Study of the state of rhodium in the potassium rhodiumundecatungstosilicate/alumina system by diffuse-reflectance IR spectroscopy

P. A. Korovchenko,[a] *R. A. Gazarov,*[a] *and L. M. Kustov*[b]*

[a]*I. M. Gubkin State University of Oil and Gas,*
65 Leninsky prosp., 117917 Moscow, Russian Federation.
Fax: +7 (095) 135 8895. E-mail: fhte@gaog.unicor.ac.ru
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: lmk@ioc.ac.ru

Adsorption of CO on the catalytic system $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ was studied by diffuse-reflectance IR spectroscopy. The electronic state of rhodium and thermal stability of the system in the redox cycles were studied. The oxidized heteropolycompound (HPC) contains the charged forms Rh^+, Rh^{2+}, and Rh^{3+}. Their ratio strongly depends on the pre-treatment temperature of the sample. In the reduced HPC two main forms of rhodium exist: the ionic Rh^+ and metallic Rh^0. The supported HPC structure is stable in an oxidative medium at temperatures below ~900 K. The properties of the $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ system are retained in the redox cycles up to ~670 K, and the highly dispersed state of rhodium is observed up to 900 K.

Key words: heteropolycompound, heteropolyanion, Keggin unit, rhodium, heteroatom, redox cycle, thermal stability, diffuse-reflectance FTIR spectroscopy, carbon monoxide, probe molecule.

Mixed 12th row heteropolycompounds (HPC) with atoms of d-metals contain acidic OH groups and highly dispersed metallic sites in the inner coordination sphere of the heteropolyanion (HPA).[1] Active bifunctional catalysts are characterized by a similar combination.[2] Previously we have studied catalytic systems based on mixed HPC with Pd and Pt atoms in the Keggin unit: $K_6[SiW_{11}PdO_{39}]/Al_2O_3$ [3] and $K_4[SiW_{11}PtO_{39}]/Al_2O_3$.[4] The supported HPC was shown to exhibit an increased thermal stability under oxidative conditions below ~800 K. The systems withstand the action of redox cycles up to ~670 K, unlike individual HPC that begin to decompose at temperatures of redox treatments close to 370 K.[1–4] The highly dispersed state of platinoids remains unchanged virtually to the complete decomposition of the HPC structure.

In this work, we studied the electronic state of rhodium in the $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ system, the thermal stability of the system, and its properties in the redox cycles by diffuse-reflectance FTIR spectroscopy using CO as the probe molecule.

Experimental

Preparation of samples. $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ samples were prepared by the impregnation of an alumina support with an aqueous solution of the individual HPC synthesized by a standard procedure.[5] The method for the preparation of $K_5[SiW_{11}RhO_{39}] \cdot 15H_2O$ has been described previously.[6,7] Alumina γ-Al_2O_3 (S_{sp} = 240—250 $m^2 g^{-1}$) with a particle size of 0.2—0.5 mm was used as the support. The content of HPC in the synthesized system $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ amounts to ~17 wt.%, which corresponds to ~0.5 wt.% Rh in the supported sample.

For measurements of IR spectra, the samples of the supported catalyst were loaded in a quartz reactor with a CaF_2 window and activated at 470—920 K *in vacuo* (10^{-4} Torr) for 1 h. Then the samples were treated with O_2 (30 Torr) at activation temperatures to prevent the reduction of rhodium. Then the catalysts were evacuated at the same temperature for 1 h to a residual pressure of 10^{-4} Torr and cooled to ~20 °C. To obtain the reduced form of rhodium, the samples (0.5 g) were activated with hydrogen for 2 h (the flow rate of H_2 was 30 mL min^{-1}) at 470—670 K. Then the samples were evacuated at temperatures chosen for the reduction to the residual pressure of 10^{-4} Torr and cooled to ~20 °C.

