ISSN 1070-4272, Russian Journal of Applied Chemistry, 2016, Vol. 89, No. 2, pp. 233−237. © Pleiades Publishing, Ltd., 2016.
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CATALYSIS

Catalytic Properties of $RhSe_2$/Ga/H-ZSM-5 System in the Reaction of Glycerol Dehydration in the Gas Phase

S. V. Volkov[a], L. B. Khar'kova[a], S. A. Baranets[a], O. G. Yanko[a], P. E. Strizhak[b], G. R. Kosmambetova[b], and V. I. Gritsenko[b]

[a] Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine,
pr. Akademika Palladina 32/34, Kyiv, 03142 Ukraine
[b] Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine,
pr. Nauki 31, Kyiv, 03028 Ukraine
e-mail: svyatium@mail.ru

Received August 17, 2015

Abstract—Catalytic properties of the $RhSe_2$/Ga/H-ZSM-5 system formed upon thermal treatment of a mechanical mixture of rhodium selenochloride $Rh_2Se_9Cl_6$ and a gallium-containing zeolite Ga/H-ZSM-5 at 300–340°C in a flow of nitrogen were studied in the course of glycerol dehydration in the gas phase. It was shown that the promotion of Ga/H-ZSM-5 with rhodium selenide $RhSe_2$ makes higher the yield of the target product acrolein.

DOI: 10.1134/S1070427216020117

Rhodium and its compounds are effective catalysts for purification of technological and exhaust gases, hydrogenation of organic compounds, oxidation of ammonia to nitric acid, etc. This is due to its high chemical stability in corrosive media and ability to form complex coordination compounds, which makes it possible to create a prescribed structure of the active center of a catalyst. The specific structural features of the complex compounds in which active metals are surrounded by ligands provide a high selectivity of the catalysts synthesized on their basis in processes of partial conversion of organic compounds [1]. The high selectivity is exhibited in this case not only by the starting complex compounds, but also by products of their thermal decomposition, in which the initial coordination of the active metal is preserved [2].

As objects promising as organic synthesis catalysts may serve chalcogenide and chalcogen-halide rhodium compounds synthesized in nonaqueous inorganic media without use of expensive templates, as well as the products of their thermal decomposition [3]. In contrast to thermally unstable organic complexes, the above inorganic coordination compounds of rhodium are thermally stable up to 300–350°C, and products of their thermal decomposition, up to 900°C, which makes substantially wider the range of their practical applicability in catalysis [4]. It can be assumed that the presence of the ligands S^{2-}, Se^{2-}, and Cl^- in the coordination compounds of this kind provides the formation of acid centers and promotes the activation of complex organic compounds.

About ten chalcogen-halide complexes of rhodium are known, but the catalytic properties have been studied only for some of its selenochlorides ($Rh_4Se_{19}Cl_{11}$, $Rh_2Se_8Cl_5$, $Rh_2Se_9Cl_5$, Rh_3Se_5Cl, Rh_3Se_3Cl) and products of their thermal decomposition on silica gel and carbon supports in the reaction of oxidative carbonylation of methane into C_1–C_3 oxygenates (methanol, methyl acetate, acetic acid) [4–6].

The need to utilize glycerol is due to the large volumes of its formation as a by-product in manufacture of biodiesel via transesterification of fats with low-molecular alcohols [7]. The following compounds may be formed in the course of dehydration: allyl alcohol as a product of splitting-off of a water molecule, acrolein as a product of splitting-off of two molecules of water, and products of glycerol decomposition. The most valuable among the above-mentioned oxygen-containing products is acrolein used in production of solid plastics, esters, and medicinal preparations.

