States of cobalt and iron in catalysts supported on TiO_2 from data of diffuse reflectance IR spectra of adsorbed carbon monoxide

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The variations in the oxidation states of cobalt and iron atoms in pure and mixed Co- and Fe-containing catalysts supported on TiO_2 as a function of the conditions in which the catalysts were prepared and preliminarily treated were studied by analysis of the IR spectra of carbon monoxide adsorbed on these catalysts. A mutual influence of the components was discovered; iron was found to promote reduction of cobalt.

Key words: Co, Fe, catalysts, TiO_2, supported catalysts, IR spectra of adsorbed CO, oxidation states of metal atoms.

Supported iron—cobalt bimetallic systems are of considerable interest as possible catalysts of direct Fischer—Tropsch conversion of CO into alcohols.[1,2]

IR spectroscopy of adsorbed probe molecules, for example, CO molecules, is one of the most useful and versatile methods of investigation of the surface properties of both solid and supported metal systems (see Refs. 3 and 4). Spectral properties of CO (ν(CO)) in surface carbonyl compounds are determined by the effective charge of the adsorption center, which, in turn, depends on the size of the metal cluster, the character of its interaction with the support, and the coordination and oxidation states of the cation.

In the present work we studied variations of the electronic properties of cobalt and iron in one- and two-component systems, formed by their deposition onto titanium dioxide, as a function of the degree of reduction of the catalysts by analyzing the IR spectra of adsorbed CO.

A large number of studies dealing with spectral manifestations of the interaction of CO with iron- (see Refs. 4—19) and cobalt-containing[19—41] systems including those supported on various carriers, SiO_2, Al_2O_3, MgO, Al/Si, *etc.*, have been reported in the literature. However, data on the state of these metals supported on TiO_2 are virtually missing. This is primarily due to methodical difficulties, since in this case, the possible reduction of the carrier (TiO_2) results in the loss of transmission of the samples, owing to the appearance of free charge carriers in the solid.[42] Consequently, it becomes practically impossible to use transmission IR spectroscopy, which has been mostly developed in recent years.

Therefore, we used diffuse reflectance spectroscopy, which makes it possible to study spectra of even slightly transmitting objects and whose sensitivity can be more than an order of magnitude higher than that of transmission spectroscopy.

We attempted to follow the variations of the states of Fe and Co complexes in the course of their genesis, *i.e.*, from the state of the active component, immediately after the preparation of systems, to the states that occur after complete reduction of the catalysts. In our opinion, this makes it possible to increase the reliability of the interpretation of the effects observed, since the state of an active component and its variations are associated with particular chemical actions on it. We took into account the published data on the IR spectra of CO, adsorbed on systems that contain iron and cobalt ions, but are supported on other materials.[4—41] This complex consideration allowed us to assign absorption bands (AB), recorded in the spectra of adsorbed CO, to particular states of the surface complexes.

Experimental

Samples of Fe : Co/TiO_2 = 5 : 5 (containing 10 % of the active component) were used in the study. The samples were prepared by depositing a mixture of cobalt carbonyl [$Co_2(CO)_8$] and iron carbonyl [$CpFe(CO)_2]_2$ taken in a corresponding ratio or by depositing the mixed carbonyl cluster $CpFe(CO)_2Co(CO)_4$ onto a titanium dioxide surface. In addition, the Fe : Co/TiO_2 (5 : 5) samples were prepared by impregnating the supporting material with the corresponding metal nitrates.

We also studied samples of monometallic catalysts, Fe/TiO_2 and Co/TiO_2 (the proportions of the active component and the

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procedures for their preparation were the same as those for Fe : Co/TiO_2).

Pretreatment of the samples was carried out in a special IR cell at 523 K in a flow of N_2 (or CO) or at 473 K in an H_2 flow normally over a period of 2 h. In the case of higher temperatures, for example, in order to reduce the catalysts, the latter were preliminarily reduced in a separate reactor under specified conditions, and then they were placed in an IR cell and were additionally reduced for 2 h in an H_2 flow at 473 K. The initial treatment of the system was carried out directly in the IR reactor in an N_2 flow at 523 K.