Measurement of IR spectra. IR spectra were recorded on a Nicolet Protégé-460 spectrophotometer equipped with a diffuse-reflectance attachment.[8] The spectra were recorded with a resolution of 8 cm^{-1}. CO was adsorbed under 30 Torr on the pre-evacuated oxidized or reduced samples. After the spectrum was recorded, the sample was evacuated with a stepwise temperature increase with an increment of 50 K, recording the spectra for each temperature of evacuation.

The spectra were processed using the Kubelka—Munk equation by the OMNIC® program according to the previously proposed procedure.[9] Computer simulation of the spectra also included the smoothening of the spectra and subtraction of the background.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1178—1181, July, 2000.

Results and Discussion

The oxidative treatment of a supported $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ system results in the appearance of the band of adsorbed CO in the IR spectrum only at temperatures >470 K, *i.e.*, under conditions where coordinatively bound water is partially removed from the HPC structure and the surface rhodium sites become accessible for the adsorption of the probe molecule (Fig. 1, spectrum *1*). The symmetric absorption band (AB) at 2130 cm^{-1} indicates the formation of the linear complexes Rh^{2+}—CO.[10] An increase in the temperature of the oxidative treatment to 520 K results in a strong increase in the intensity of this band (Fig. 1, spectrum *2*), which is explained by a more complete removal of structurally bonded water. The stepwise increase in the temperature of evacuation during pumping of adsorbed CO decreases the intensity of the AB at 2130 cm^{-1}, and at 470 K (Fig. 2) this band completely disappears. The position of the maximum of the band remains unchanged, indicating the highly dispersed ionic state of the metal.[3,4] Further increase in the temperature of the oxidative treatment of the sample to 570 K results in a decrease in the intensity of the band of CO at 2130 cm^{-1}, but the band itself broadens and becomes asymmetric from the side of low frequencies (Fig. 1, spectrum *3*). This suggests the presence of an additional band in the region of 2100 cm^{-1} corresponding to vibrations of CO in the linear complex Rh^0—CO.[10–12]

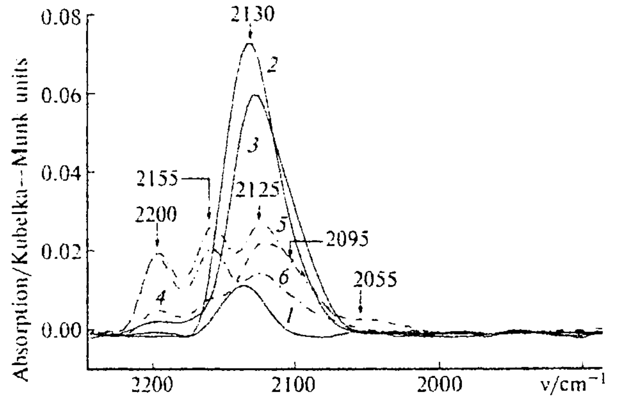

Fig. 1. IR spectra of CO (30 Torr) adsorbed on a Rh-HPC/Al_2O_3 sample oxidized at different temperatures: 470 (*1*), 520 (*2*), 570 (*3*), 670 (*4*), 820 (*5*), and 920 K (*6*).

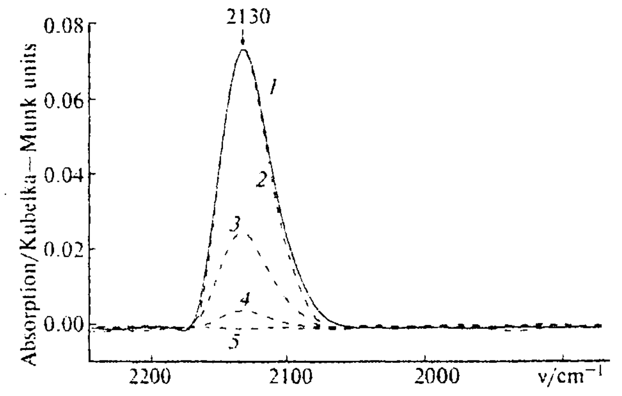

Fig. 2. IR spectra of CO (30 Torr) adsorbed on a Rh-HPC/Al_2O_3 sample oxidized at 520 K: *1*, before evacuation and *2*—*5*, after evacuation at 290 (*2*), 370 (*3*), 420 (*4*), and 470 K (*5*).