As catalysts for dehydration of glycerol in the gas phase serve oxide systems: modified, natural, and synthetic zeolites, aluminosilicate and silicate mesoporous materials, and systems based on solid heteropolyacids having acid surface properties, which is due to the specific features of glycerol activation [8]. The high catalytic activity of zeolites of the type of ZSM-5 and its hydrogen forms H–ZSM-5 in the course of glycerol dehydration is due to the specific features of their structure and, in particular, to the 3D system of open channels and separation of cations at a large Si/Al ratio, and also to the presence of acid centers [9]. One of ways to raise the activity of systems of the H–ZSM-5 type is by modification with gallium additives for making higher the concentration of acid centers and improving the catalytic properties of the material in the reactions of the acid-base type, including the dehydration of glycerol to acrolein [10–12].

There have been several reports that metal-modified bifunctional catalysts also having redox properties are promising for application in glycerol transformation processes [13, 14]. It was noted that a specific feature of bifunctional systems is the certain structure of an active center, which is an active metal surrounded by ligands.

Previously, it has been found in a study of the catalytic properties of rhodium chalcogen-halides in the course of oxidative carbonylation of methane that the active centers of catalysts of this kind have the form of metallic rhodium and Rh^{3+} in the coordination environment of Cl and Se, which can serve as catalytic centers [3].

The specific features of the chemical composition and structure of metal chalcogen-halides and products of their thermal decomposition suggest that systems of this kind may possess not only redox, but also acid properties, thereby exhibiting bifunctionality. It is noteworthy that the acid properties of rhodium chalcogen-halides and products of their thermal decomposition have not been studied previously.

The goal of our study was to examine the catalytic properties of the $RhSe_2$/Ga/H–ZSM-5 system formed as a result of a thermal treatment of a mechanical mixture of Rh2Se9Cl6 and a gallium-containing zeolite Ga/H–ZSM-5 in the course of glycerol dehydration to acrolein in the gas phase.

EXPERIMENTAL

Rhodium selenochloride of composition $Rh_2Se_9Cl_6$ was produced by the procedure dscribed in [15]. A thermographic study of rhodium selenochloride was carried out on an MOM Q-1500 instrument (Hungary) in the temperature range 20–1000°C (sample heating rate 5 deg min^{-1}, sensitivity 250 μV, weighed portion 0.5–1 g) in special cuvettes under reduced pressure, with condensation of gaseous decomposition products in a trap submerged in liquid nitrogen. To isolate solid thermolysis products, the starting compound was kept at temperatures fixed in the thermogram of the effects for 16–24 h until a constant mass of the solid residue was reached.

An elemental composition of the $Rh_2Se_9Cl_6$ complex and products of its thermal transformations was made with an ElvaX Light X-ray fluorescence spectrometer. IR spectra of the compounds in the form of suspensions in Nujol were recorded with Nicolet Magna-IR 750 spectrometer. Diffraction patterns were obtained on an STOE STADI P diffractometer with a linear position-precision detector.

The acid properties of the surface of the samples were determined by the method of temperature-programmed desorption of ammonia (TPDA). Preliminarily, the samples were heated in a flow of helium at 400°C for 1 h and then cooled to 100°C and saturated with ammonia for 1 h. The thermal desorption of ammonia was examined in the temperature range 100–700°C at a heating rate of 10 deg min^{-1}.

The catalysts were prepared by mechanical mixing of rhodium selenochloride $Rh_2Se_9Cl_6$ (10 wt %, which corresponds to 1.8% Rh in terms of the metal) and high-silica gallium-containing zeolite Ga/H–ZSM-5 (90 wt %). The Si/Al ratio in Ga/H–ZSM-5 was 40/1, and the total concentration of acid centers, 2.341 mM NH_3/g.

The catalytic properties of Ga/H–ZSM-5 and a sample containing rhodium selenochloride $Rh_2Se_9Cl_6$ were studied in a flow-through kinetic installation at various experimental temperatures of 300, 320, and 340°C. A 0.5-cm^3 weighed portion of the catalyst (1–2-mm fraction) was placed between layers (0.5 cm^3 each) of quartz with grain size of 2–3 mm. Three samples were examined at each temperature, with averaged data used in calculations. Preliminarily, a sample was treated in a flow of nitrogen at the experimental temperature, and, therefore, the final formation of the catalyst and the decomposition of $Rh_2Se_9Cl_6$ to rhodium selenide $RhSe_2$ occurred in the course of its thermal treatment in the atmosphere of nitrogen.

