ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 6, pp. 893–897. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © E.M. Churakova, S.D. Badmaev, P.V. Snytnikov, A.I. Gubanov, E.Yu. Filatov, P.E. Plyusnin, V.D. Belyaev, S.V. Korenev, V.A. Sobyanin, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 6, pp. 923–928.

YOUNG SCIENTISTS' SCHOOL

Bimetallic Rh–Co/ZrO_2 Catalysts for Ethanol Steam Reforming into Hydrogen-Containing Gas

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Received December 15, 2009

Abstract—The properties of supported bimetallic Rh–Co/ZrO_2 catalysts in ethanol steam reforming into hydrogen-containing gas were studied. The particles of Rh–Co solid solutions on the catalyst surface were prepared by the thermal decomposition of the double complex salt $[Co(NH_3)_6][Rh(NO_2)_6]$ and the solid solution $Na_3[RhCo(NO_2)_6]$. It was found that the bimetallic Rh–Co/ZrO_2 catalysts exhibited high activity in the reaction of ethanol steam reforming. The equilibrium composition of reaction products was attained at 500–700°C and a reaction mixture space velocity of 10000 h^{-1}.

DOI: 10.1134/S0023158410060157

INTRODUCTION

Recently, attention has been focused on the development of power plants based on various types of fuel cells. This is due to the fact that fuel cells have a number of advantages over traditional electric energy sources. The most important of these advantages are a high efficiency of the conversion of chemical fuel energy into electrical energy, silence in operation, modular construction, and high environmental characteristics.

Hydrogen or hydrogen-containing gas is a fuel for fuel cells. However, the use of hydrogen for feeding fuel cells is currently complicated because of the absence of well-developed infrastructure and technologies for its safe storage and transportation. To overcome these difficulties, it was proposed to use a fuel processor—a device for the on-site generation of hydrogen-containing gas from various raw materials (natural gas, gasoline, diesel fuel, bioethanol, methanol, dimethyl ether, etc.) using catalytic methods. Of these raw materials, bioethanol is a renewable fuel. It can be obtained by the biochemical conversion of various agricultural commodities or wood and food wastes. The resulting bioethanol is an aqueous solution containing to 12–14 vol % ethanol.

Steam reforming is the most efficient process for producing hydrogen-containing gas from ethanol; it results in a maximum yield of hydrogen. A great number of supported catalysts based on both common metals (Cu, Co, and Ni) and noble metals (Pd, Pt, Ru, Rh, and Ir) have been proposed to perform this reaction [1–19]. The nature of the support has a considerable effect on the reaction of ethanol steam reforming. It has been shown [3, 7, 14] that a side reaction of ethanol dehydration can occur on Al_2O_3; this reaction leads to ethylene formation and, finally, catalyst carbonization. Recently, ZrO_2 and CeO_2–ZrO_2 have been frequently used as supports. It was found [4, 9, 12, 13, 20] that these supports are characterized by high thermal stability, and they provide high dispersity of an active component to prevent its agglomeration.

Of the test systems, Co- and Rh-containing catalysts are considered most promising [18]. Rhodium catalysts are stable and highly active [7, 8, 14, 15, 18, 19]. It was found that the activity of Rh catalysts is due to the ability of Rh to cleave the C–C bond in the ethanol molecule [11, 14]. Cobalt-containing catalysts are active in ethanol steam reforming; however, they undergo carbonization, and their productivity is lower than that of rhodium catalysts [3, 10, 15, 18, 21]. In addition, it was noted [2, 4] that Co-containing catalysts are prone to the formation of by-products such as acetaldehyde.