Increase in the temperature of the oxidative treatment of the sample to 670 K further decreases the intensity of the bands of adsorbed CO; however, new bands appear in the spectrum (Fig. 1, spectrum *4*). For example, along with the asymmetric AB at 2130 cm^{-1} with a shoulder in the region of 2100 cm^{-1}, AB at 2200, 2155, and 2055 cm^{-1} appear in the spectrum (Fig. 3, spectrum *1*). The position of the first band and its behavior during thermovacuum treatment allow us to ascribe it, according to the previous data,[3,4] to CO adsorption on Lewis acidic sites of the support. Two other bands are attributed to the linear complexes Rh^{3+}—CO and Rh^0—CO, respectively.[10,12] During vacuum treatment of the sample at ~20 °C, the intensity of the AB at 2130 cm^{-1} decreases, the AB at 2200 and 2155 cm^{-1} disappear, and that at 2055 cm^{-1} is shifted to 2030 cm^{-1}. Subsequent temperature increase during evacuation of the sample to 370 K results in a further decrease in the intensity of the asymmetric AB at 2130 cm^{-1} and a simultaneous increase in the AB at 2030 cm^{-1}. The latter band can characterize, most likely, the antisymmetric vibrations of CO (ν_{as}) in the geminal dicarbonyl complex Rh^+—$(CO)_2$.[10–12] Then we may assume that the shoulder of the asymmetric AB at 2130 cm^{-1} masks the AB at 2095 cm^{-1} corresponding to the symmetric vibration of CO (ν_s) in the Rh^+—$(CO)_2$ complex.[10–12] This implies that new *gem*-dicarbonyl complexes Rh^+—$(CO)_2$ are formed along with the linear Rh^{2+}—CO complexes under these conditions. The complexes of both types exhibit high thermal stability and decompose at temperatures of vacuum treatment higher than 470 K (Fig. 3, spectrum *4*).

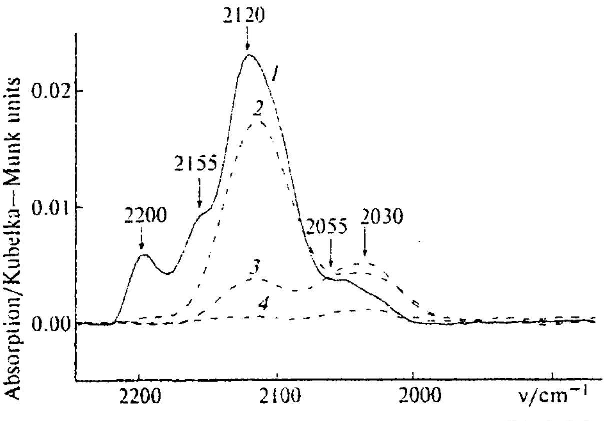

Fig. 3. IR spectra of CO (30 Torr) adsorbed on a Rh-HPC/Al_2O_3 sample oxidized at 670 K: *1*, before evacuation and *2*—*4*, after evacuation at 290 (*2*), 370 (*3*), and 470 K (*4*).