The reactor had the form of a quartz tube with inner diameter of 10 mm. A water–glycerol mixture (10 vol % glycerol, which corresponds to 12.6 wt %) was delivered at a rate of 0.033 mL min^{-1} into the mixer heated to 200°C, with nitrogen gas fed therein at a rate of 30 mL min^{-1}. The

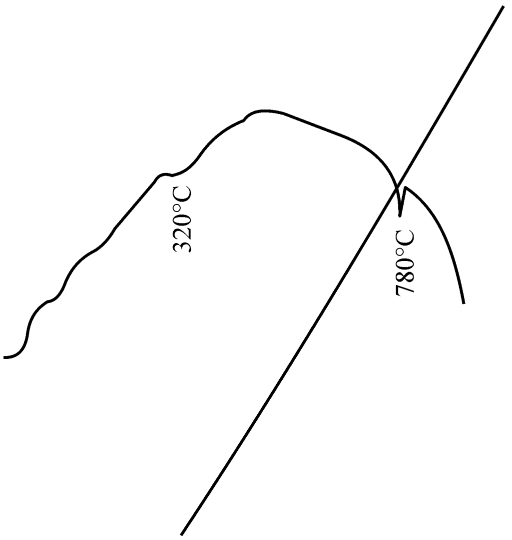

Fig. 1. Thermogram of $Rh_2Se_9Cl_6$ decomposition.

content of glycerol and liquid reaction products (acrolein, allyl alcohol, and acetaldehyde) was monitored with a Khrom-5 chromatograph equipped with a flame-ionization detector on a column packed with Carbopac (B). The gaseous products (CO, CO_2) were analyzed on an LKhM-80 chromatograph with a heat-conductivity detector.

RESULTS AND DISCUSSION

The structure of the starting rhodium selenochloride can be represented as packing of structural units of $Rh_2Se_9Cl_6$ composition. The metal atoms are in the deformed octahedral environment $[RhCl_3Se_3]$ characteristic of Rh(III). Two $[RhCl_3Se_3]$ octahedral are connected at faces of selenium atoms bound into an annular crown-like Se_9 structure. The μ_3-Se and μ_3-Rh fragments form a structure with a cubane-like structure: D_3-trishomocubane [15, 16].

When $Rh_2Se_9Cl_6$ is heated to 160°C, evolution of Se_2Cl_2 vapor is observed. A dip of the endothermic effect is observed in the thermogram (Fig. 1) at around 320°C and corresponds to the decomposition of rhodium selenochloride with sublimation of selenium, evolution of Se_2Cl_2 vapor, and its condensation on cold parts of the reactor. The black powder obtained as a result of the thermal treatment has the following experimentally found composition (%): Rh 40.20, Se 59.80 at a composition calculated for $RhSe_2$ (%): Rh 39.345 and Se 60.55. This compound is rather thermally stable, with an endothermic effect observed only at 780°C. In this case, a gray product with metallic shine is formed, which has an experimentally found composition (%): Rh 57.03 and Se 42.97 at a composition calculated for RhSe (%): Rh 56.58 and Se 43.42.