To increase catalyst activity and to decrease the concentration of expensive noble metals in catalysts for ethanol steam reforming remain a problem of considerable current interest. This problem can be solved by using more complex bimetallic catalysts. Thus, Pereira et al. [21] studied the reaction of ethanol steam reforming on Co/SiO_2, Rh/SiO_2, CoRh/SiO_2, Ru/SiO_2, and CoRu/SiO_2 catalysts with the addition of oxygen to the reaction mixture. They found that the CoRu/SiO_2 and CoRh/SiO_2 catalysts were more active in this process than the monometallic catalysts. In the course of reaction, all of the catalysts were carbonized and their activity decreased. The presence of oxygen in

Characteristics of the support and bimetallic Rh–Co catalysts

Sample	S_{BET}, m^2/g	Metal content, wt %	
		Co	Rh
ZrO_2	35	–	–
Rh–Co(DCS)/ZrO_2	23	0.59	1.01
Rh–Co(SS)/ZrO_2	23	0.59	1.05

the reaction mixture resulted in the oxidation of Co particles to CoO; this is undesirable because CoO is active in the reaction of ethanol dehydrogenation to acetaldehyde. In the CoRh and CoRu catalysts, the platinum group metals prevented the oxidation of cobalt by the formation of bimetallic Co–Rh or Co–Ru particles. This makes it possible to regenerate a carbonized catalyst by oxidative treatment with the retention of its initial catalytic properties.

In this work, we studied the reaction of ethanol steam reforming into hydrogen-containing gas on bimetallic Rh–Co/ZrO_2 catalysts. The main goal was to develop the target-oriented synthesis of bimetallic Rh–Co particles on the support surface. Double complex salts (compounds containing a complex cation and a complex anion, where different metals (Rh and Co) are central atoms) and isostructural Rh and Co salts that form solid solutions were used as the precursors of catalyst active components. The advantage of the above compounds is that the stoichiometry of a complex precursor is responsible for the composition of the resulting polymetallic phase; this allowed us to expect the formation of bimetallic particles with a specified composition in the catalyst.

EXPERIMENTAL

Catalyst Preparation

The ZrO_2 support was prepared by precipitation from an aqueous solution of zirconyl nitrate at a constant value of pH 10. A 5% aqueous solution of ammonia was used as a precipitating agent. The resulting precipitate was filtered off and washed on filter with water and then with ethanol. The resulting mass was dried in air for two days; thereafter, it was calcined at 500°C in air for 4 h.

The bimetallic rhodium–cobalt catalysts were prepared by impregnating the ZrO_2 support with aqueous solutions of complex compounds containing Rh and Co.

The first method consisted in the use of aqueous solutions of isostructural $Na_3[Rh(NO_2)_6]$ and $Na_3[Co(NO_2)_6]$ salts. The $Na_3[Rh_xCo_{1-x}(NO_2)_6]$ solid solution can be obtained upon mixing depending on the initial ratio between the components. The thermal decomposition of this solid solution results in the formation of RhCo solid solution particles. In particular, we used an equimolar ratio between the Rh and Co salts in this study to obtain the $Na_3[Rh_{0.5}Co_{0.5}(NO_2)_6]$ complex. The resulting samples were held in a flow of a mixture of 5 vol % H_2 + 95 vol % He at 600°C for 2 h. Henceforth, the catalyst thus prepared is referred to as Rh–Co(SS)/ZrO_2.

The second method consisted in the use of aqueous solutions of $Na_3[Rh(NO_2)_6]$ and $[Co(NH_3)_6]Cl_3$ complex salts. As a result of mixing these salts, the double complex salt $[Co(NH_3)_6][Rh(NO_2)_6]$ was formed, the thermal decomposition of which led to the formation of RhCo solid solution particles. The resulting samples were held in a flow of a mixture of 5 vol % H_2 + 95 vol % He at 600°C for 2 h. Henceforth, the catalyst thus prepared is referred to as Rh–Co(DCS)/ZrO_2.

Using these methods, we obtained catalyst samples with the atomic ratio Rh : Co = 1 and a total metal content of ~1.6 wt % (see the table).

The catalytic properties of the synthesized bimetallic Rh–Co/ZrO_2 systems in the reaction of ethanol steam reforming were compared with the properties of preciously studied monometallic Rh/ZrO_2 [19] and Co/ZrO_2 catalysts [22].