The previous studies of the thermostability of alumina-supported Pd-HPC and Pt-HPC showed that the HPC structure remains unchanged to 700—800 K and begins to change irreversibly at 800—900 K.[3,4] To reveal the limits of thermal stability of the supported rhodium complex, the subsequent oxidative treatment was carried out at 820 and 920 K. The IR spectrum of CO adsorbed on the sample oxidized at 820 K repeats the spectral pattern for the sample oxidized at 670 K (Fig. 1, spectrum *5*). The intensity of all bands observed previously (and especially, the AB at 2155 cm^{-1}) considerably increases, indicating an increase in the number of rhodium sites accessible for CO adsorption. The stepwise increase in the oxidation temperature from 670 to 820 K does not change the behavior of the sample during evacuation. The step of the intermediate formation of the $Rh^+—(CO)_2$ complexes is also retained. Thus, the shape of the bands in the IR spectrum of the sample oxidized at 820 K and their behavior during thermovacuum treatment suggest that the HPC structure and the highly dispersed state of the metal in the catalytic system are retained. The spectra exhibit an increase in the intensity of the bands of adsorbed CO, which has previously been observed for the Pt-HPC/Al_2O_3 system.[13,14] The oxidative treatment of the sample at 920 K does not change the position of the bands in the IR spectrum but is accompanied by a sharp decrease in the intensity of the bands characteristic of CO adsorption on charged forms of rhodium (Fig. 1, spectrum *6*). For example, the intensity of the AB at 2155 cm^{-1} ($Rh^{3+}—CO$) decreases by approximately 30%, and the AB at 2125 cm^{-1} is halved. This decrease indicates a decrease in the total concentration of the sites accessible for CO adsorption and can be related to processes of strong condensation of the HPC structure in the dehydrated state.

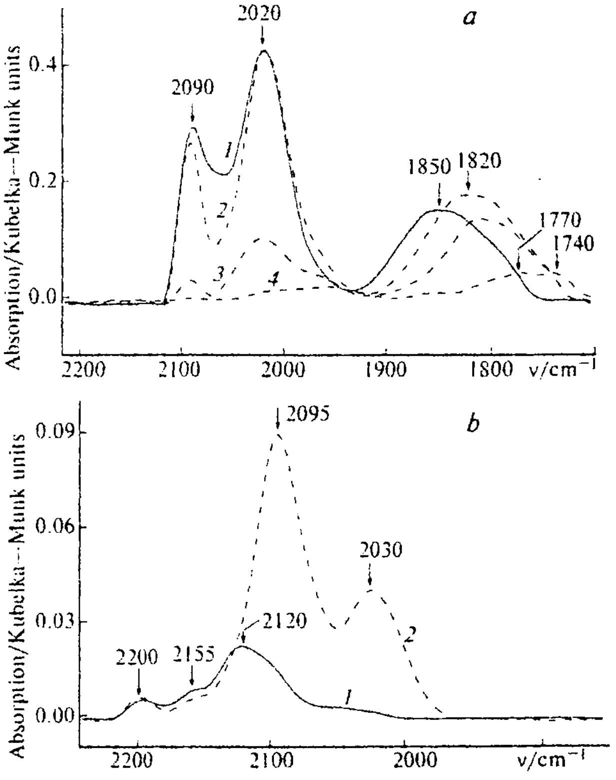

Fig. 4. IR spectra of CO (30 Torr) adsorbed on the Rh-HPC/Al_2O_3 sample (*a*) reduced at 470 K before (*1*) and after evacuation (*2—4*) at 290 (*2*), 370 (*3*), and 420 K (*4*); (*b*) oxidized (*1*) and reoxidized (*2*) at 670 K.