The IR spectroscopic study of adsorption of CO was carried out using a Bruker FTS-85 IR Fourier spectrometer. The diffuse reflectance IR spectra were recorded on a standard reflection accessory (Harrick Scientific), equipped with a special flow cell for studying IR spectra of adsorbed molecules under elevated pressures.[43] This cell makes it possible to treat catalysts in a controlled gas flow at temperatures up to 573 K. CO was adsorbed at 293 K from a flow of pure carbon oxide. To record a spectrum without gaseous CO, the carbon monoxide flow was stopped, and the samples were kept at ambient temperature (or at 373 K) for 15 min to 1 h in a flow of N_2 or H_2. The reflectance spectra were converted into absorption modes using special programs that take the Kubelka—Munk function into account.

Results and Discussion

Fe/TiO_2 samples were prepared by impregnation and prior to adsorption, they were processed for 2 h in a nitrogen flow at 523 K. Adsorption of CO on a Fe/TiO_2 sample at 523 K results in the appearance of a number of IR AB at 2174, 2104, 2054, and 1996 cm^{-1} (Fig. 1, spectrum *1*), recorded in the IR spectrum after removal of gaseous CO with a nitrogen flow. The assignment of these bands to ν(CO) in carbonyl and related Fe^{n+}—CO complexes is beyond question.[3,4] Since the spectrum contains no AB typical of Ti^{4+}—CO complexes, which are exhibited, as a rule, in the 2190—2205 cm^{-1} region,[3,19] one may assume that the surface Ti^{4+} ions are entirely blocked by an oxide phase of the iron supported on titanium dioxide (anatase).

The AB observed in the spectra of adsorbed CO were assigned by taking into account the scheme suggested previously[3] to interpret ν(CO) in carbonyl and related surface complexes of late transition metals of Period III of the Periodic System, as a function of their oxidation states. According to this scheme, bands recorded in the region above 2170—2180 cm^{-1} are due to M^{n+}—CO complexes in which $n > 2$; those recorded in the region close to ν(CO) of the free molecule are associated with M^{1+}—CO complexes, and absorption below 2100 cm^{-1} normally corresponds to M^0CO complexes. Besides, it was assumed that bridging carbonyl groups are manifested at frequencies below 1900 cm^{-1}, whereas bands corresponding to linear carbonyl groups are within the 1900—2100 cm^{-1} range. This scheme is in agreement with previously reported[4] data.

Taking into account the foregoing scheme and published data dealing with IR-spectrometric studies of adsorption of CO on iron oxides of various reduction degrees, on iron clusters, supported on various materials and subjected to various (including oxidation) treatments, and on films,[4—19] we may suggest the following assignment of the maxima observed: 2174 cm^{-1} to Fe^{2+}—CO, 2104 cm^{-1} to Fe^{1+}—CO, 2054 cm^{-1} to $Fe^{\delta+}$—CO, and 1996 cm^{-1} to Fe^0_{clust}—CO.

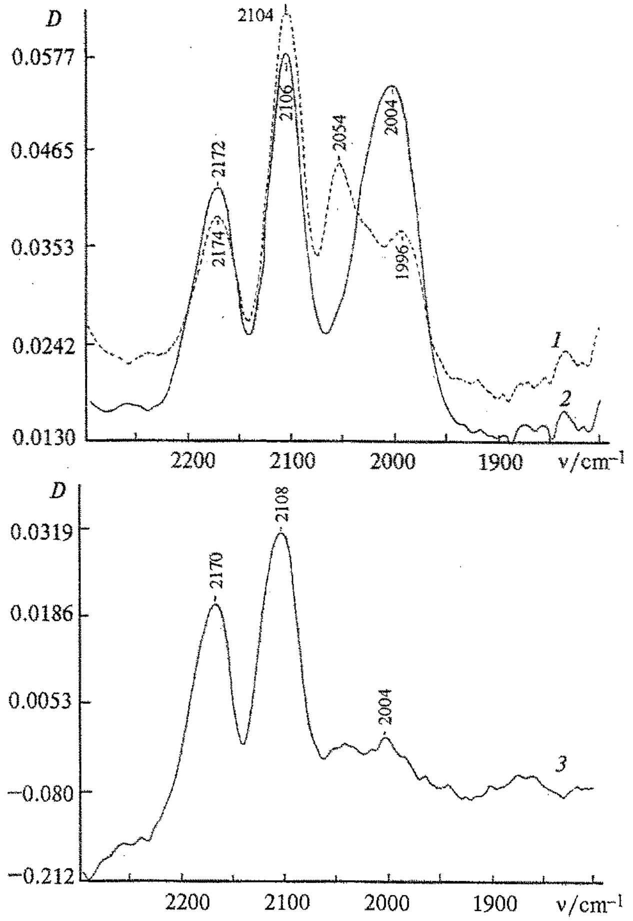

Fig. 1. Diffuse reflectance IR spectra of CO adsorbed at 293 K on a Fe/TiO_2 sample prepared by impregnation and processed in an N_2 flow for 2 h at 523 K (*1*); reduced in H_2 for 2 h at 453 K (*2*); reduced in H_2 for 2 h at 423 K (*3*).

