d  $E_{\rm b}$  = 57.0 eV must be associated with the Se<sub>2</sub>Cl<sub>2</sub> molecule, in which the strong "electrophile," chlorine, makes greater the positive charge on selenium atoms, with the complexation acting in the same direction.

Selenium derivatives are characterized by formation of multinuclear complexes whose structure is based on a cubane-like core  $[Rh_4(\mu_3-Se)_4]$  [10]. The "cubane" structure [Rh<sub>4</sub>( $\mu_3$ -Se)<sub>4</sub>] is due to a specific electronic structure of the selenium atom, which has free, comparatively low-lying *d*-orbitals capable of additional bonding [11]. Therefore, analysis of the vibrational and XPS spectra suggests that the structure of the compounds obtained is Rh<sub>4</sub>( $\mu_3$ -Se)<sub>4</sub>( $\mu$ -Se<sub>2</sub>)<sub>3</sub>Cl<sub>4</sub>(Se<sub>2</sub>Cl<sub>2</sub>)<sub>3</sub> and Rh<sub>4</sub>( $\mu_3$ -Se)<sub>4</sub>( $\mu$ -Se<sub>2</sub>)<sub>4</sub>Cl<sub>4</sub>(Se<sub>2</sub>Cl<sub>2</sub>)<sub>3</sub>. The intensity ratio of the lines in the Se3*d* spectrum, 0.23 : 0.53 : 0.24, approximately corresponds to the selenium distribution among the fragments.

The Se3*d* spectra of the thermal decomposition products, Rh<sub>3</sub>Se<sub>3</sub>Cl and Rh<sub>3</sub>Se<sub>5</sub>Cl, have two components with Se3*d*  $E_b$  = 54.6 and 55.3 eV. The binding energy of 54.6 eV is typical of metal selenides. This means that the charge on selenium is close to -2e and confirms the conclusion furnished by vibrational spectroscopy, according to which the molecules of the starting selenochlorides undergo a deep transformation in thermal decomposition to give "selenide" fragments  $\mu$ -Se<sup>2-</sup> and  $\mu$ -Se<sup>2-</sup>. The value of 55.3 eV can be attributed to the  $\mu_3$ -Se<sup>2-</sup> fragment.

On heating rhodium selenochlorides,  $Se_2Cl_2$ molecules and  $Se_2$  "dumbbells" are eliminated and the remaining molecular structure is constituted by the  $\mu_3$ -Se fragment linking three rhodium atoms, between which the fragments  $\mu$ -Se and  $\mu$ -Se<sub>2</sub> are situated. The structure of the compounds can be represented as Rh<sub>3</sub>( $\mu_3$ -Se)( $\mu$ -Se)<sub>2</sub>Cl and Rh<sub>3</sub>( $\mu_3$ -Se)( $\mu$ -Se)<sub>2</sub>( $\mu$ -Se<sub>2</sub>)Cl.

The compositions of these compounds might indicate that rhodium is in the oxidation state +1 and  $\mu$ -SE and  $\mu$ -Se<sub>2</sub> fragments have zero charges. However, the IR and XPS spectra more likely correspond to selenide fragments  $\mu$ -Se<sup>2-</sup> and  $\mu$ -Se<sup>2-</sup><sub>2</sub>. In this case, rhodium retains the oxidation state +3.

A decomposition of the Rh3 $d_{5/2}$  XPS spectrum of a sample synthesized in Se<sub>2</sub>Cl<sub>2</sub> in the presence of a carbon support gave two lines indicating that there exist two different states of rhodium (Fig. 2c, Table 1). Presumably, the line Rh3 $d_{5/2}$   $E_b$  = 308.3 eV with the highest intensity (b) belongs to rhodium which is possibly in the oxidation state Rh<sup>2+</sup> in a ligand environment of selenium and chlorine, and the lowlying weak line Rh3 $d_{5/2}$   $E_b$  = 306.4 eV is associated with Rh<sup>0</sup> (a), i.e., with metallic rhodium. The second line lies at somewhat lower energies, compared with Rh3 $d_{5/2}$   $E_b$  = 307.2 eV for pure metallic rhodium, which may be due to interaction of adsorbed rhodium with the carbon of the substrate. The presence of three lines in the spectrum indicates that the thermal decomposition of Rh<sub>4</sub>Se<sub>18</sub>Cl<sub>10</sub> in the presence of carbon