To study the stability of the $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ system in redox cycles, we performed two of these cycles at 670 and 920 K. The temperature regime of the first cycle was chosen according to the previously obtained data on the retention of the structure and reversibility of the properties of the Pd- and Pt-HPC/Al_2O_3 systems in redox cycles at 670 K. The reductive treatment at 470 K of the initially oxidized (at 670 K) rhodium sample followed by CO adsorption results in the formation of the *gem*-dicarbonyl complexes $Rh^+—(CO)_2$ and bridged CO complexes with metallic rhodium. This is indicated by the bands at 2090 and 2030 cm^{-1} and at 1850 cm^1 appearing after CO adsorption (Fig. 4, *a*). During the thermovacuum treatment of the sample, the intensities of the AB at 2090 and 2030 cm^{-1} decrease, and the bands completely disappear at 470 K. The maxima of the bands are not shifted, which indicates a highly dispersed state of the Rh^+ ions. The AB at 1850 cm^{-1}, whose maximum is shifted by 30—50 cm^{-1} towards low frequencies, exhibits different behavior. This is explained by the weakening of the dipole-dipole interaction between the CO molecules when the surface coverage decreases. The spectrum of the reoxidized sample contains the bands corresponding to the reduced state of the sample (Fig. 4, *b*), which indicates an incomplete reoxidation of rhodium under these conditions. The absence of bands of bridged CO complexes with Rh^0 in the spectrum of the reoxidized sample and the high intensity of the bands of CO adsorbed on charged rhodium suggest the absence of any irreversible changes in the HPC structure and indicate that a highly dispersed state of the metal is retained.

The second redox cycle was carried out under more severe conditions, where irreversible processes related to partial decomposition of the HPC structure ($T_{ox,reox}$ = 920 K, T_{red} = 670 K) were observed for the Pt-HPC/Al_2O_3 system.[4] The obtained spectral data differ slightly from those of the first redox cycle for the Rh-HPC/Al_2O_3 system (Fig. 5, *a* and *b*). An additional AB at 2070 cm^{-1} (Fig. 5, *a*) appears in the spectrum of the sample reduced at 670 K, which can be attributed to the linear $Rh^0—CO$ complexes (these complexes are unstable and disappear after vacuum treatment at 290 K). The data obtained barely indicate the decomposition of the HPC structure and sintering of the metallic particles or formation of an oxide metallic phase on the catalyst surface. However, the substantial decrease in the inten-

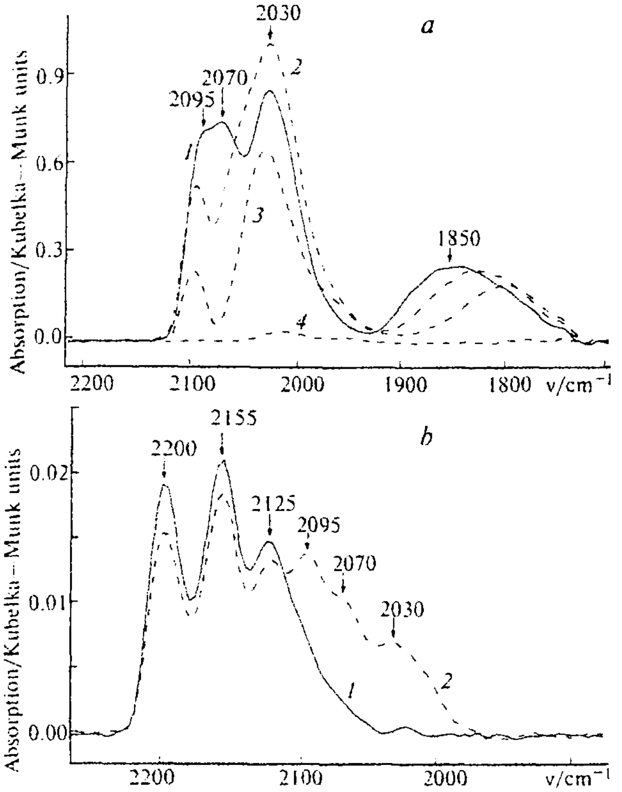

Fig. 5. IR spectra of CO (30 Torr) adsorbed on a Rh-HPC/Al_2O_3 sample (*a*) reduced at 670 K before (*1*) and after evacuation (*2*—*4*) at 290 (*2*), 370 (*3*), and 470 K (*4*); (*b*) oxidized (*1*) and reoxidized (*2*) at 920 K.

sity of the bands of adsorbed CO in the spectrum of the reoxidized sample indicates a decrease in the number of rhodium atoms accessible for CO adsorption. This indicates the strong irreversible condensation of the HPC structure. The absence of changes in the positioning of the bands of adsorbed CO indicates the highly dispersed state of the metal, which is retained until the onset of decomposition of the Keggin unit.