This assignment is supported by the variations of the spectrum after reducing the system with H_2 for 2 h at 453 K (see Fig. 1, spectrum *2*). It can be seen that the proportion of reduced Fe^0 centers, responsible for the AB at ~2000 cm^{-1}, substantially increases, whereas the concentrations of Fe^{1+}—CO complexes (AB at ~2105 cm^{-1}) and $Fe^{\delta+}$—CO complexes (AB at ~2054 cm^{-1}) decrease; the latter band even disappears entirely. The variations of the intensity of the AB at ~2170 cm^{-1} are more difficult to follow. It may even increase on the reduction in H_2, which can be explained by the reduction of some Fe^{3+} ions on the surface to Fe^{2+} ions. In conformity with the viewpoint, stated in other papers,[3,17] one may assume that the Fe^{3+} cations in iron oxide are coordinatively saturated and do not adsorb CO, and the Fe^{2+} ions, resulting from reduction of Fe^{3+}, stabilize CO as the Fe^{2+}—CO complex (AB at ~2170 cm^{-1}).

When the temperature of the reduction with H_2 is increased further, even to 523—543 K, the intensities of all of the AB of the adsorbed CO, present in the spectrum, substantially decrease (see Fig. 1, spectrum *3*). The decrease in the intensity (*D*) of the AB at 2170 and 2108 cm^{-1} is associated with the reduction of the oxidized surface centers of Fe^{2+} and Fe^{1+} types to Fe^0. The decrease in the intensity of the AB at ~2000 cm^{-1} is probably caused by the decrease in the concentration of Fe^0 type adsorption centers due to agglomeration of metal particles during sintering and, consequently, to a decrease in the metal surface area. It should be noted that the overall reflectance of the sample dramatically decreases. This may be caused by the absorption, which is due to reduction of the supporting material (TiO_2) and appearance of free charge carriers (electrons) in it; these carriers absorb the IR radiation. The spectra of samples with greater degrees of reduction could not be recorded at all, which results most likely from the complete absorption of the IR radiation by the reduced supporting material.

The character of interaction of CO with a Fe/TiO_2 sample prepared from iron carbonyl differs qualitatively from that described above. Adsorption of CO on this catalyst, pretreated at 523 K for 2 h in an N_2 flow, with subsequent removal of CO with a nitrogen flow reveals mainly one intense AB at ~2000 cm^{-1} (shoulders at ~2020 and 2035 cm^{-1} can also appear) (Fig. 2), which corresponds to ν(CO) in a $Fe^0{}_{clust}$—CO complex. Thus, clusters of iron metal, probably stabilized near Ti^{4+} acceptor centers or at them, are the predominating state of the active component of this type of catalyst, since the spectra of adsorbed CO exhibit no AB peculiar to Ti^{4+}—CO complexes, which are observed with the pure support.

The reducing treatment of a sample with H_2 at 453 K (see Fig. 2, spectrum *2*) leads to some increase in the intensity of the AB at 2000 cm^{-1}, corresponding to the adsorbed CO, compared to the reduced sample. However, treatment with H_2 for 2 h at 523 K (see Fig. 2, spectrum *3*) dramatically decreases the intensity of this band (*D* ~0.02), which can be explained by sintering of iron particles. It should be noted that now this is not accompanied by a substantial change in the location of the ν(CO) AB, corresponding to the carbonyl complex, as has been observed, for example, for $Pt/Al_2O_3(SiO_2)$ (see Ref. 44); however, a certain trend for increase in the frequency can be followed (from 2000 cm^{-1} to 20008 cm^{-1}). The difference in the increase in frequency between Pt- and Fe-containing catalysts is caused by the fact that the size of particles in Pt-containing systems varies from 10 to 100 Å ($\Delta\nu$ = 30 to 40 cm^{-1}), while in the case of Fe-containing systems, the variations are less pronounced (probably, only 2—3 times), and they occur with larger particles (~100 Å). The possibility that the support is reduced cannot be ruled out even when the sample has been treated under the above-mentioned conditions (523 K in H_2). The latter should deteriorate optical properties of the sample: most of the incident energy is absorbed on conduction electrons of the support, and that is why the recorded reflection signal decreases. More stringent conditions of reduction result in that the spectrum cannot be recorded at all.

