Chemical transformations of a SiO_2-supported $[Fe_5RhC(CO)_{16}]^-$ cluster and catalysis of propylene hydroformylation

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Chemical transformations of SiO_2-supported $[Fe_5RhC(CO)_{16}]^-$ and $[Fe_4RhC(CO)_{14}]^-$ clusters in Ar, CO, and synthesis gas are studied by IR spectroscopy, Mössbauer spectroscopy, and transmission electron microscopy. It is shown that partial transformation of the $[Fe_5RhC(CO)_{16}]^-$ cluster to the $[Fe_4RhC(CO)_{14}]^-$ cluster occurs immediately after its deposition on the substrate surface with the simultaneous formation of Fe^{2+} ions. The complete conversion of the supported $[Fe_5RhC(CO)_{16}]^-$ cluster to $[Fe_4RhC(CO)_{14}]^-$ is observed at 323 K in the synthesis gas. At 373 to 423 K $[Fe_5RhC(CO)_{16}]^-$ transforms into a mixture of $Fe_4Rh_2C(CO)_{16}$, $[Fe_4RhC(CO)_{14}]^-$, and $[Fe_3Rh_3C(CO)_{15}]^-$ clusters. In the 523 to 623 K range, the supported $[Fe_5RhC(CO)_{16}]^-$ cluster decarbonylates completely to form bimetallic species $\leq$ 5 Å in size. Silica-supported FeRh clusters are active in propylene hydroformylation at 423 to 473 K and form a mixture of butyl alcohols and butyraldehydes.

Key words: carbonyl clusters, silica gel, propylene, hydroformylation; IR spectroscopy; Mössbauer spectroscopy.

The development of the chemistry of metal carbonyl clusters has made it possible to study them extensively. These compounds can be considered as potential catalysts of chemical reactions. There is an analogy between metal carbonyl clusters and metallic surfaces.[1] Carbonyl clusters can exhibit unusual catalytic properties, for example, in reactions involving CO and H_2 (CO hydrogenation or olefin hydroformylation), because carbon monoxide and hydrogen in fact form "inherent ligands" with them.[2] The metallic framework of the cluster is stabilized in the presence of CO above room temperature, when the rates of the majority of chemical reactions become noticeable. However, the prospects for using carbonyl clusters in catalysis turned out to be more limited than expected, because fragmentation of cluster compounds occurs under the conditions of catalytic reactions and these systems are catalytically active only due to mononuclear metallocomplexes.[3] There are only a few exceptions to this rule.[4,5]

Inorganic substrates are known to stabilize supported metal carbonyl clusters, especially cluster anions.[6—13] Such catalytic systems are active in CO hydrogenation to form products, whose molecular weight distribution does not obey the Schulz—Flory equation.[9—12] Some of these catalysts are active in gas-phase hydroformylation of olefins.[14,15]

This work is devoted to the study of the properties of systems prepared by deposition of the carbonyl clusters $[Fe_5RhC(CO)_{16}]^-$ and $[Fe_4RhC(CO)_{14}]^-$ on a silica gel surface. The stoichiometric transformations of the supported clusters are studied under conditions modelling the process of catalyst activation. The catalytic properties of the family of supported hexanuclear FeRh carbidocarbonyl clusters are studied during the gas-phase hydroformylation of propylene.

Experimental

Silica gel (specific surface 250 $m^2 g^{-1}$, sodium and iron content less than 0.01 wt. %) was dehydrated at 873 K *in vacuo*. The carbonyl clusters $[TEA][Fe_5RhC(CO)_{16}]$ and $[TEA][Fe_4RhC(CO)_{14}]$ (see Ref. 16), $Fe_4Rh_2C(CO)_{16}$ and $[TEA][Fe_3Rh_3C(CO)_{15}]$ (see Ref. 17) (TEA is tetraethyl ammonium) were synthesized according to the known procedures.

Carbonyl clusters were deposited by the impregnation of silica gel according its moisture capacity from solutions of the clasters in acetone (for ionic compounds) or hexane. The contents of the supported clusters were 2 wt. % calculated as the sum of Fe and Rh. The analysis was performed by X-ray fluorescence spectroscopy.

Transformations of supported clusters were studied by recording IR spectra of carbonyl compounds extracted with methylene chloride or acetonitrile from the surfaces of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 632—641, April, 1995.

[TEA][$Fe_5RhC(CO)_{16}$]/SiO_2 or [TEA][$Fe_4RhC(CO)_{14}$]/SiO_2 after various treatments of the latter. In a typical experiment, ~0.5 g of SiO_2 with a supported cluster was heated in a flow of CO, argon, or synthesis gas (CO : H_2 = 1 : 1) for 2 to 3 h, cooled to room temperature in the same atmosphere in which the treatment was carried out, a sample was extracted with 2.5 mL of MeCN or CH_2Cl_2, and the IR spectrum of the extract was recorded. The IR spectra of the solid residue that remained after evaporation of the extract (in pellets with KBr) were obtained in several cases.

Some studies were performed using an EMB-100B electron microscope with the limiting resolution of points of 3 Å, according to the procedure described previously.[18] Samples were prepared in air by mechanical fragmentation followed by ultrasonic dispergation in ethanol. The suspension was placed on carbon substrates on copper nets. The photography was performed in a light-field regime with an accelerating voltage of 75 kV, the aperture of the objective lens was $6 \cdot 10^{-3}$ rad. To rule out the effect of the carbon substrate on the degree of contrast of the display, the portions of the sample in the holes of the carbon substrate were studied. The microscope magnification was $2 \cdot 10^5$. The final magnification in the photographs was $10^6 \pm 5$ %.

The studies of supported and crystalline carbonyl clusters by Mössbauer spectroscopy were performed on a spectrometer with a constant acceleration drive for the source and with a non-linearity of scale ~0.05 %. ^{57}Co in a matrix of metallic chromium with the natural line width of ~0.17 mm s^{-1} was used as the source. All spectra were obtained at room temperature for the natural content of the ^{57}Fe isotope. The registration time of one spectrum was 72 h. The components were isolated from the spectra obtained by a special computer program assuming the Lorentz shape of the lines and symmetry of quadrupole doublets. The resulting chemical shifts were reduced to the shift of sodium nitroprusside.

Mössbauer spectra of samples were obtained in a hermetically sealed cell with windows of metallic beryllium. In addition, the Mössbauer spectrum of the crystalline cluster [TEA][$Fe_5RhC(CO)_{16}$] was recorded in a cell with Dacron windows. Several spectra were recorded in a cell with windows of metallic magnesium.

All procedures involving cluster deposition on SiO_2, the high-temperature treatments in various gaseous media, and the studies of the samples by IR and Mössbauer spectroscopic methods were performed under conditions that exclude contact with air oxygen. Before use, all samples were stored in an argon atmosphere in sealed glass tubes.

Hydroformylation of propylene was carried out in a flow installation in the 420 to 470 K temperature range and a total pressure of the reaction mixture of 1 atm. The molar ratio CO : H_2 : olefin : Ar was 1 : 1 : 1 : 7. The volume velocity of the reaction mixture flow was selected in such a way that the degree of conversion of propylene did not exceed 5 %.