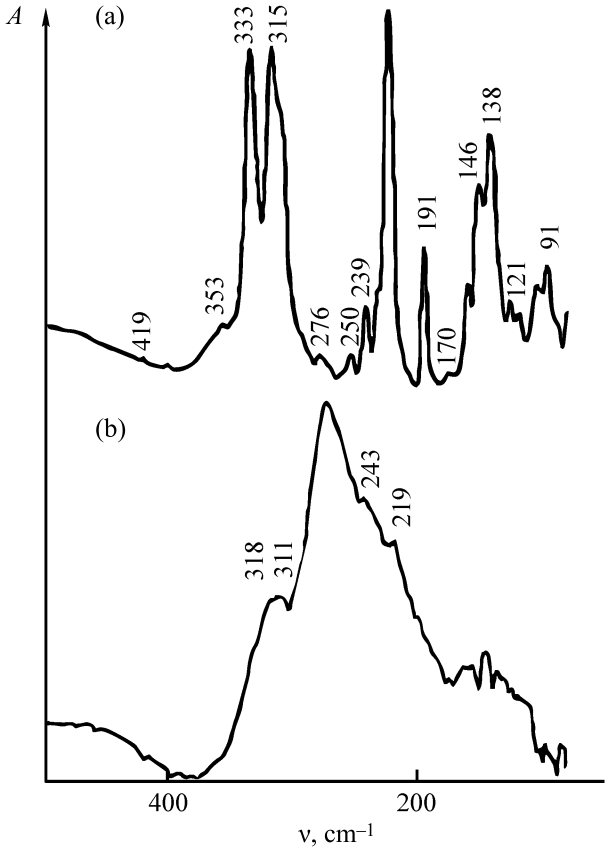

Fig. 2. IR spectra of (a) $Rh_2Se_9Cl_6$ and (b) $RhSe_2$. (*A*) Absorption and (ν) wave number.

Thus, the thermal transformations of rhodium selenochloride $Rh_2Se_9Cl_6$ occur by the scheme

$$Rh_2Se_9Cl_6 \xrightarrow{320°C} RhSe_2 \xrightarrow{780°C} RhSe.$$

The IR spectrum of the decomposition product $RhSe_2$ (Fig. 2) is markedly different from that of the starting rhodium selenochloride $Rh_2Se_9Cl_6$ (an interpretation of the latter was reported in [15]), which points to profound changes in the molecular structure. The doublet at 318 and 311 cm^{-1} corresponds to bond vibrations ν(Rh–Se) with somewhat lowered frequency. The broad absorption band peaked at 270 cm^{-1} is associated with the vibrations ν(Se–Se).

It should be noted that $RhSe_2$, product formed in the thermal decomposition of $Rh_2Se_9Cl_6$ at 320°C, has low crystallinity, which hinders an unambiguous identification of its structure. However, the positions and intensities of broadened diffraction peaks (Fig. 3) indicate that the cubic

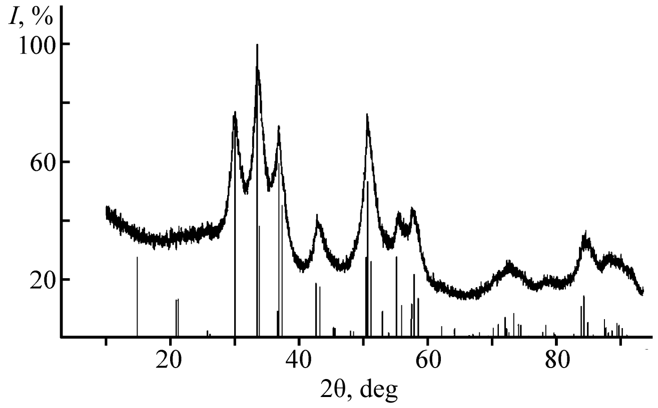

Fig. 3. X-ray diffraction pattern of $RhSe_2$, product of thermal transformations of rhodium selenochloride $Rh_2Se_9Cl_6$ at T = 320°C. (I) Relative intensity and (2θ) Bragg angle.

phase $RhSe_2$ is present in this product [17]. The diffraction pattern of the product formed in thermal transformation of $Rh_2Se_9Cl_6$ at 780°C shows that it contains the RhSe hexagonal phase [18] of the NiAs structural type and elementary rhodium.

The presence of the selenium and chlorine ligands in $Rh_2Se_9Cl_6$ may indicate that acid centers are present on its surface [19]. However, it seems to be impossible to obtain the spectrum of thermal desorption of ammonia from the starting $Rh_2Se_9Cl_6$ compound because selenium and Se_2Cl_2 vapors are released as the temperature increases from 160 to 320°C.