Catalytic Experiments

Ethanol steam reforming was studied in a quartz flow reactor at atmospheric pressure over the temperature range of 300–700°C. The reactor was a U-shaped tube with an inner diameter of 4 mm. The experiments were performed using a reaction mixture containing 16 vol % C_2H_5OH, 64 vol % H_2O, and 20 vol % N_2 at a space velocity of 10000 h^{-1}. Nitrogen was used as an internal standard in chromatographic analysis.

The concentrations of reactants and reaction products were determined on two Tsvet-500 chromatographs equipped with thermal-conductivity detectors. Ethanol, water, acetaldehyde, ethylene, and carbon dioxide were separated at 125°C on a column with Porapak T; hydrogen, nitrogen, carbon monoxide, and methane were separated at room temperature on a column with NaX molecular sieves. Argon was used as a carrier gas.

Before the experiments, the catalysts were reduced in a flow of a mixture of 5 vol % H_2 + 95 vol % N_2 at 400°C and a flow rate of 90 ml/min for 2 h.

Investigation Techniques

For the X-ray diffraction (XRD) analysis of support and catalyst samples, diffraction patterns were obtained on an HZG-4C apparatus (CuK_α radiation; graphite monochromator in a reflected beam). The diffraction patterns were measured by point-by-point scanning over the angle range of $2\theta = 10°–90°$ at a step of 0.05° and a 10-s accumulation time at a point. The qualitative phase composition of the samples was determined using the JCPDS data cards [23]. The sizes of coherent-scattering regions (CSRs) were calculated from the broadening of diffraction peaks due to the detected phases.

The XRD analysis of $[Rh(NO_2)_6][Co(NH_3)_6]$ and $Na_3[Rh_{0.5}Co_{0.5}(NO_2)_6]$ polycrystals and their thermolysis products (after treatment with a mixture of 5 vol % H_2 + 95 vol % He at 400°C for 2 h) was performed on DRON-3M and DRON-RM4 instruments (R = 192 mm; CuK_α radiation; Ni filter; scintillation detector with amplitude discrimination) over the angle range of $2\theta = 5°–90°$. The samples were prepared as a thin layer on a polished side of a standard quartz cell. An analogously prepared Si sample was used as an external standard.

The high-resolution transmission electron microscopy (HR TEM) images were obtained on a JEM-2010 electron microscope (with a grid resolution of 0.14 nm at an accelerating voltage of 200 kV). Before measurements, the catalyst samples were supported onto copper gauze coated with a perforated carbon film using a UZDN-144.2 ultrasonic disperser. The high-resolution images of periodic structures were analyzed by the Fourier method. The energy dispersive X-ray microanalysis (EDX) of samples was performed using characteristic energy dispersive X-ray spectroscopy on an EDAX spectrometer (EDAX) equipped with a Si(Li) detector with an energy resolution of 130 eV.

The specific surface area (S_{BET}) was determined on a TriStar 3000 instrument using the full isotherms of low-temperature nitrogen adsorption (–196°C).

The concentrations of metals in the catalysts were determined by X-ray fluorescence analysis on a VRA-30 instrument with a Cr anode in the X-ray tube using an external standard technique.