Type of Preparation		T, °C	Output capacity, $\mu mol g_{cat}^{-1} h^{-1}$			
support method	CH <sub>3</sub> OH		C <sub>2</sub> H <sub>5</sub> OH	СН <sub>3</sub> СООН	C <sub>2</sub> H <sub>5</sub> COOH	
<b>S</b> 1	II	400	_	_	_	_
		450	_	_	_	_
		500	_	0.0412	0.026	_
		550	_	0.018	0.009	_
<b>S</b> 1	III	400	_	-	_	_
		450	_	0.077	_	_
		500	_	0.006	_	_
		550	_	-	_	_
<b>S</b> 1	IV	400	-	—	0.047	_
		450	-	—	0.971	_
		500	-	0.103	0.090	_
		550	-	—	0.125	_
S2	IV	400	-	—	-	_
		450	0.040	1.391	0.050	0.04
		500	-	—	-	_
		550	0.04	0.001	0.015	0.04
F1	IV	400	-	—	_	—
		450	-	0.022	0.014	—
		500	-	0.08	_	—
		550	-	—	_	—
F2	IV	400	-	0.038	0.028	—
		450	0.031	_	0.056	_
		500	0.019	_	_	_
		550	_	_	_	_

**Table 4.** Catalytic properties of rhodium selenochlorides on carbon supports in oxidative carbonylation of methane [reaction mixture (MPa): CH<sub>4</sub> 0.066, CO 0.027, O<sub>2</sub> 0.007; volumetric flow rate of the process 6000  $h^{-1}$ ]

supports yields three potentially possible catalytically active centers.

Tests with various catalyst supports (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, MgO) in synthesis of rhodium selenochlorides demonstrated that only carbon materials are stable in Se<sub>2</sub>Cl<sub>2</sub>.

Catalysts containing rhodium compounds on carbon supports (SKT-1 carbon: S1,  $S_{sp} = 700 \text{ m}^2 \text{ g}^{-1}$ ; spherical enterosorbent: S2,  $S_{sp} = 1400 \text{ m}^2 \text{ g}^{-1}$ ; and two fractions of fullerene black: F1,  $S_{sp} = 20 \text{ m}^2 \text{ g}^{-1}$ and F2, 65 m<sup>2</sup> g<sup>-1</sup>, produced by pyrolysis of styrene and a copolymer of divinylbenzene) were prepared by the following four methods. The first included impregnation of carbon supports with an aqueous solution of RhCl<sub>3</sub> and subsequent thermal decomposition at 120°C for 5 h and 320°C for 40 h (method I). The second was based on thermal decomposition of a mechanical mixture of a preliminarily synthesized Rh<sub>4</sub>Se<sub>18</sub>Cl<sub>10</sub> and carbon supports (method II). In the third technique, rhodium selenochloride Rh<sub>4</sub>Se<sub>18</sub>Cl<sub>10</sub> was synthesized on the surface of carbon supports and then subjected to thermal destruction (method III). Finally, the fourth procedure included mechanical mixing of the thermal decomposition product Rh<sub>3</sub>Se<sub>5</sub>Cl with carbon supports (method IV).

The thermal decomposition of samples prepared using methods II and III was carried out at 320°C for 40 h.

The data on the catalytic activity of the samples are listed in Table 4. The first set of catalysts was prepared by ordinary impregnation of carbon supports with an aqueous solution of rhodium chloride (method I). Tests of impregnated samples in oxidative carbonylation of methane revealed that  $CO_2$  is the only reaction product.

It was found in a study of catalysts containing rhodium selenochlorides that methanol and acetic and propionic acids are formed in addition to the main reaction product,  $CO_2$  (Table 4). A comparison of the data in Table 4 demonstrated that the activity and

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 80 No. 2 2007



**Fig. 3.** Output capacity of  $Rh_3Se_3Cl/SiO_2$  catalysts for (a) methanol, (b) ethanol, and (c) acetic acid in relation to the process temperature *T* and support pore size. (*A*) Output capacity and (*r*) pore radius.

selectivity of rhodium selenochlorides on carbon supports largely depends on the catalyst preparation technique. This result can be illustrated by the example of a catalyst deposited on an S1 support by three different methods. It can be seen from Table 4 that  $C_2$ -ox-

Table 5. Texture characteristics of silica supports

Support	$S, m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$	Pore diameter, nm
KSK	270	0.76–0.93	12–15
KSS-3	520	0.920	7
KSS-4	650	0.76	5
KSS-5	500	0.71	3
ShSM	720	0.40	1.1–1.2

ygenates are formed on the samples synthesized by methods II and IV, but the quantitative composition of the products depends on the catalyst preparation method. A higher output capacity for acetic acid  $(0.971 \ \mu\text{mol g}_{cat}^{-1} \text{h}^{-1})$  is observed in the case when the support is mixed with the thermal destruction product (method IV), compared with the starting selenochloride (method II). Only ethanol is found in liquid reaction products formed on a sample synthesized by introducing a support into the starting reaction mixture RhCl<sub>3</sub> · 4H<sub>2</sub>O : Se<sub>2</sub>Cl<sub>2</sub> = 1 : 10 (method III). A test in the reaction of samples prepared by method IV on other carbon supports demonstrated that acetic acid and alcohols are formed on all the catalysts, but the output capacity of the process depends on the nature of a carbon support.