Figures 4a and 4b show spectra of thermal desorption of ammonia from the products $RhSe_2$ and RhSe formed in the thermal decomposition of rhodium selenochloride. Analysis of the spectra shows that the $RhSe_2$ sample contains acid centers of varied strength, with peaks of the thermal desorption of ammonia at 150, 350, and 480°C. The total concentration of the acid centers is 0.023 mmol NH_3/g. The spectrum of thermal desorption of ammonia from the RhSe sample has no pronounced peaks, and the total concentration of acid centers sharply decreases to become only 0.008 mmol NH_3/g. Thus, rhodium is reduced in the course of thermal transformation at 780°C to the oxidation states +2 and 0, and the product being formed loses its acid properties.

The results obtained in the study indicate that rhodium selenochloride mostly decomposes to $RhSe_2$ in the course of a preliminary treatment of a catalyst formed by

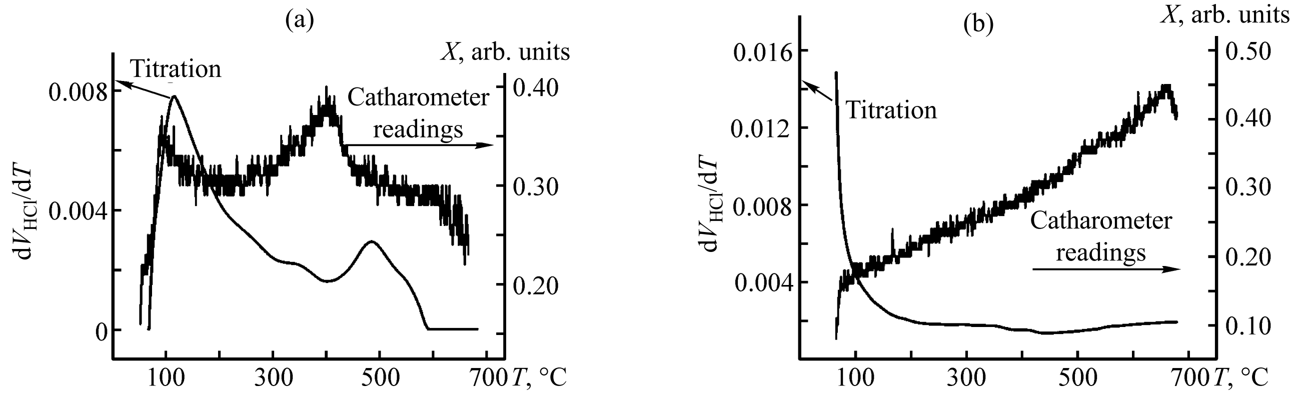

Fig. 4. Spectra of thermal desorption of ammonia for (a) $RhSe_2$ and (b) RhSe. (X) Signal from catharometer and (T) temperature. Total acidity (mmol NH_3/g): (a) 0.023 and (b) 0.008.

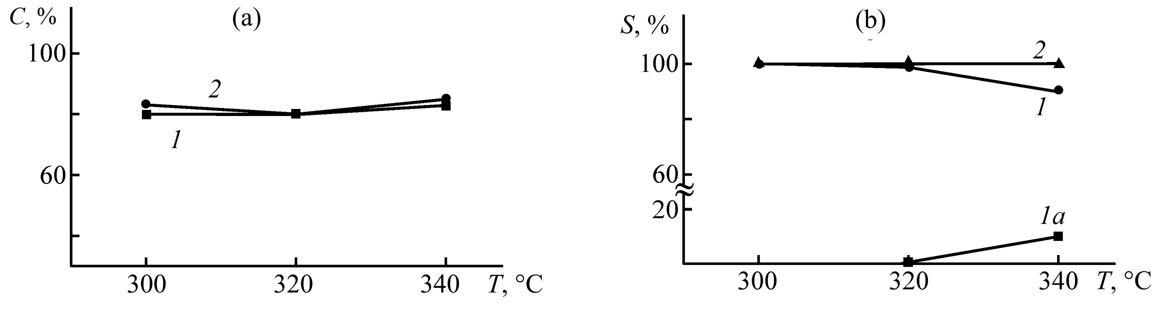

Fig. 5. (a) Conversion C of glycerol and (b) selectivity S for liquid reaction products (1) acrolein and ($1a$) acetaldehyde on the catalysts (1) Ga/H–ZSM-5 and (2) RhSe2/Ga/H–ZSM-5 vs. temperature T.