Results and Discussion

The IR spectra of the clusters [$Fe_5RhC(CO)_{16}$][TEA] and [$Fe_4RhC(CO)_{14}$][TEA] dissolved in methylene chloride and acetonitrile, respectively, and the spectra of the clusters extracted from the silica gel surface with methylene chloride two weeks after deposition of the cluster [$Fe_5RhC(CO)_{16}$][TEA] on the silica gel surface and after 1 h exposure of the system [$Fe_5RhC(CO)_{16}$][TEA]/SiO_2 at 323 K in a flow of synthesis gas are presented in Fig. 1.

Absorption bands (AB) at 1843, 1985, 2008, and 2062 cm^{-1} are observed in the ν(CO) range of the IR spectrum of the dissolved cluster [$Fe_5RhC(CO)_{16}$][TEA] (see Fig. 1, curve *1*), while AB at 1886, 1930, 1956, 1982, 2002, 2025, and 2062 cm^{-1} are observed in the spectrum of [$Fe_4RhC(CO)_{14}$][TEA] (see Fig. 1, curve *4*). AB at 1841, 1886, 1982, 2004, 2024, and 2064 cm^{-1} appear in the IR spectra of the carbonyl compounds extracted from the surface of the system [$Fe_5RhC(CO)_{16}$][TEA]/SiO_2 two weeks after the deposition of the cluster on the substrate (see Fig. 1, curve *2*). The curves at 1886 and 2024 cm^{-1} indicate that $[Fe_4RhC(CO)_{14}]^-$ also is present in the extract, and its

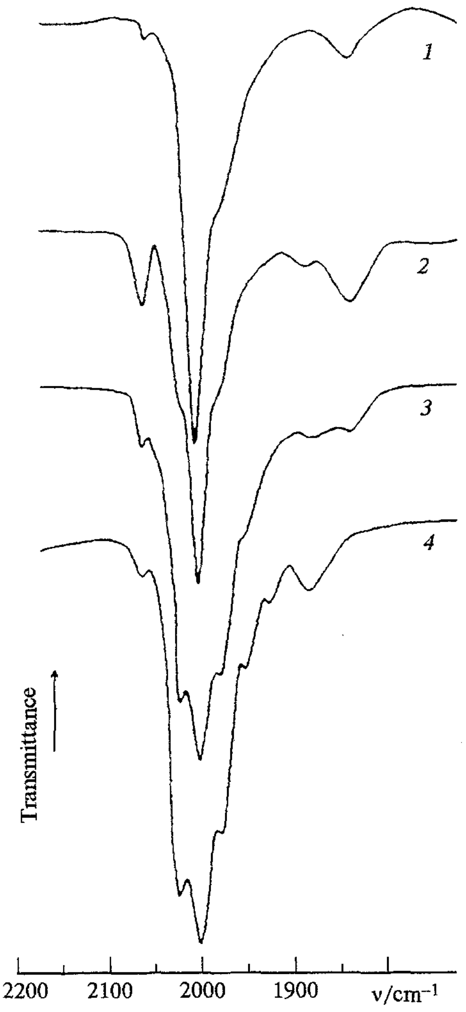

Fig. 1. IR spectra of clusters [TEA][$Fe_5RhC(CO)_{16}$] (*1*) and [TEA][$Fe_4RhC(CO)_{14}$] (*4*) dissolved in methylene chloride and acetonitrile, respectively, and the clusters obtained by the extraction of the catalyst [TEA][$Fe_5RhC(CO)_{16}$]/SiO_2 with methylene chloride two weeks after its preparation (*2*) and after its exposure for 1 h at 323 K in a flow of synthesis gas (*3*).

relative concentration increases as the exposure time of the sample increases. The treatment of this sample with synthesis gas at 323 K for 1 h results in the complete coincidence of the IR spectrum of the extract with that of the individual cluster $[Fe_4RhC(CO)_{14}]^-$. Only the AB at 1841 cm^{-1} (see Fig. 1, curve *3*) indicates the presence of a small amount of $[Fe_5RhC(CO)_{16}]^-$ in the extract.

Since $[Fe_4RhC(CO)_{14}]^-$ can be obtained by the elimination of the $Fe(CO)_2$ group from $[Fe_5RhC(CO)_{16}]^-$, the presence of synthesis gas during thermolysis is not necessary. In fact, the decomposition of the supported cluster $[Fe_5RhC(CO)_{16}]^-$ at 323 K in an argon atmosphere results in the same compound.

No rhodium was found on the SiO_2 surface after the thermolysis of the $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ system at 323 K in a synthesis gas atmosphere or in an argon atmosphere after the extraction of the supported carbonyl compounds with methylene chloride. This testifies that the formation of the pentanuclear cluster $[Fe_4RhC(CO)_{16}]^-$ from $[Fe_5RhC(CO)_{16}]^-$ is highly selective. It is noteworthy that the transformation of $[Fe_5RhC(CO)_{16}]^-$ into $[Fe_4RhC(CO)_{14}]^-$ in solution is well known.[5,17] However, the selectivity of the process in this case is noticeably lower and is 70 % for the reaction at 363 K in diglyme[17] and 92 % as the sum of the clusters $[Fe_4RhC(CO)_{14}]^-$ and $Fe_4Rh_2C(CO)_{16}$, whose formation was observed in the hydroformylation of 1-pentene involving $[Fe_5RhC(CO)_{16}]^-$ (373 K, 60 atm, $1CO + 1H_2$)[5].

No absorption bands that could be assigned to the cluster $[Fe_5RhC(CO)_{16}]^-$ were observed in the range where carbonyl vibrations appear in the IR spectrum of the extract after the treatment of the supported cluster $[Fe_5RhC(CO)_{16}][TEA]$ with synthesis gas at 373 K for 7 h. However, weak bands of the neutral cluster $Fe_4Rh_2C(CO)_{16}$ were observed in this range, which indicates the presence of a mixture of the clusters $[Fe_4RhC(CO)_{14}]^-$ and $Fe_4Rh_2C(CO)_{16}$ in the extract. The same bands were observed in the thermolysis of the supported cluster $[Fe_5RhC(CO)_{16}]^-$ at 373 K in an argon atmosphere. In neither of the two cases was rhodium found on the SiO_2 after the extraction of the carbonyl clusters with methylene chloride.