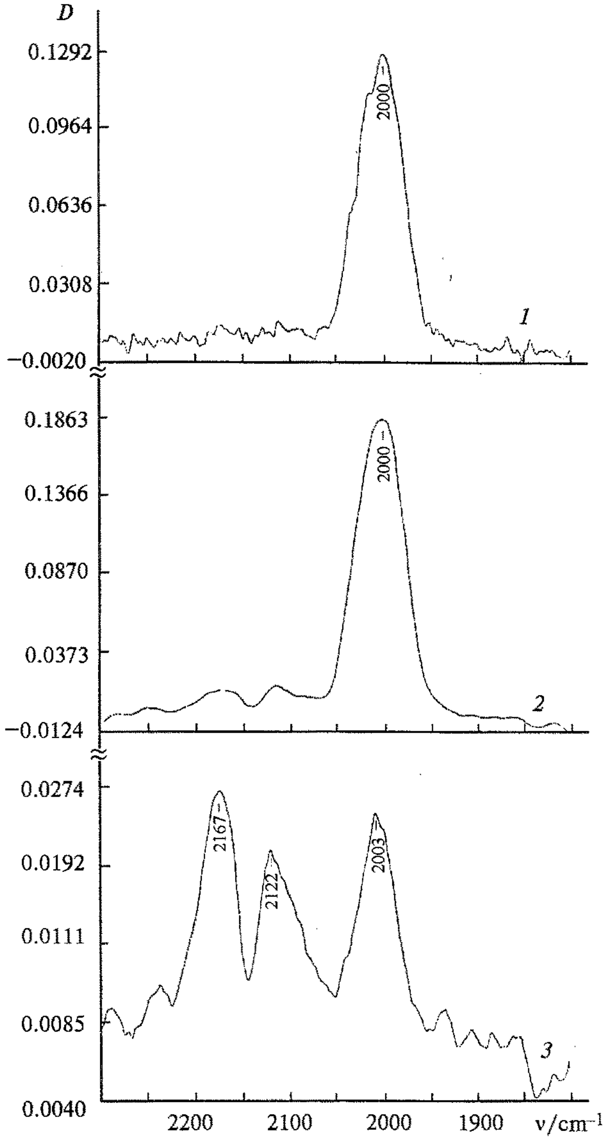

Fig. 2. Diffuse reflectance IR spectra of CO adsorbed at 293 K on Fe/TiO_2 samples prepared by deposition of the carbonyl and processed in an N_2 flow for 2 h at 523 K (*1*); reduced in H_2 for 2 h at 453 K (*2*); reduced in H_2 for 2 h at 523 K (*3*).

Co/TiO_2. Unlike the above-considered interaction of $[CpFe(CO)_2]_2$ with TiO_2, in which the formation of iron metal clusters on the TiO_2 surface is the main process, formation of the Co/TiO_2 system by reaction of $Co_2(CO)_8$ with TiO_2 involves other processes. The results obtained by us (Fig. 3, spectrum *1*), resorting to published data