The data obtained show that the widest variety of reaction products (methanol, ethanol, acetic and propionic acids) is observed when the catalyst is prepared by mechanical mixing of the thermal destruction product  $Rh_3Se_5Cl$  with carbon support S2, spherical enterosorbent.

The next series of experiments was devoted to catalytic properties of rhodium selenochlorides on silica supports, synthesized by their mechanical mixing with  $Rh_3Se_3Cl$ , which is a product of thermal destruction of a cluster selenochloride  $Rh_4Se_{16}Cl_{10}$ , and of samples prepared by impregnation of the KSS-5 support with rhodium trichloride and its mixture with ammonium metavanadate. As supports for rhodium selenochlorides served the following silicas: KSS-5, KSS-4, KSS-3, ShSM, and KSK, which differ in specific surface area, volume, and average pore size (Table 5).

It has been shown previously that pure silica supports are inactive in oxidative carbonylation of methane carbonylation and insignificant amounts of methyl acetate  $(0.05-0.5 \ \mu mol \ g_{cat}^{-1} \ h^{-1})$  are formed on samples prepared by introduction of ammonium metavanadate in template synthesis of MCM-41 mesoporous silica [8]. Only gaseous products, carbon oxides, were formed on catalysts prepared by impregnation of the supports KSS-5, KSS-4, KSS-3, ShSM, and KSK supports with a rhodium trichloride solution. Trace amounts of acetic acid  $(0.02 \ \mu mol \ g_{cat}^{-1} \ h^{-1})$ were found on a catalyst synthesized by joint deposition of rhodium trichloride and ammonium metavanadate onto a KSS-5 silica, with the catalyst strongly carbonized in the course of the reaction. Methanol, ethanol, and acetic acid were formed in oxidative carbonylation of methane on samples prepared by mixing Rh<sub>3</sub>Se<sub>3</sub>Cl with silicas. Figure 3

shows how the output capacity of the catalysts for methanol, ethanol, and acetic acid depends on the process temperature and support pore size. As can be seen in Fig. 3a, the highest output capacity for methanol (1.5  $\mu$ mol g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>) is observed on the Rh<sub>3</sub>Se<sub>3</sub>Cl/KSS-3 sample with a support pore size of 3 nm. Acetic acid is mostly formed on Rh<sub>3</sub>Se<sub>3</sub>Cl/KSS-4 and Rh<sub>3</sub>Se<sub>3</sub>Cl/KSS-5 samples with a pore size of 7–8 nm. As the support pore size increases to 12 nm, ethanol becomes the main liquid product of the process.

It was shown in [12] that single-stage synthesis from methane and carbon monoxide yields methanol in the presence of nitrogen(II) oxide as oxidizing agent and iron(III) phosphate as catalyst, and methyl acetate upon addition of highly dispersed  $Rh_2O_3$  to the catalyst. A conclusion was made on the basis of these data that presence of a single active center (FePO<sub>4</sub>) on the catalyst surface leads to activation of methane to give a methyl radical and, subsequently,  $C_1$ -oxygenate. Presence of a second closely lying active center (Rh<sub>2</sub>O<sub>3</sub>) enables carbonylation and makes it possible to obtain longer-chain  $C_2$ - $C_3$ -oxygenates.

It was experimentally demonstrated that oxygencontaining products are formed in oxidative carbonylation of methane either on a rhodium selenochloride or in the joint presence of rhodium and vanadium oxides. The formation of acetic acid on the rhodium-vanadium catalyst can be attributed, by analogy with [12], to presence of two active centers responsible for activation of methane and its subsequent carbonylation into acetic acid. Use of rhodium selenochloride instead of rhodium and vanadium oxides can improve the output capacity for acetic acid by more than an order of magnitude. In addition, the reaction of oxidative carbonylation of methane yields ethanol and ethanol.