Figure 2 shows the absorption regions of the carbonyl groups of the cluster $Fe_4Rh_2C(CO)_{16}$ dissolved in *n*-hexane and of the clusters extracted from the surface of the $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ sample, which was treated at 423 K for 2 h in a $CO + H_2$ atmosphere. The IR spectrum of the cluster $[Fe_4RhC(CO)_{14}]^-$ dissolved in acetonitrile is presented for a comparison. The IR spectrum of the cluster $Fe_4Rh_2C(CO)_{16}$ contains AB at 1965, 1982, 1998, 2018, 2028, 2042, 2055, and 2074 cm^{-1}. The bands at 1886, 1956, 1982, 2002, 2017, 2026, 2045, 2055, and 2075 cm^{-1} present in the spectra of the carbonyl compounds extracted after the treatment of the $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ sample with synthesis gas at 423 K. A comparison of this spectrum and the IR spectra of the clusters $[Fe_5RhC(CO)_{16}][TEA]$, $[Fe_4RhC(CO)_{14}][TEA]$, and $Fe_4Rh_2C(CO)_{16}$ (see Figs. 1 and 2) shows that the cluster $[Fe_5RhC(CO)_{16}]^-$ is absent and a mixture of the clusters $[Fe_4RhC(CO)_{14}]^-$ (AB at 1886, 1956, 1982, 2002, and 2026 cm^{-1}) and $Fe_4Rh_2C(CO)_{16}$ (AB at 2017, 2026, 2045, 2955, and 2075 cm^{-1}) is present in the extract. Only trace amounts of rhodium were observed on the substrate after the extraction of the carbonyl compounds from the $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ sample. The presence of rhodium on the substrate may be caused by the decomposition of the cluster during thermolysis or by incomplete extraction of the carbonyl compounds from the SiO_2 surface. Increasing in the duration of the thermolysis of $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ at 423 K to 5 h results in the appearance of $[Fe_3Rh_3C(CO)_{15}][TEA]$. This compound is identified by the presence of AB at 780 and 750

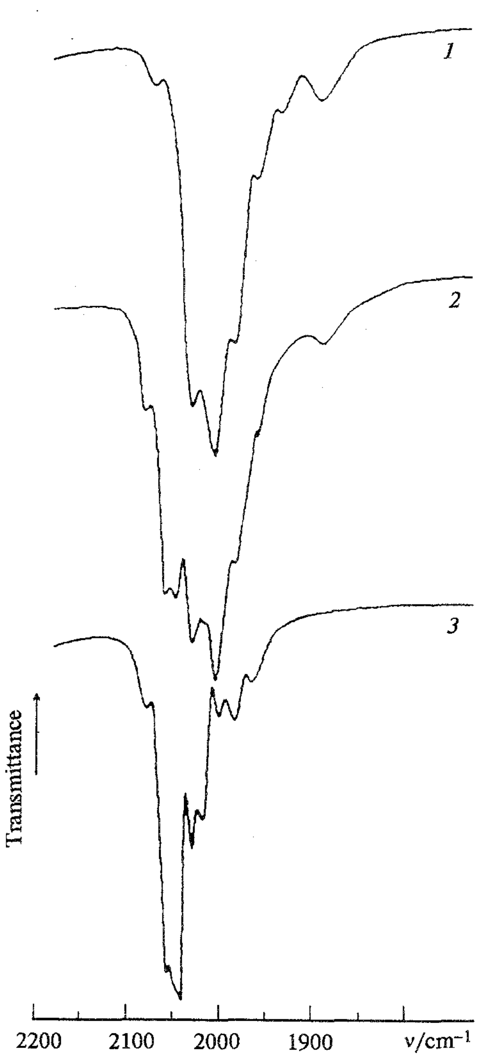

Fig. 2. IR spectra of clusters $[TEA][Fe_4RhC(CO)_{14}]$ in acetonitrile (*1*) and $Fe_4Rh_2C(CO)_{16}$ in *n*-hexane (*3*) and the solution obtained by the extraction of the catalyst $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ with methylene chloride (*2*) after its exposure for 2 h at 423 K in a flow of synthesis gas ($CO : H_2 = 1 : 1$).

cm^{-1} in the IR spectrum of the solid substance remaining after evaporation of the extract to dryness. Stretching vibrations of the metal—carbide carbon bonds appear in this spectral range. The thermolysis of $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ at 423 K in an argon atmosphere instead of CO + H_2 does not result in any changes in the composition of the products. However, an insignificant amount of rhodium remains on the SiO_2 surface after the extraction of the carbonyl compounds.

Increasing the treatment temperature of the $[Fe_5RhC(CO)_{16}]^-/SiO_2$ system to 523 K results in the decomposition of the surface molecular carbonyl clusters, because there are no AB in the IR spectrum of the acetonitrile extract that can be assigned to stretching vibrations of CO groups.

The SiO_2-supported cluster $Fe_4RhC(CO)_{14}][TEA]$ undergoes no noticeable transformations in a synthesis gas atmosphere below 423 K. Additional AB of the CO groups, which are not related to the cluster $[Fe_4RhC(CO)_{14}]^-$, are observed in the IR spectrum of the extract only after 3-h exposure in a flow of synthesis gas at 423 K followed by extraction with methylene chloride.

Figure 3 shows the IR spectrum of the carbonyl clusters extracted with methylene chloride from $[Fe_4RhC(CO)_{14}][TEA]/SiO_2$ after a 10-h exposure of the system to a CO + H_2 flow at 423 K (AB at 1852, 1877, 1956, 1980, 2002, 2016, and 2033 cm^{-1}) and the spectra of $[Fe_3Rh_3C(CO)_{15}][TEA]$ dissolved in methylene chloride (AB at 1852, 1878, 1924, 1934, 1980, 2016, and 2033 cm^{-1}) and $[Fe_4RhC(CO)_{14}][TEA]$ dissolved in acetonitrile. The AB at 2016 cm^{-1} and the doublet of the bands at 1878 and 1850 cm^{-1} corresponding to the stretching vibrations of the bridge CO ligands[17] convincingly prove that the pentanuclear cluster $[Fe_4RhC(CO)_{14}]^-$ transforms into the hexanuclear cluster $[Fe_3Rh_3C(CO)_{15}]^-$ on the silica gel surface.

No AB that could be assigned to rhodium or iron homonuclear clusters were observed in the spectra of the extracts studied. However, it is known[5] that iron pentacarbonyl $Fe(CO)_5$ is formed in the transformations of the clusters $[Fe_5RhC(CO)_{16}][P(C_6H_5)_4]$ and $[Fe_4RhC(CO)_{14}][P(C_6H_5)_4]$ under the conditions of hydroformylation of 1-pentene.

The change in the state of iron in the thermolysis of the FeRh clusters on the SiO_2 surface was studied by Mössbauer spectroscopy.

Figure 4 presents the Mössbauer spectra of the crystalline and supported clusters $[Fe_4RhC(CO)_{14}][TEA]$ and $[Fe_5RhC(CO)_{16}][TEA]$ subjected to different treatments. The parameters obtained from the computational resolution of the spectra into the Lorentz components are listed in Table 1.

The spectrum of the cluster $[Fe_5RhC(CO)_{16}][TEA]$ in the crystalline state is a superposition of two doublets, which testifies that the iron atoms in this cluster are chemically non-equivalent. The ratio of the surface areas of these doublets is equal to 4 (see Table 1), which makes it possible to assume that they belong to the iron atoms at the *cis*- and *trans*-positions to the rhodium atom in the octahedral carbonyl $[Fe_5RhC(CO)_{16}]^-$. It should be noted that in the Mössbauer spectra the chemical shift and quadrupole splitting of the Fe^{III} ions in the Fe—Rh/SiO_2 catalysts prepared using $RhCl_3 \cdot xH_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ and reduced at 850 K are 0.76 and 0.94 mm s^{-1}, respectively,[19,20] which are close to the parameters of the iron state denoted in Table 1 as Fe^0_1 (δ = 0.50 mm s^{-1}, ε = 0.94 mm s^{-1}).