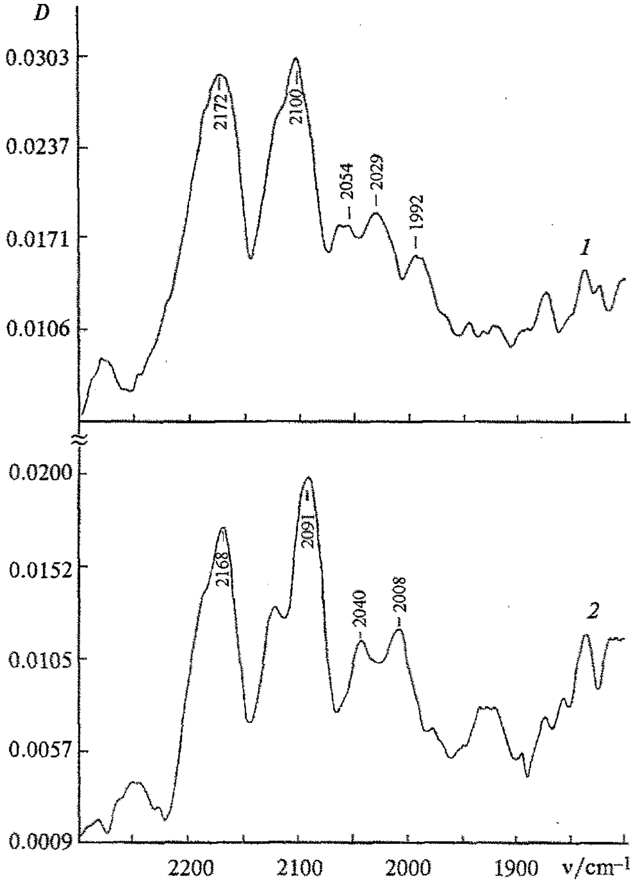

Fig. 3. Diffuse reflectance IR spectra of CO adsorbed at 293 K on Co/TiO_2 samples prepared by deposition of the carbonyl and processed in N_2 for 2 h at 523 K (*1*) and in H_2 for 2 h at 453 K (*2*).

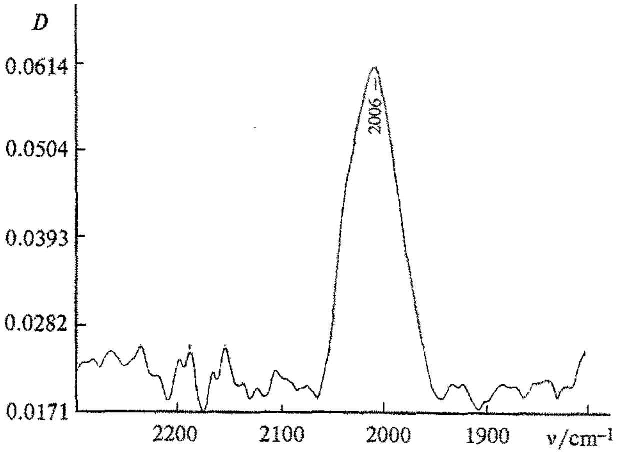

Fig. 4. Diffuse reflectance IR spectrum of CO, obtained by subtracting the spectrum recorded for a sample processed in H_2 for 2 h at 453 K from the spectrum of a sample processed in N_2 for 2 h at 523 K.

on IR-spectroscopic manifestations of CO adsorbed on cobalt-containing systems,[19—41] indicate that AB located at frequencies below 2000 cm^{-1} undoubtedly characterize adsorption of CO (ν(CO)) on metal clusters, whereas ν(CO) AB located above 2100 cm^{-1} are due to complexes of CO with Co atoms in an oxidized state. From this it follows that the proportion of cobalt metal in the starting sample, processed in an N_2 flow for 2 h at 523 K, is very low, and oxidized states of cobalt predominate, though their concentration is small. In our opinion, this may imply that cobalt reacts with TiO_2, possibly, to give a chemical compound, for example, $CoTiO_3$; the possibility of this reaction has been reported previously.[45] A substantial proportion of the oxidized states of cobalt is retained in the sample even after its reducing treatment in H_2 at 523 K (see Fig. 3, spectrum *2*). According to the published data,[19—40] these can be characterized as follows: 2170 cm^{-1} corresponds to ν(CO) in Co^{2+}—CO complex; 2091 cm^{-1} is due to ν(CO) in Co^{1+}—CO; and 2033 cm^{-1} is due to ν(CO) in $Co^{\delta+}$—CO. At the same time, the proportion of reduced cobalt, characterized by the AB at ~2000 cm^{-1} (Co^0_{clust}—CO), increases as the extent to which the sample has been reduced in H_2 increases. In fact, the increase in the intensity (*D*) of the AB at ~2006 cm^{-1} on going from a sample processed in nitrogen at 523 K to a sample reduced in H_2 for 2 h at 453 K indicates that the degree of reduction of cobalt has increased (Fig. 4).