A detailed study of the structure of active centers of the reaction of oxidative carbonylation of methane on rhodium selenochlorides is beyond the scope of this study. The suggested structure of both the starting rhodium selenochlorides,  $Rh_4(\mu_3-Se)_4(\mu-Se_2)_3Cl_4(Se_2Cl_2)_3$ and  $Rh_4(\mu_3-Se)_4(\mu-Se_2)_4Cl_4(Se_2Cl_2)_3$ , and products of their thermal transformations,  $Rh_3(\mu_3-Se)(\mu-Se)_2Cl$ and  $Rh_3(\mu_3-Se)(\mu-Se)_2(\mu-Se_2)Cl$ , leads to a conclusion that the starting reagents are activated not only on rhodium atoms, but on selenium as well. The subsequent transformations of the activated complex and the qualitative composition of the reaction products strongly depend both on the nature of a support and on its texture characteristics. This makes it possible to regard nanovoids in porous silicas and carbon materials as nanoreactors whose size affects the selectivity of oxidative carbonylation of methane on rhodium selenochlorides [13]. It should be noted that none of the catalyst samples containing rhodium seleno-chlorides was carbonized in the tests, in contrast to the catalyst prepared by impregnation with rhodium trichloride and ammonium metavanadate.

#### CONCLUSIONS

(1) New cluster-type cubane-like rhodium selenochlorides  $Rh_4Se_{16}Cl_{10}$  and  $Rh_4Se_{18}Cl_{10}$  were synthesized and products of their thermal transformations,  $Rh_3Se_3Cl$  and  $Rh_3Se_5Cl$ , were obtained. An analysis of the vibrational (IR, Raman) and  $Rh_3d_{5/2}$ ,  $Se_3d$ , and  $Cl2p_{3/2}$  XPS spectra of these compounds suggested the following structure of the rhodium selenochlorides obtained:  $Rh_4(\mu_3-Se)_4(\mu-Se_2)_3Cl_4(Se_2Cl_2)_3$ and  $Rh_4(\mu_3-Se)_4(\mu-Se_2)_4Cl_4(Se_2Cl_2)_3$ , based on the "cubane" core  $[Rh_4(\mu_3-Se)_4]$ .

(2) The catalytic properties of  $Rh_4Se_{18}Cl_{10}$  and a product of its thermal destruction,  $Rh_3Se_5Cl$ , deposited on various carbon supports were studied in the reaction of oxidative carbonylation of methane. It was shown that, in contrast to samples prepared by impregnation of supports with rhodium trichloride, rhodium selenochlorides exhibit catalytic activity in carbonylation of methane. The output capacity of the process for methanol, ethanol, and acetic acid depends on the method of catalyst preparation and type of a carbon support.

(3) A study of the catalytic properties of a mechanical mixture of rhodium selenochloride  $Rh_3Se_3Cl$ and silicas with various texture characteristics demonstrated that support nanopores can be regarded as nanoreactors whose size affects the output capacity and selectivity of oxidative carbonylation of methane.

#### REFERENCES

- Kosmambetova, G.R., Gritsenko, V.I., Strizhak, P.E., et al. *The Eur. Catalysis Forum "EuropaCat-VI"*, 31.08–4.09, 2003, Austria, Innsbruck, CD: Abstracts, 2003, Poster 1546.
- 2. Kosmambetova, G.R., Gritsenko, V.I., Strizhak, P.E., et al., *Ukr. Khim. Zh.*, 2004, vol. 70, no. 2, pp. 75–80.
- Sheldon, R.A., Chemicals from Synthesis Gas: Catalytic Reactions of CO and H<sub>2</sub>, Dordrecht: Reidel, 1983.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 80 No. 2 2007

- 4. Lin, M. and Sen, F., *Nature*, 1994, vol. 368, pp. 613–615.
- 5. Wilcox, E.M., Roberts, G.W., and Sprivey, J.J., *Catal. Today*, 2003, vol. 88, pp. 83–90.
- 6. Wang, Y., Katagiri, M., and Otsuka, K., Chem. Commun., 1997, pp. 1187–1188.
- Otsuka, K. and Wang, Y., *Appl. Catal., Ser. A*, 2001, vol. 222, pp. 145–161.
- 8. Pavlenko, N.V., Kosmambetova, G.R., Gritsenko, V.I., et al., *Ukr. Khim. Zh.*, 2003, vol. 69, no. 11, pp. 27–32.
- 9. Nefedov, V.I., Rentgenoelektronnaya spektroskopiya

khimicheskikh soedinenii (X-ray Photoelectron Spectroscopy of Chemical Compounds), Moscow: Khimiya, 1984.

- Pekhn'o, V.I., Stepanenko, I.N., Fokina, Z.A., et al., *Zh. Neorg. Khim.*, 2004, vol. 49, no. 5, pp. 813–816.
- 11. Schulz, S., Andruh, M., and Pape, T., *Organometallics*, 1994, vol. 13, pp. 4005–4007.
- 12. Yuan, Q., Zhang, Q., and Wang, Y., J. Catal., 2005, vol. 233, pp. 221–233.
- 13. Buchachenko, A.L., *Usp. Khim.*, 2003, vol. 72, no. 5, pp. 420–437.