The peculiarities of the spatial structures of the metallopolyhedron of the $[Fe_4RhC(CO)_{14}]^-$ molecule (tetragonal pyramid with a rhodium atom at one of the vertices of the base[17]) allow one to draw the conclusion that there are iron atoms of three types: two atoms at the *cis*-position relative to the rhodium in the base of the

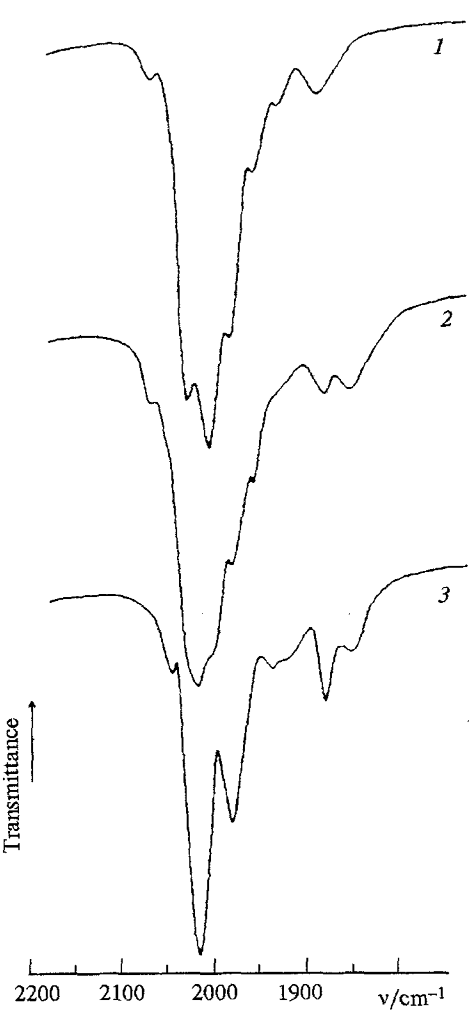

Fig. 3. IR spectra of clusters $[TEA][Fe_4RhC(CO)_{14}]$ in acetonitrile (*1*) and $[Fe_3Rh_3C(CO)_{15}][TEA]$ in methylene chloride (*3*), and the solution obtained by the extraction of the catalyst $[Fe_4RhC(CO)_{14}][TEA]/SiO_2$ with methylene chloride (*2*) after its exposure for 10 h at 423 K in a flow of synthesis gas (CO : H_2 = 1 : 1).

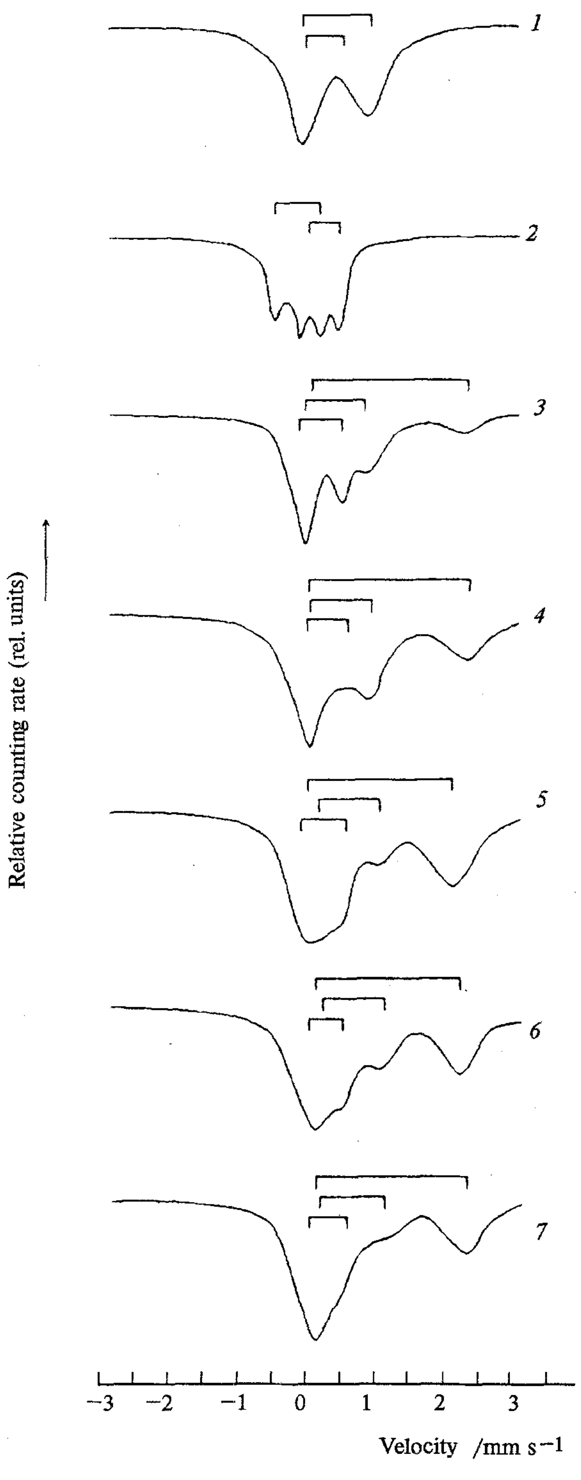

Fig. 4. Mössbauer spectra of crystalline clusters $[Fe_5RhC(CO)_{16}][TEA]$ (*1*), $[Fe_4RhC(CO)_{14}][TEA]$ (*2*), SiO_2-supported cluster $[Fe_5RhC(CO)_{16}][TEA]$ (*3*), and the samples obtained by the treatment of the catalyst $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ with the synthesis gas at 323 K (*4*), 423 K (*5*), 523 K (*6*), and 623 K (*7*) for 3 h.

square pyramid, an atom at the vertex of the pyramid, and an atom at the *trans*-position to the rhodium atom in the base of the square pyramid. However, the Mössbauer spectrum of the $[Fe_4RhC(CO)_{14}][TEA]$ cluster in the crystalline state can be satisfactorily resolved only into doublets. This testifies that the parameters of the Mössbauer spectra of the iron atoms at the *cis*-position to the rhodium in the base of the square pyramid and the atom at the pyramid vertex are similar. The fact that the ratio of the surface areas of the corresponding quadrupole doublets is equal to 7/3 (see Table 1) instead of 3/1 (three Fe atoms at the *cis*-position and one Fe atom at the *trans*-position relative to the rhodium) can be considered as quite satisfactory, taking into account the accuracy of the determination of these surface areas, which is 5 to 10 %.