Thus, the studies performed allow us to draw the following conclusions.

1. The electronic state of rhodium in the oxidized $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ sample corresponds to the charged forms Rh^+, Rh^{2+}, and Rh^{3+}, but their ratio strongly depends on the pre-treatment temperature. Below 570 K rhodium exists predominantly as the Rh^{2+} ion, whereas at temperatures up to 920 K the Rh^{3+} form prevails.

2. The reduced samples contain the ionic Rh^{1+} species along with Rh^0, which forms with CO mainly bridged complexes.

3. The system $K_5[SiW_{11}RhO_{39}]/Al_2O_3$ exhibits a high thermal stability and does not decompose to 700—800 K.

4. The properties of the system remain unchanged during redox cycles at temperatures as high as 600—700 K.

5. The highly dispersed state of the rhodium ions is retained up to 900 K, when the first irreversible changes occur in the HPC structure.

It should be noted in conclusion that the synthesis of mixed HPC with platinoid ions in the internal coordination sphere of the Keggin HPA makes it possible to obtain thermostable catalytic systems with controlled acidic properties and a high dispersion of platinoid ions.

References

1. E. A. Nikitina, *Geteropolisoedineniya* [*Heteropolycompounds*], Goskhimizdat, Moscow, 1962, 424 pp. (in Russian).
2. I. V. Kozhevnikov, *Usp. Khim.*, 1993, **62**, 510 [*Russ. Chem. Rev.*, 1987, **56** (Engl. Transl.)].
3. P. A. Korovchenko, R. A. Gazarov, A. Yu. Stakheev, and L. M. Kustov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1271 [*Russ. Chem. Bull.*, 1999, **48**, 1261 (Engl. Transl.)].
4. P. A. Korovchenko, R. A. Gazarov, and L. M. Kustov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 2017 [*Russ. Chem. Bull.*, 1999, **48**, 1994 (Engl. Transl.)].
5. C. Tourne, *C. R. Acad. Sci. (Paris)*, 1968, **702**, 266.
6. R. A. Gazarov, Doct. Sci. (Chem.) Thesis, I. M. Gubkin Institute of Oil and Gas, Moscow, 1989, 289 pp. (in Russian).
7. RF Patent No. 2064828, 1996 (in Russian).
8. L. M. Kustov, A. A. Alekseev, V. Yu. Borovkov, and V. B. Kazanskii, *Dokl. Akad. Nauk SSSR*, 1981, **261**, 1374 [*Dokl. Chem.*, 1981 (Engl. Transl.)].
9. V. Yu. Borovkov, Doct. Sci. (Chem.) Thesis, N. D. Zelinsky Institute of Organic Chemistry, RAS, Moscow, 1989, 336 pp. (in Russian).
10. J. P. Wey, W. C. Neely, and S. D. Worley, *J. Catal.*, 1992, **134**(1), 378.
11. H. A. Pearce, Ph. D. Thesis, University of East England, Norwich, England, 1974.
12. A. C. Yang and C. W. Garland, *J. Phys. Chem.*, 1957, **61**, 1504.
13. P. Rabette and D. Olivier, *J. Less-Common Metals*, 1974, **36**, 299.
14. T. A. Karpukhina, V. F. Chuvaev, G. K. Mailieva, and I. N. Pinchuk, in *Fiziko-khimicheskie osnovy prakticheskogo ispol'zovaniya izo- i geteropolisoedinenii* [*Physicochemical Fundamentals of the Practical Use of Iso- and Heteropolycompounds. Collection of Works*], Dnepropetrovsk, 1983, 42 pp. (in Russian).

Received December 29, 1999