Fe:Co/TiO_2. Binary systems prepared by impregnation differ appreciably from those prepared from metal carbonyls. Irrespective of the percentages of the components (Fe : Co = 1 : 1 or 5 : 5), the samples, prepared by impregnation, contain initially (after processing in an N_2 flow for 2 h at 523 K) a set of states of the cations in various oxidation states (Fig. 5, spectrum *1*). In conformity with the above consideration, the AB, observed in the spectra, most likely characterize the following vibrations: ~2170 cm^{-1}, ν(CO) in Me^{2+}—CO; 2102 cm^{-1}, ν(CO) in $Me^{\delta+}$—CO; 1994 cm^{-1}, ν(CO) in Me^0_{clust}—CO.

Since the locations of ν(CO) in the spectra of complexes of iron and cobalt metals with carbon oxide are close, it is practically impossible to find out, what particular element is incorporated in one or another complex. Note that the AB at ~2048 cm^{-1} apparently characterizes the $Co^{\delta+}$—CO complex, since it is also exhibited in the spectra of CO adsorbed on mixed samples, after they have been reduced in H_2 (see Fig. 5, spectrum *2*), which is typical of cobalt-containing systems. In the case of iron-containing catalysts, this AB was observed only in the spectra of the initial unreduced samples (see Fig. 1, spectrum *1*) and disappeared immediately after reduction in H_2 (see Fig. 1, spectrum *2*).

Binary Co—Fe-containing systems, prepared by the interaction of a mixture of cobalt and iron carbonyls or by the interaction of $CpFe(CO)_2Co(CO)_4$ cluster with TiO_2, almost do not differ from one another, as regards the spectra of CO adsorbed on these systems; their spectral characteristics are very similar to those of CO,

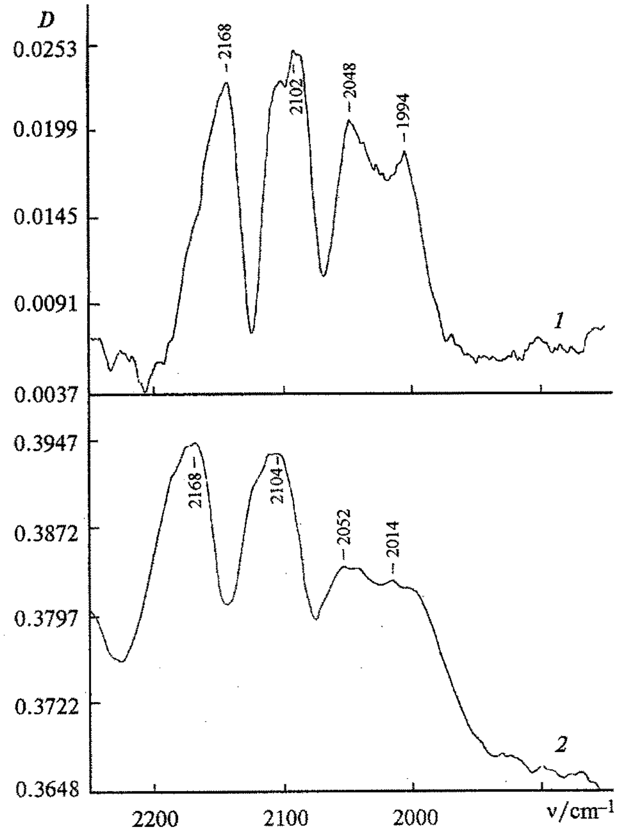

Fig. 5. Diffuse reflectance IR spectra of CO adsorbed at 293 K on Fe : Co = 5 : 5 samples prepared by impregnation and processed in N_2 for 2 h at 523 K (*1*) and in H_2 for 1 h at 453 K (*2*).