When the $[Fe_5RhC(CO)_{16}][TEA]$ cluster is supported on a silica gel surface, the quadrupole doublet of Fe^{2+} appears in its Mössbauer spectrum. The relative contribution of this state of iron increases after the treatment of the $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ sample with synthesis gas at 323 K (see Table 1). As shown by IR spectroscopy, this treatment results in the predominant transformation of the $[Fe_5RhC(CO)_{16}]^-$ cluster into $[Fe_4RhC(CO)_{14}]^-$ (see Fig. 1). Note that the parameters of the state of iron in samples **4** and **5** (see Table 1) conventionally denoted as $Fe^0{}_1$ are intermediate between those of the state of iron $Fe^0{}_1$ in the crystalline cluster $[Fe_5RhC(CO)_{16}][TEA]$ and the Fe^{3+} ions on the silica gel surface.[19,20] At the same time, the similarity of the parameters of the $Fe^0{}_1$ and Fe^{3+} states does not allow one to determine reliably the contribution of each of them, assuming that both of them exist in samples **4** and **5**.

At moderate temperatures and in the absence of oxygen, the only reason for the appearance of iron atoms on the surface of dehydrated SiO_2 is the oxidation of atoms of the formally zero-valence iron, which eliminate from the octahedral cluster $[Fe_5RhC(CO)_{16}]^-$ when it is transformed into the cluster $[Fe_4RhC(CO)_{14}]^-$, by the surface hydroxyl groups (reactions (1a) and (1b)).

$$[Fe_5RhC(CO)_{16}]^- \rightarrow [Fe_4RhC(CO)_{14}]^- + [Fe(CO)_2] \qquad (1a)$$

$$\begin{aligned}&[Fe(CO)_2] + n(\equiv Si-OH) \rightarrow \\ &\rightarrow (\equiv Si-O^-)_nFe^{n+} + (n/2)H_2 + 2CO \qquad (1b)\end{aligned}$$

Reaction (1b) occurs in the case of supported homonuclear iron carbonyls.[21–23] A comparison of the oxidation potentials of the Fe^{2+}/Fe^0 and Fe^{3+}/Fe^0 systems with the potential of the $2H^+/H_2$ system shows that the oxidation of zero-valence iron to Fe^{3+} is thermodynamically improbable at a low concentration of protons (hydroxyl groups).[24] It has been shown[25] that the temperature-programmed decomposition of the γ-Al_2O_3-supported $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ carbonyls in a helium flow in the 295 to 873 K temperature range results in the oxidation of iron. The valent state of iron changes from 1.6 to 2.4 depending on the type of

Table 1. Parameters of the Mössbauer spectra of the sample studied

Sample	Composition of the cluster (catalyst)	Type of treatment	State of Fe	δ	ε	S (%)
				/mm s^{-1}		
1	$[Fe_5RhC(CO)_{16}][TEA]$, crystalline	—	Fe^0	0.33	0.57	20
			$Fe^0{}_1$	0.50	0.9	80
2	$[Fe_4RhC(CO)_{14}][TEA]$, crystalline	—	Fe^0	0.27	0.56	70
			$Fe^0{}_2$	−0.07	0.65	30
3	$[Fe_5RhC(CO)_{16}]^-/SiO_2$	—	Fe^0	0.26	0.63	45
			Fe^{2+}	1.26	2.28	15
			$Fe^0{}_1(Fe^{3+})^*$	0.46	0.88	40
4	$[Fe_5RhC(CO)_{16}]^-/SiO_2$	CO + H_2, 3 h, 323 K	Fe^0	0.35	0.63	14
			Fe^{2+}	1.25	2.32	36
			$Fe^0{}_1(Fe^{3+})^*$	0.55	0.88	50
5	$[Fe_5RhC(CO)_{16}]^-/SiO_2$	CO + H_2, 3 h, 423 K	Fe^0	0.28	0.65	20
			Fe^{2+}	1.10	2.10	65
			$Fe^0{}_1(Fe^{3+})^*$	0.65	0.90	15
6	$[Fe_5RhC(CO)_{16}]^-/SiO_2$	CO + H_2, 3 h, 523 K	Fe^0	0.30	0.56	18
			Fe^{2+}	1.20	2.06	55
			Fe^{3+}	0.65	0.90	27
7	$[Fe_5RhC(CO)_{16}]^-/SiO_2$	H_2, 3 h, 623 K	Fe^0	0.33	0.55	57
			Fe^{2+}	1.25	2.23	18
			Fe^{3+}	0.68	0.95	25

Note. δ is the chemical shift, ε is the quadrupole splitting, S is the relative surface area of the signal corresponding to the given state of iron.

* The presence of both of the states is possible, the similarity of their parameters does not allow one to determine reliably the contribution of each of them.

carbonyl compound, the method of its deposition on the substrate, and the experimental conditions. Only Fe^{2+} and Fe^0 states were found[26] on the MgO surface by Mössbauer spectroscopy after the decomposition of the supported $Fe_3(CO)_{12}$. It is noteworthy that in the decomposition of supported carbonyls a portion of the CO hydrogenates to form hydrocarbons.[23,25] The appearance of Fe^{3+} ions on the substrate surface, for example, according to reaction (2), cannot be ruled out.

$$4\ Fe^0 + 2\ CO + 6\ {\equiv}Si{-}OH \rightarrow$$
$$\rightarrow 2\ {\equiv}Si{-}OFeO + 2\ ({\equiv}Si{-}O)_2Fe + C_2H_6 \qquad (2)$$

However, hydrogenation of carbon monoxide becomes noticeable[23] above 423 K. In any event, if the transformation of the cluster $[Fe_5RhC(CO)_{16}]^-$ into $[Fe_4RhC(CO)_{14}]^-$ is the only reaction on the SiO_2 surface (this seems to be true for temperatures below 323 K), the maximum amount of iron that can exist in the oxidized state cannot exceed 20 % of its total amount (see Eq. (1a)). Therefore, samples **3** and **4** can contain only an insignificant amount of iron as Fe^{3+} ions (see Table 1), and its state with δ = 0.46 to 0.55 and ε = 0.88 probably corresponds to the $Fe^0{}_1$ state in the crystalline cluster $[Fe_5RhC(CO)_{16}]^-$. However, it is likely that even this interpretation overestimates the amount of Fe^{2+} in samples **3** and **4**, if it is assumed that only reaction (1a) can occur under these conditions. It is also unclear why the ratio $Fe^0/Fe^0{}_1$ changes from 0.25 for sample **1** to 1.33 for sample **5**. This fact needs further study.