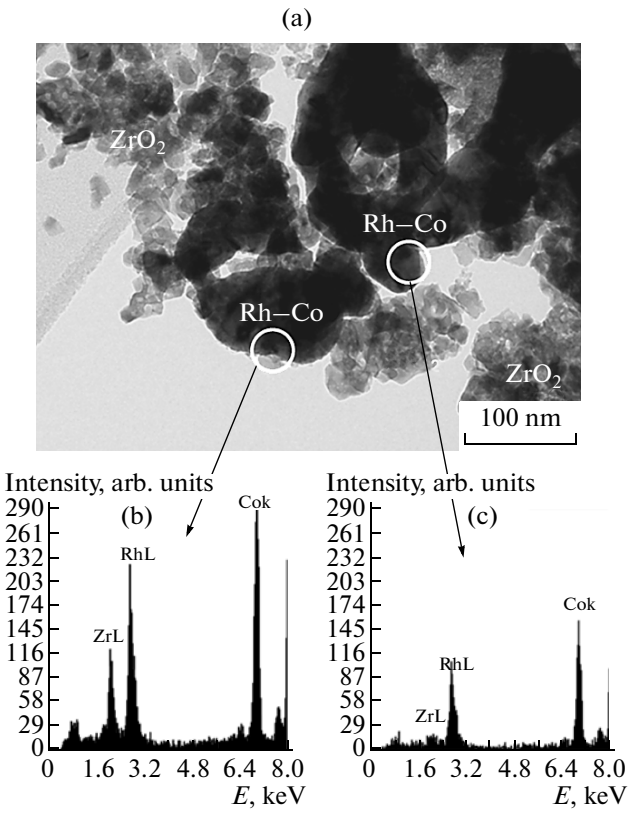

Fig. 1. (a) TEM micrograph of the Rh–Co(DCS)/ZrO_2 catalyst and (b, c) the EDX spectra of marked regions.

RESULTS AND DISCUSSION

Physicochemical Properties

An analysis of the diffraction pattern of the synthesized ZrO_2 demonstrated that the support consisted of two zirconium oxide phases: monoclinic m-ZrO_2 (90 wt %) and tetragonal t-ZrO_2 (10 wt %) structures with CSR sizes of 150 and 100 Å, respectively. The unit cell parameters of the zirconia phases were consistent with standard values [23].

Unfortunately, the XRD analysis of the Rh–Co/ZrO_2 catalysts did not allow us to identify the formation of bimetallic phases. This was due to the fact that the main reflections of Rh and Co coincided with the reflections of the ZrO_2 support and the integrated intensity of metal peaks was small because of low metal contents of the catalyst.

At the same time, the XRD analysis of the samples obtained after drying an equimolar mixture of the aqueous solutions of $Na_3[Rh(NO_2)_6]$ and $Na_3[Co(NO_2)_6]$ complex salts, as well as of the precipitate obtained upon mixing the aqueous solutions of $Na_3[Rh(NO_2)_6]$ and $[Co(NH_3)_6]Cl_3$ complex salts, demonstrated the formation of single-phase compounds: a $Na_3[Rh_{0.5}Co_{0.5}(NO_2)_6]$ solid solution and a $[Co(NH_3)_6][Rh(NO_2)_6]$ double complex salt, respectively. The XRD analysis of the thermal decomposition products of these complex compounds revealed the formation of a mixture of $Rh_{0.65}Co_{0.35}$ and $Rh_{0.55}Co_{0.45}$ solid solutions with CSR sizes of ~90 Å. These results suggest that Rh–Co solid solutions can also be formed on the support surface in the course of the preparation of bimetallic Rh–Co/ZrO_2 catalysts.

To study in more detail the morphology and structure of the Rh–Co/ZrO_2 catalysts, we used HR TEM and EDX. Particles of sizes from 20 to 100 nm as larger agglomerates were observed in a micrograph of the Rh–Co(DCS)/ZrO_2 catalyst (Fig. 1a). As an example, Figs. 1b and 1c show the EDX spectra that characterize the elemental compositions of marked regions in the micrographs. The spectra contained lines due to Zr, Rh, and Co; in this case, the ratio between the integral intensities of Rh and Co corresponding to the atomic ratio between the elements was 1.

Interplanar distances for ZrO_2 support particles and bimetallic Rh–Co particles were determined using the Fourier transform. The observed interplanar distances of 3.61 and 3.05 Å correspond to distances between the (011) and (111) planes of the monoclinic phase of ZrO_2 (PCPDF ICSD no. 371484). The observed interplanar distances of 2.74 and 3.38 Å correspond to the tetragonal phase of ZrO_2 (PCPDF ICSD no. 170923). A reflection corresponding to the