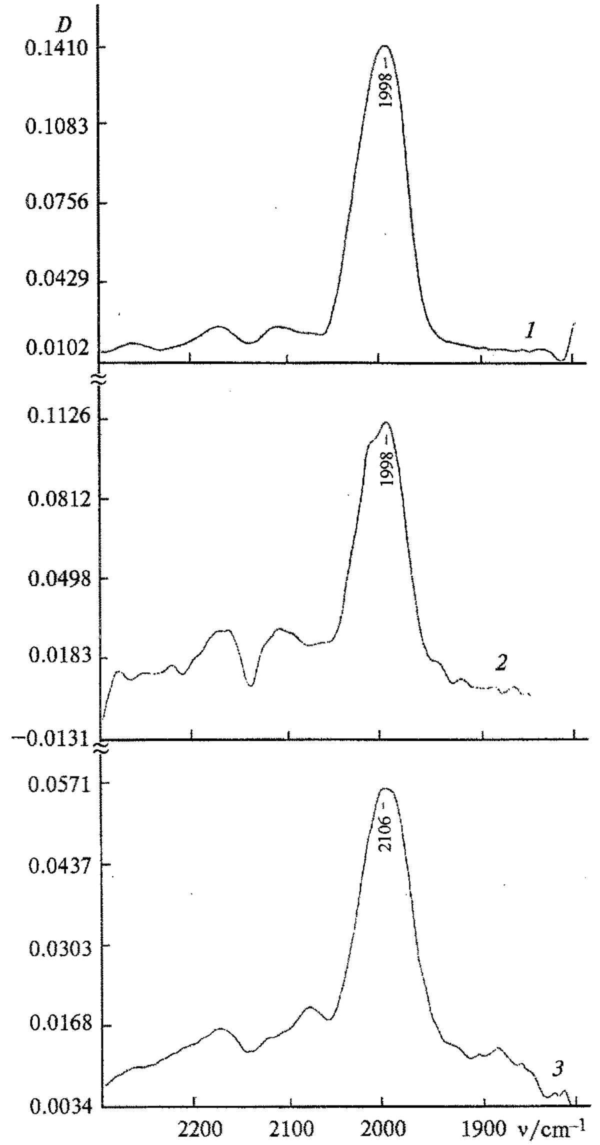

Fig. 6. Diffuse reflectance IR spectra of CO adsorbed at 293 K on binary systems prepared by interaction of the carbonyls or the $CpFe(CO)_2Co(CO)_4$ cluster with TiO_2 and processed in N_2 for 2 h at 523 K (*1*); in H_2 for 1 h at 453 K (*2*); and in H_2 for 2 h at 523 K (*3*).

adsorbed on $[CpFe(CO)_2]_2/TiO_2$. One may believe that metal clusters supported on TiO_2 are the major state of the active component in these systems, which is indicated, for example, by the spectra of CO, adsorbed at 293 K even on samples processed in N_2 only for 2 h at 523 K (Fig. 6, spectrum *1*). It should be noted that the distribution of metal particles in these catalysts is monodisperse; the spectra exhibit only one AB at ~2000 cm^{-1}, but this band is rather broad, which may indicate that the sizes of the particles are somewhat nonuniform. A comparison of the intensities of the AB at ~2000 cm^{-1} recorded for these samples prior to and after reduction at $T < 473$ K implies that already in the initial samples, virtually the whole metal exists in the reduced state, since no considerable increase in the intensity of this AB is observed, when a sample is reduced. Starting with 523 K, reduction in H_2 results in a substantial diminution of the intensity of the AB under consideration, which points to sintering of the metal particles. Since the AB at ~2000 cm^{-1} is rather broad, no noticeable change in its location occurs, although in the case of high-temperature reduction, a high-frequency component appears. Virtually no oxidized states of cobalt or iron cations are manifested in the spectra of initial samples of these catalysts or in the spectra of their reduced samples. It is likely that metal clusters effectively block titanium cations, near which they are stabilized, since the IR spectra of adsorbed CO exhibit no AB corresponding to ν(CO) in Ti^{n+}—CO complexes, which are normally recorded after absorption of CO on TiO_2.

One more important feature of the spectral manifestations of CO adsorbed on the catalysts, prepared from the cluster or from a mixture of cobalt and iron carbonyls, deserves attention. In these samples, as in the supported iron carbonyl, virtually no oxidized states of iron and cobalt are found. This is not characteristic of cobalt, since it is mostly stabilized in an ionic state both in the case of supported systems and in the case when Co/TiO_2 catalyst is prepared by reacting cobalt carbonyl with TiO_2. However, in the above-considered examples in which binary systems were prepared by reacting a mixture of carbonyls or cluster carbonyl, practically no ionic states of cobalt were found. In our opinion, this experimental fact indicates that in these systems cobalt interacts with iron (possibly to give an alloy*), which prevents cobalt from interacting with the support, *i.e.*, in binary systems, cobalt is protected by iron (probably, through interaction) against oxidation, or the presence of iron promotes reduction of cobalt.

Thus, the results obtained in this work imply that iron has a promoting effect on the reduction of cobalt.

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* The effect of interaction between the components cannot be directly detected in the IR spectra of the adsorbed CO, since ν(CO) corresponding to Co^0—CO and Fe^0—CO complexes overlap.