As follows from the IR spectroscopic data, the supported cluster $[Fe_5RhC(CO)_{16}]^-$ transforms predominantly into $[Fe_4RhC(CO)_{14}]^-$ below 373 K. The analysis of the Mössbauer spectra of the crystalline clusters $[Fe_5RhC(CO)_{16}][TEA]$ and $[Fe_4RhC(CO)_{14}][TEA]$ (Fig. 4, Table 1) shows that their parameters are similar (spread is less than 5 %). This makes it impossible to establish their ratio with sufficient accuracy from the Mössbauer spectra of the samples obtained by the deposition of $[Fe_5RhC(CO)_{16}][TEA]$ on the SiO_2 surface (see Table 1, samples **3** and **4**). Nevertheless, the computational simulation allows one to draw the qualitative conclusion that these clusters exist in samples **3** and **4** (see Table 1). When the spectra are interpreted according to the model, which consists of only one component corresponding to the $[Fe_5RhC(CO)_{16}][TEA]$ clusters, the "residual noise" obtained as a result of the interpretation contains a component corresponding to the $[Fe_4RhC(CO)_{14}][TEA]$ cluster. This confirms that both of the components exist in the initial Mössbauer spectrum.

Increasing the temperature of the treatment of the $[Fe_5RhC(CO)_{16}]^-/SiO_2$ sample in CO + H_2 from 323 to 423 K results in a still greater increase in the contribution of the Fe^{2+} state to the resulting spectrum (see Table 1, samples **4** and **5**). According to the data of IR spectroscopy, the $[Fe_5RhC(CO)_{16}]^-$ cluster is transformed into a mixture of $[Fe_4RhC(CO)_{14}]^-$ and $Fe_4Rh_2C(CO)_{16}$ at 423 K. Assuming that complete transformation takes place (this contradicts the IR spectroscopic data), only 60 % of the initial iron can be in the oxidized form, *i.e.,* in this case, the fraction of oxidized iron in sample **5** is overestimated as well.

When the spectrum of sample **6** (see Table 1) is interpreted, it should be kept in mind that the supported carbonyl clusters completely decompose after treatment with a CO + H_2 mixture at 523 K. Under these conditions, the hydrogenation of carbon monoxide to form hydrocarbons occurs with a noticeable rate. The observed ratio between the different states of Fe is due to competition between the processes that lead to iron oxidation (for example, the reactions with hydroxyl groups and the oxygen formed on the surface due to CO dissociation) and the processes of iron reduction (reaction with hydrogen).

The reduction of the $[Fe_5RhC(CO)_{16}]^-/SiO_2$ system by hydrogen at 623 K results in an increase in the fraction of Fe^0 in the Mössbauer spectrum of the sample to 57 % (see Table 1, sample **7**), and the fraction of Fe^{2+} decreases to 18 %. Note that the Mössbauer parameters of the Fe^{3+} state in samples **6** and **7** are very close to those for the Fe^{3+} ions on the SiO_2 surface (δ = 0.76 mm s^{-1}, ε = 0.94 mm s^{-1}).[19,20]

The electron microscopic study of the $[Fe_5RhC(CO)_{16}]^-/SiO_2$ catalyst reduced at 623 K (see Table 1, sample **7**) shows that it contains uniform metallic particles $\leq$ 0.5 nm in size. This value is close to the sizes of the metallic cluster framework of Fe_5Rh. The experimental data obtained (small size and homogeneity of metallic particles, iron ions, and the previously established possibility of the stabilization of metallic clusters bonded to the substrate surface by metal ions[27]) make it possible to assume that the reduced sample contains bimetallic FeRh particles, which interact with the SiO_2 surface *via* the iron atoms.

Based on the aforesaid, the following scheme of the transformations of the SiO_2-supported cluster $[Fe_5RhC(CO)_{16}]^-$ below 423 K can be suggested (Scheme 1).

It should be kept in mind that the ≡Si—OH group of the substrate also acts as a reagent, and CO, H_2, and probably hydrocarbons should be in the reaction products. Although no attempts have been made to detect gaseous products, their formation is required for the mass balance and has been previously[17,21–23] found for similar transformations.

Thus, the SiO_2-supported cluster $[Fe_5RhC(CO)_{16}]^-$ can transform *via* the monomolecular route to form the pentanuclear cluster $[Fe_4RhC(CO)_{14}]^-$ (reaction (3a)) and *via* the bimolecular route to form the hexanuclear cluster $Fe_4Rh_2C(CO)_{16}$ (reaction (3b)). It is likely that the activation energy of the second process is higher; therefore, its contribution becomes noticeable only at high temperatures. It should be mentioned that $[Fe_4Rh_2C(CO)_{15}]^{2-}$ can be obtained from $[Fe_4RhC(CO)_{14}]^-$ by thermolysis in diglyme at 383 K (20 h, yield 53 % with respect to Rh).[28]

The cluster $[Fe_5RhC(CO)_{16}]^-$ is transformed into $[Fe_4RhC(CO)_{14}]^-$ in diglyme at 363 K (see Ref. 17), also forming metallic iron and carbon monoxide probably *via* the decomposition of the short-lived $\{Fe(CO)_2\}$ particle, which eliminates from the $[Fe_5RhC(CO)_{16}]^-$ cluster. It cannot be ruled out that when this reaction is performed in a carbon monoxide atmosphere, the intermediate $\{Fe(CO)_2\}$ can form stable homonuclear carbonyls. In particular, this is supported by the observation of,[5] in addition to the FeRh cluster carbonyls, iron pentacarbonyl in the transformation of the $[Fe_5RhC(CO)_{16}]^-$ cluster under the conditions of hydroformylation of 1-pentene. It can also be assumed that reaction (1a) is reversible at moderate temperatures in a CO atmosphere. In this case, the oxidation of the Fe^0 atoms shifts the equilibrium to the right. It is likely that it is the oxidation of $\{Fe(CO)_2\}$ formed *via* reaction (1a) by the hydroxyl groups of the substrate that causes reaction (1a) to proceed on the SiO_2 surface even at room temperature.

$$\begin{aligned}&\{Fe(CO)_2\} + 2\ {\equiv}Si{-}OH \rightarrow\\&\rightarrow ({\equiv}Si{-}O^-)_2Fe^{2+} + H_2 + 2\ CO \qquad (4)\end{aligned}$$

Reaction (3b), *i.e.,* the transformation of the $[Fe_5RhC(CO)_{16}]^-$ cluster into the $Fe_4Rh_2C(CO)_{16}$ cluster has been poorly studied. This transformation has been found[5] only for hydroformylation of 1-pentene in a mixture of CH_2Cl_2, C_5H_{10}, and C_6H_6 at 373 K and 60 atm of 1CO + 1H_2. No propositions concerning the mechanism of this transformation have been advanced.