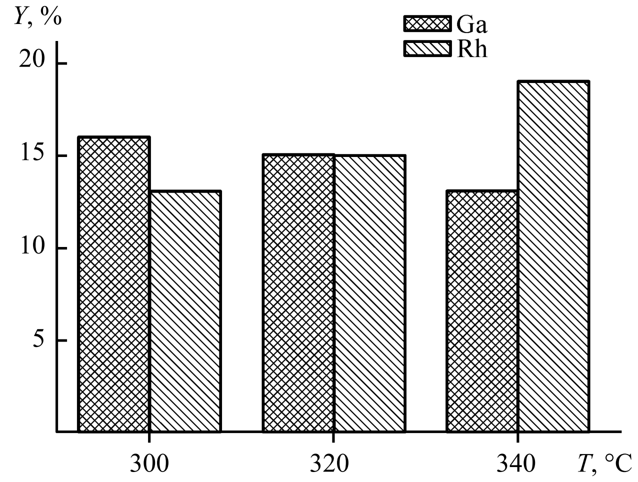

Fig. 6. Yield *Y* of acrolein formed on Ga/H–ZSM-5 and $RhSe_2$/Ga/H–ZSM-5 catalysts in relation to the experimental temperature *T*.

mechanical mixing of $Rh_2Se_9Cl_6$ and Ga/H–ZSM-5 in a flow of nitrogen.

Figure 5 compares the conversion of glycerol and the selectivity for liquid reaction products on the starting Ga/H–ZSM-5 zeolite and on the modified $RhSe_2$/Ga/H–ZSM-5 catalytic system. The promotion of Ga/H–ZSM-5 with rhodium selenide $RhSe_2$ hardly affects the conversion of glycerol, which was about 80% at any of the experimental temperatures (Fig. 5a). Both samples are distinguished by high selectivity (Fig. 5b): in the temperature range 300–320°C, the only liquid reaction product is acrolein, with acetaldehyde found at 340°C. It should be noted that both samples are strongly carbonized in the course of the reaction.

Comparison of the acrolein yields on the Ga/H–ZSM-5 and RhSe2/Ga/H–ZSM-5 catalysts (Fig. 6) shows that the promotion of Ga/H–ZSM-5 with rhodium selenide only slightly affects the yield of acrolein at 300–320°C, and on raising the experimental temperature to 340°C, the yield of acrolein grows from 13 to 19%. Raising the experimental temperature further results in that the conversion of glycerol increases, but the yield of liquid reaction products decreases, which is presumably due to their decomposition to solid carbonaceous formations.

CONCLUSIONS

The catalytic properties of the $RhSe_2$/Ga/H–ZSM-5 system in dehydration of glycerol to acrolein in the gas phase at 300–340°C were studied for the first time. The catalyst is formed as a result of a preliminary thermal treatment of a mechanical mixture of rhodium selenochloride $Rh_2Se_9Cl_6$ and a gallium-containing zeolite Ga/H–ZSM-5 in a flow of nitrogen at the process temperatures. It was shown that the starting rhodium selenochloride $Rh_2Se_9Cl_6$ is stable up to 160°V. Raising the temperature to 320°C results in its decomposition to rhodium selenide, the presence of which provides an increase in the catalytic activity of Ga/H–ZSM-5 in the reaction under study. It was found that the promotion of Ga/H–ZSM-5 with rhodium selenide $RhSe_2$ raises the yield of the target product acrolein from 13 to 19% at 340°C.

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