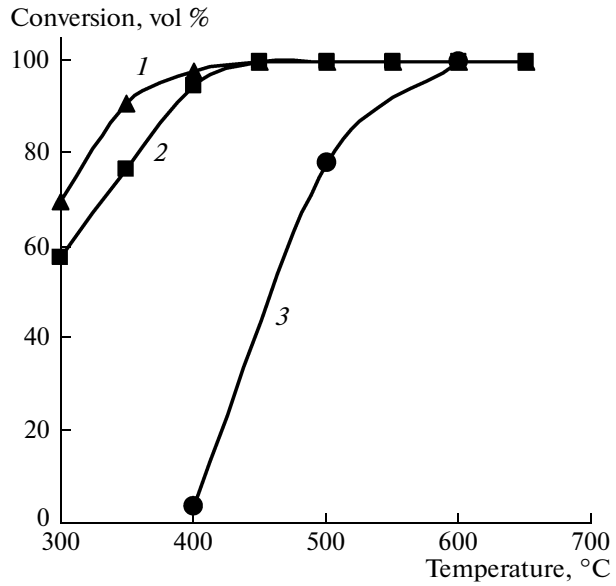

Fig. 2. Dependence of the conversion of ethanol on temperature on the (*1*) Rh–Co(SS)/ZrO_2 and (*2*) Rh–Co(DCS)/ZrO_2 catalysts and (*3*) ZrO_2.

interplanar distance d = 2.11 Å was observed in the Fourier diffraction pattern of a metal particle; this distance is inconsistent with both Co (Fm3m d_{111} = 2.0467 Å, PCPDF ICSD no. 150806; $P6_3/mmc$ d_{100} = 2.17026 Å, PCPDF ICSD no. 52935) and Rh (d_{111} = 2.1960 Å, PCPDF ICSD no. 050685). A comparison with EDX data in the same particle region allowed us to conclude that this interplanar distance corresponds to the interplanar distance of a solid solution with the ratio Rh : Co = 1 : 1 (Fm3m d_{111} = 2.1188 Å, PCPDF ICSD no. 102635).

The results of the analysis allowed us to state that dark spots of size 20–50 nm, which are observed in Fig. 1a, are bimetallic Rh–Co solid solutions with the ratio Rh : Co = 1 : 1. Analogous data were also obtained for the Rh–Co(SS)/ ZrO_2 sample.

Thus, the use of the double complex salt $[Co(NH_3)_6][Rh(NO_2)_6]$ and the solid solution $Na_3[Rh_{0.5}Co_{0.5}(NO_2)_6]$ as precursor compounds resulted in the formation of bimetallic Rh–Co particles in the catalyst. As found in the studies of the catalysts after the reaction of ethanol steam reforming, no detectable changes occurred in the particles of Rh–Co solid solutions (particle size or composition) under reaction conditions. The formation of carbon on the surface of the bimetallic catalyst did not exceed 0.5 wt %, as determined by the combustion of the samples after catalytic experiments; at the same time, the amount of carbon on the monometallic cobalt catalyst was about 10 wt % [22]. The lower carbonization of the Rh–Co/ZrO_2 catalyst was due to the formation of bimetallic Rh–Co particles, which resulted in changes in the catalytic properties. It is likely that these bimetallic particles enhanced the ability to cleave the C–C bond in the ethanol molecule, as compared with monometallic cobalt systems.

Catalytic Activity

Figure 2 compares the conversion of ethanol on the Rh–Co(DCS)/ZrO_2 and Rh–Co(SS)/ZrO_2 catalysts and the ZrO_2 support. It can be seen that the bimetallic catalysts exhibited high activity. The conversion of ethanol into hydrogen-containing gas on these catalysts was as high as 100% even at 450°C, and it then remained unchanged.

On the ZrO_2 support, 100% ethanol conversion was reached at 600°C; in this case, the main products were acetaldehyde and ethylene formed in the following reactions:

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O;$$
$$C_2H_5OH \longrightarrow CH_3COH + H_2.$$

The temperature dependences of the concentrations of the reaction products of ethanol steam reforming on the Rh–Co(DCS)/ZrO_2 and Rh–Co(SS)/ZrO_2 catalysts were found identical. In the temperature range of 300–650°C, the main products were H_2, CO, CO_2, and CH_4. Acetaldehyde and ethylene occurred in trace amounts (<0.1 vol %) only at 300–400°C.