Scheme 1

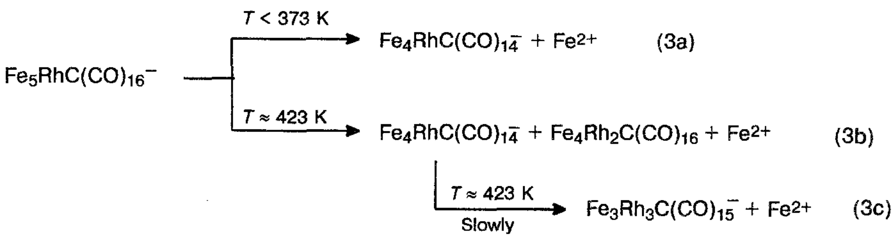

Table 2. Catalytic properties of samples reduced at 573 K, obtained by the deposition of FeRh carbonyl clusters on SiO_2 in the reaction of propylene gas-phase hydroformylation at 473 K

Cluster	Formation rate/mol (mol cluster)$^{-1}$ h^{-1}		*S* (%)		Ratio
	C_3H_6	C_3H_7CHO + + $C_3H_7CH_2OH$	Aldehydes	Alcohols	*n/iso*
$[Fe_5RhC(CO)_{16}][TEA]$	1.43	0.96	5.2	27.8	1.85
$[Fe_4RhC(CO)_{14}][TEA]$	4.47	3.82	14.5	31.5	2.3
$Fe_4Rh_2C(CO)_{14}$	5.99	5.45	14.7	33.3	2.74
$[Fe_3Rh_3C(CO)_{15}][TEA]$	3.78	2.52	20.0	20.0	3.0

Reaction (3c) is more complicated. Studying it is hampered by the low reactivity of the $[Fe_4RhC(CO)_{14}]^-$ cluster in reaction (3c). This results in side reactions related to the decomposition of the initial substance, found by traces of rhodium on the SiO_2 surface after the extraction of carbonyl compounds.

SiO_2-supported FeRh clusters exhibit noticeable catalytic activity in the gaseous hydroformylation of propylene above 423 K, *i.e.,* above the limits of the thermal stability of the supported clusters. Butanal, 2-methylpropanal, butanol, 2-methylpropanol-1, and propane are the reaction products. The catalytic properties of the pre-reduced samples are shown in Table 2.

A typical example of the change over time of the activity of SiO_2-supported carbonyl clusters in the absence of a pre-reduced catalyst is presented in Fig. 5.

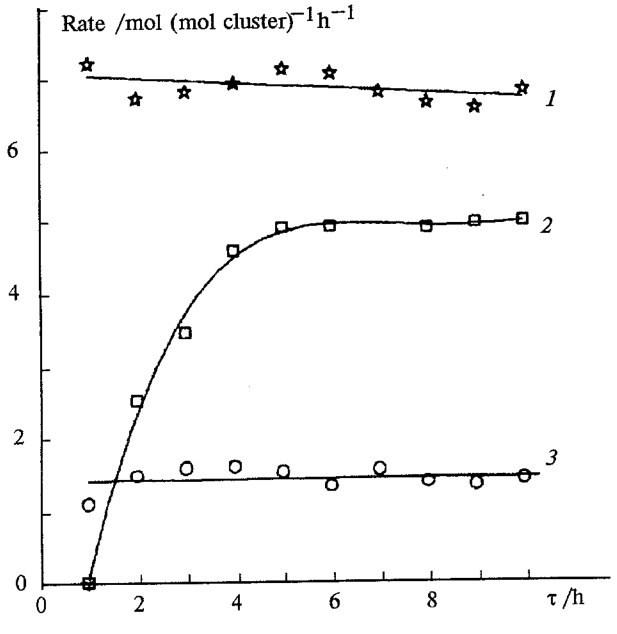

Fig. 5. Change over time in the rate of formation of the products of propylene gas-phase hydroformylation at 473 K in the presence of $Fe_4Rh_2C(CO)_{16}/SiO_2$: propane (*1*); butyl alcohols (*2*); butyric aldehydes (*3*).

Without pre-activating the supported clusters their catalytic activity increases over time and tends to the activity of the samples pre-reduced at 573 K in a H_2 flow. Therefore, the activities of the initial cluster compounds on the substrates are noticeably lower than the activities of the products of their decomposition in a reducible atmosphere. The character of the change in the rates of formation of butyl alcohols, butyric aldehydes, and propane can differ significantly. For example, the rate of hydrogenation of propylene on the catalyst obtained using the $Fe_4Rh_2C(CO)_{16}$ cluster changes slightly over 10 h (see Fig. 5). It is known that molecular rhodium clusters on oxide substrates[29] and heterogeneous rhodium-containing metallic catalysts[30] are active in olefin hydrogenation. Since a portion of the supported cluster molecules decomposes in the reaction, the character of the change over time in the rate of propane formation is determined by the ratio of the rates of propylene hydrogenation on the two types of active centers, "cluster" and metallic. In this case, the fact that the hydrogenation activity is constant over time may indicate that the activities of these centers are approximately the same.

The rates of formation of butyric and isobutyric aldehydes (see Fig. 5) depend on two components: the rate of aldehyde formation *via* the hydroformylation of propylene (reaction (5a))

$$2CH_3CH{=}CH_2 + 2CO + 2H_2 \rightarrow \\ \rightarrow CH_3CH_2CH_2CHO + (CH_3)_2CHCHO \qquad (5a)$$

and the rate of hydrogenation of the aldehydes to butyl alcohols (reaction (5b)).

$$C_3H_7CHO + H_2 \rightarrow C_3H_7CH_2OH \qquad (5b)$$

If the rates of aldehyde formation *via* reaction (5a) and their consumption *via* reaction (5b) are equal, the observed rate of aldehyde formation is time-independent. It is noteworthy that 1 h after the beginning of the hydroformylation of propylene on the $Fe_4Rh_2C(CO)_{16}/SiO_2$ sample the transformation rate *via* route (5b) is close to zero, *i.e.,* reaction (5b) has an induction period that is necessary for the formation of the active centers responsible for hydrogenation of aldehydes to alcohols.

A comparison of the catalytic activities of the supported FeRh clusters after their reduction by hydrogen at 573 K shows that the $Fe_4Rh_2C(CO)_{16}/SiO_2$ system is the most active and the $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ system is the least active. The activities of the $[Fe_4RhC(CO)_{14}][TEA]/SiO_2$ and systems based on $[Fe_3Rh_3C(CO)_{16}][TEA]/SiO_2$ differ to a smaller extent (see Table 2). It is known[5] that when hydroformylation of 1-pentene occurs under the conditions of homogeneous catalysis, the dissolved clusters $Fe_4Rh_2C(CO)_{16}$ and $[Fe_3Rh_3C(CO)_{16}][PPh_4]$ are the most active, while $[Fe_5RhC(CO)_{16}][PPh_4]$ and $[Fe_4RhC(CO)_{14}][PPh_4]$ are considerably less active. In the case of the first two clusters, 1-pentene is transformed selectively into aldehydes, whereas in the case of the latter, approximately one-third of the olefin introduced into the reaction isomerizes to 2-pentene (see Ref. 5). When propylene is hydroformylated in the gaseous phase on heterogeneous FeRh catalysts, the selectivity with respect to oxygen-containing compounds is noticeably lower than for homogeneous systems of similar composition. The selectivity with respect to oxygen-containing products does not exceed 50 % due to the contribution of the side reaction of olefin hydrogenation, and a considerable portion of the aldehydes is hydrogenated to the corresponding alcohols (see Table 2). The ratio of linear and α-branched oxygen-containing products of the hydroformylation of propylene on the heterogeneous catalysts studied ranges from 1.85 to 3.0 (see Table 2). This ratio is equal to 1 for the homogeneous catalysts $Fe_4Rh_2C(CO)_{16}$ and $[Fe_3Rh_3C(CO)_{16}][PPh_4]$ and increases to 2.7 for $[Fe_5RhC(CO)_{16}][TEA]$ and $[Fe_4RhC(CO)_{14}][TEA]$ (see Ref. 5).