As an example, Fig. 3 shows the dependence of the concentrations of H_2, CO, CO_2, and CH_4 on temperature in the course of reaction on Rh–Co(DCS)/ZrO_2. Figure 3 also shows the equilibrium concentrations of ethanol steam reforming products, which were calculated based on the assumption that the following reactions occurred in the system:

$$C_2H_5OH = CO + H_2 + CH_4;$$
$$CO + H_2O = CO_2 + H_2;$$
$$CH_4 + H_2O = CO + 3H_2.$$

It can be seen that the concentrations of all reaction products are close to equilibrium values in the temperature range of 500–650°C. At low temperatures (300–400°C), CO_2 was almost not observed in the reaction products; the main products were H_2, CO, and CH_4 in the molar ratio $H_2 : CO : CH_4 = 2 : 1 : 1$. As the temperature was increased to 650°C, the concentration of methane decreased to ~1 vol %; in this case, the concentrations of H_2 and CO_2 increased to ~45 and 13 vol %, respectively.

Thus, to obtain a maximum yield of hydrogen in the absence of methane from the reaction products, the reaction of ethanol steam reforming on the Rh–Co/ZrO_2 catalysts should be performed in the temperature range of 600–700°C. In this case, the concentration of CO in the mixture is at a level of 10 vol %. This mixture is suitable for feeding high-temperature fuel cells [18, 24].

The Rh–Co/ZrO_2 samples are similar to rhodium catalysts in catalytic characteristics [19]; they contain

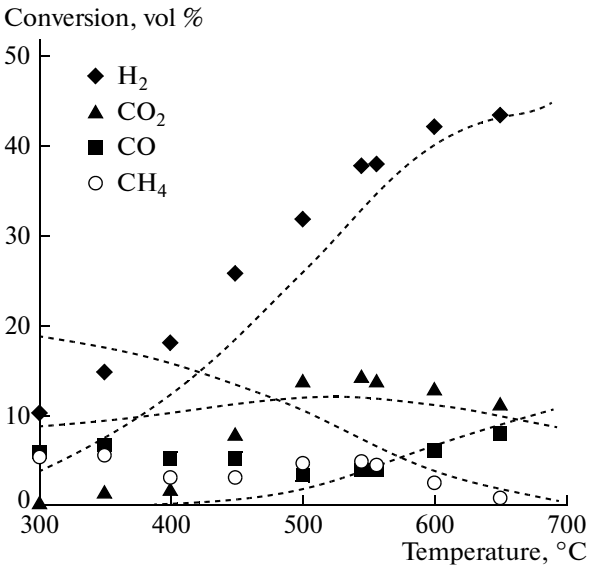

Fig. 3. Dependence of product concentrations on temperature in the course of ethanol stream conversion on the Co(DCS)/ZrO_2 catalyst. Points and dashed lines refer to experimental data and calculated equilibrium values, respectively.

a smaller amount of Rh and are less prone to carbonization than monometallic cobalt systems.

CONCLUSIONS

We found that the use of the double complex salt $[Co(NH_3)_6][Rh(NO_2)_6]$, as well as isostructural Rh and Co salts that form the solid solution $Na_3[Rh_{0.5}Co_{0.5}(NO_2)_6]$, as compound precursors makes it possible to obtain bimetallic RhCo solid solution particles in the catalyst by the thermal decomposition of the precursor.

The bimetallic Rh–Co/ZrO_2 catalysts were found to exhibit high activity in ethanol steam reforming. The equilibrium composition of reaction products was reached at 500–650°C and a reaction mixture space velocity of 10000 h^{-1}.

ACKNOWLEDGMENTS

We are grateful to V.P. Pakharukova, Yu.I. Amosov, and A.V. Ishchenko for their assistance in performing experiments. This study was supported by the Siberian Branch of the Russian Academy of Sciences (integration project no. 112) and the Federal Goal-Oriented Program "Scientific and Educational Cadres of Innovative Russia" for 2009–2013 (state contract no. P999 of August 20, 2009).

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