The catalysts obtained by the deposition of iron carbonyl clusters on SiO_2 are known[15] to be inactive in olefin hydroformylation. If the reaction rates on the supported FeRh catalysts are calculated not per mole of the cluster, but per mole of Rh, the highest activity in propylene hydroformylation is observed for the reduced $[Fe_4RhC(CO)_{14}][TEA]/SiO_2$ catalyst. Despite the fact that a little above room temperature the supported cluster $[Fe_5RhC(CO)_{16}]^-$ rapidly transforms into $[Fe_4RhC(CO)_{14}]^-$, the total activity of the reduced $[Fe_5RhC(CO)_{16}][TEA]/SiO_2$ catalyst is more than three times lower than that of the reduced $[Fe_4RhC(CO)_{14}][TEA]/SiO_2$ sample (see Table 2). This can be related to the fact that the excess Fe^{n+} ions that are formed on the SiO_2 surface in the transformation of $[Fe_5RhC(CO)_{16}]^-$ into $[Fe_4RhC(CO)_{14}]^-$ in the process of catalyst activation, are localized near the active centers formed and exert an inhibiting effect on the activity of rhodium. The conclusion that the activity of rhodium is suppressed by iron in olefin hydroformylation can be also drawn from a comparison of the reaction rates in the presence of dissolved FeRh clusters[5] and homogeneous rhodium catalysts.[31]

This work was financially supported by the Krasnoyarsk Region Science Foundation (Grant No. 1F0020).

References

1. E. L. Muetterties, *Bull. Soc. Chem. Belg.*, 1975, **84**, 959.
2. S. P. Gubin, *Khimiya klasterov. Osnovy klassifikatsii i stroenie* [*The Chemistry of Clusters: Classification Principles and Structure*], Nauka, Moscow, 1987 (in Russian).
3. W. L. Gladfelter and K. J. Roesselet, in *The Chemistry of Metal Cluster Complexes,* Eds. D. F. Shriver, D. Kaesz, and R. D. Adams, VCH, Weinheim, 1990, 329.
4. S. Attaly and R. Mathieu, *J. Organomet. Chem.*, 1985, **291**, 205.
5. M. K. Alami, F. Dahan, and R. Mathieu, *J. Chem. Soc., Dalton Trans.*, 1987, 1983.
6. H. H. Lamb and B. C. Gates, *J. Am. Chem. Soc.*, 1986, **108**, 81.
7. H. Knoezinger and B. C. Gates, in *Metal Clusters in Catalysis,* Eds. B. C. Gates, L. Guczi, and H. Knoezinger, Elsevier, Amsterdam, 1986, 531.
8. R. Patrini, J. Puga, K. Sanchez, and B. Gates, *Abstr. VI Int. Symp. on Relations between Homogen. and Heterogen. Catalysis,* Pisa, Italy, 1989, 131.
9. P.-L. Zhou and B. C. Gates, *J. Chem. Soc., Chem. Commun.*, 1989, 347.
10. P.-L. Zhou, S. D. Maloney, and B. C. Gates, *J. Catal.*, 1991, **129**, 315.
11. T. J. Lee and B. C. Gates, *Catal. Lett.*, 1991, **8**, 15.
12. S. Kawi, J.-R. Chang, and B. C. Gates, *J. Catal.*, 1993, **142**, 585.
13. T. Beutel, S. Kawi, S. K. Purnell, H. Knoezinger, and B. C. Gates, *J. Phys. Chem.*, 1993, **97**, 7284.
14. E. J. Rode, M. E. Davis, and B. E. Hanson, *J. Catal.*, 1985, **96**, 563, 574.
15. A. Fukuoka, T. Kimura, N. Kosugi, H. Kuroda, Y. Minai, Y. Sakai, T. Tominaga, and M. Ichikawa, *J. Catal.*, 1990, **126**, 434.
16. V. E. Lopatin, N. M. Mikova, and S. P. Gubin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1407 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 1276 (Engl. Transl.)].
17. S. P. Gubin, N. M. Mikova, M. Ts. Tsybenov, and V. E. Lopatin, *Koord. Khim.*, 1984, **10**, 625 [*Sov. J. Coord. Chem.,* 1984, **10** (Engl. Transl.)].
18. V. I. Zaikovskii, Yu. A. Ryndin, V. I. Koval'chuk, L. M. Plyasova, B. N. Kuznetsov, and Yu. I. Ermakov, *Kinet. Katal.*, 1981, **22**, 443 [*Kinet. Catal.,* 1981, **22** (Engl. Transl.)].
19. J. W. Niemantsverdriet, J. A. C. van Kaam, C. F. J. Flipse, and A. M. van der Kraan, *J. Catal.*, 1985, **96**, 58.
20. J. W. Niemantsverdriet, J. van Grondelle, and A. M. van der Kraan, *Hyperfine Interaction*, 1986, **28**, 867.
21. A. Brenner and R. L. Burwell, Jr., *J. Catal.*, 1978, **52**, 353.
22. A. Brenner, D. A. Hucul, and S. J. Hardwick, *Inorg. Chem.*, 1979, **18**, 1478.
23. J. M. Basset, B. Besson, A. Choplin, F. Hugues, M. Leconte, D. Rojas, A. K. Smith, A. Theolier, Y. Chauvin, D. Commereuc, R. Psaro, R. Ugo, and G. M. Zanderighi, in *Fundam. Res. Homogeneous Catal.*, New York — London, 1984, **4**, 19.
24. Yu. Yu. Lur'e, in *Spravochnik po analiticheskoi khimii* [*Handbook on Analytical Chemistry*], Khimiya, Moscow,

1971, 271—287 (in Russian).
25. A. Brenner and D. A. Hucul, *Inorg. Chem.*, 1979, **18**, 2836.
26. F. Hugues, J. A. Dalmon, P. Bussiere, A. K. Smith, J. M. Basset, and D. Olivier, *J. Phys. Chem.*, 1982, **86**, 5136.
27. Yu. I. Yermakov and B. N. Kuznetsov, *J. Mol. Catal.*, 1980, **18**, 13.
28. M. Ts. Tsybenov, S. P. Gubin, V. E. Lopatin, and N. S. Erdyneev, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1987, **32**, 104 [*Mendeleev Chem. J.*, 1987, **32** (Engl. Transl.)].
29. R. Psaro, C. Dossi, L. Sordelli, and R. Ugo, *Chim. e ind.*, 1992, **74**, 154.
30. *Kataliticheskie svoistva veshchestv* [*Catalytic Properties of Substances*], Manual, Ed. V. A. Roiter, Naukova Dumka, Kiev, 1968 (in Russian).
31. R. L. Pruett, *Adv. Organomet. Chem.*, 1979, **17**, 1.

Received April 26, 1994;
in revised form October 10, 1994