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Properties of Catalysts Prepared by Pyrolysis of $Co_2(CO)_8$ on Silica Containing Surface Ti Ions

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Catalysts prepared by thermal decomposition of $Co_2(CO)_8$ on modified silica were studied by magnetic susceptibility and by IR and ESR spectroscopy, and were tested in CO hydrogenation. The modification of SiO_2 by Ti ions made it possible to diminish the size of metallic Co particles. The effect was the most pronounced for modification by hydride complexes of a low-valent titanium. An increase of Co dispersion was accompanied by a drop in the metal activity in CO hydrogenation and by a rise of the relative yield of light hydrocarbons and alcohols, especially that of ethanol.

INTRODUCTION

As one of the methods of preparation of supported metal catalysts, thermal decomposition of carbonyl complexes on oxide supports currently attracts great attention. This technique of catalyst preparation provides a number of advantages, as compared with the traditional methods, and, in some cases, has resulted in preparation of samples with unusual properties (*1–4*).

Supported Co catalysts obtained via pyrolysis of dicobaltoctacarbonyl showed specific behavior in hydroformylation (*5, 6*), hydrocarboxylation (*7*), and the CO + H_2 reaction (see Refs. (*8–10*) and refs. therein). The chemical nature of the support was found to be one of the factors affecting the state of Co in the samples and its catalytic properties. For example, Al_2O_3, MgO, TiO_2, ZrO_2 as supports provided the formation of smaller Co particles than SiO_2 (*10, 11*).

Besides variation in the bulk composition of a support, another method to regulate the properties of the metal in supported catalysts is the modification of the support surface, e.g., by anchoring elements in a low-valent state (*12*).

Here we report and discuss data on the properties of catalysts prepared by thermal decomposition of $Co_2(CO)_8$ on SiO_2 modified by Ti ions.

EXPERIMENTAL

Modification of SiO_2

An initial silica (BET surface 200 m^2/g, pore radius ≈ 100 Å) was heated at 670 K and 10^{-2} Torr for 4 h. The modification of the surface was performed by reaction of $TiCl_4$, $Ti(OBu)_4$, and $Ti(CH_2C_6H_5)_4$ with surface hydroxyl groups:

$$n(\text{Si–OH}) + TiR_4 \rightarrow (\text{Si–O})_nTiR_{4-n} + n\text{HR} \quad (1)$$

where Si is a silicon atom of the surface, R = Cl, OBu, or $CH_2C_6H_5$. Commercial samples of $TiCl_4$ and $Ti(OBu)_4$ were used. Tetrabenzyltitanium was prepared as described in Ref. (*13*).

Four samples of modified silica were prepared:

TiO_2–SiO_2(I). The mixture of SiO_2 and $TiCl_4$ was heated in a sealed ampoule at 420 K for 5 h. An excess of $TiCl_4$ was then removed under vacuum at the same temperature. The sample was treated with water at 295 K and dried at 670 K under vacuum.

TiO_2–SiO_2(II). SiO_2 was treated with a pentane solution of $Ti(OBu)_4$ at 295 K for 24

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h. An excess of $Ti(OBu)_4$ was washed off by pentane. The sample was treated with water at 295 K and dried at 670 K under vacuum.

TiO_2–SiO_2(III). SiO_2 precovered by pentane was treated with a pentane solution of $Ti(CH_2C_6H_5)_4$ at 295 K. After decoloration of the solution, the solvent was removed under vacuum. The sample was treated with O_2 at 770 K and then outgassed at 670 K.

TiH_x–SiO_2. After anchoring $Ti(CH_2C_6H_5)_4$ (see above), the sample was treated with H_2 at 430 K. According to IR, ESR, oxygen adsorption data, and mass-spectrometry analysis (*14–15*), the sample prepared by this technique contained hydride complexes of Ti^{3+} and Ti^{4+} in approximately equal amounts.

Preparation of the Catalysts

So as the interaction of titanium compounds with silica, the addition of carbonyl complex to the prepared supports was performed in an all-glass system with breakable partitions (for a detailed description of the system see, e.g., Ref. (*16*)). It completely prevented the samples from contact with air and allowed further operations to be performed under vacuum. Pentane, used as a solvent, was dried over molecular sieves and was then outgassed.

The sample based on TiH_x–SiO_2 as a support was prepared via *adsorption* of $Co_2(CO)_8$ from pentane solution. The partitions between the ampoules with support and solution were broken (the volume between the partitions was previously outgassed) and some quantity of the solvent was distilled to cover the support. Then, the solution was gradually added to the slurry of the support in pentane. When decoloraton of the last portion of the added solution was seen to occur very slowly, addition was stopped and an excess of Co carbonyl was washed off by the solvent. The atomic Co-to-Ti ratio in the sample reached unity.

Irreversible adsorption of Co carbonyl on TiO_2–SiO_2 supports was considerably smaller and the Co/Ti ratio did not exceed 0.3 (wt% of Co was below 0.4). Unmodified SiO_2 and silica containing anchored benzyl complexes of Ti were quite inert to adsorb $Co_2(CO)_8$ from the solution. Therefore, to obtain the Co/SiO_2 and Co/TiO_2–SiO_2 catalysts with a Co content close to that in the Co/TiH_x–SiO_2 sample, the *impregnation* technique was used.

Pyrolysis of the supported carbonyl complexes was carried out at 530 K for 0.5 h in a preheated furnace and with outgassing CO evolved. The catalyst obtained in this way was distributed under vacuum into several sealed ampoules supplied with thin glass partitions for further operations with the catalyst in the absence of air (loading into the reactor and initial treatment for recording IR spectrum).

Elemental analysis of Co and Ti was performed by atomic absorption. Within the accuracy of the determination (±5%), there was no difference in the data for initial pyrolyzed samples and those which had been used in CO + H_2 reaction.

Study of the physical and catalytic properties of the samples was performed as described earlier (*10, 17*). *IR spectra* were recorded for the slurry of sample in Nujol. To diminish contact of the sample with air, it was initially placed under vacuum into Nujol (previously outgassed) and then was rapidly ground in an Ar atmosphere and placed between NaCl disks. *Magnetization* of catalysts was measured on a magnetic balance by the Faraday method. Before measurements at 77 K, the sealed tube with sample was kept in liquid nitrogen for 2–3 h. *ESR spectra* were recorded on a ER-200 D (Bruker) spectrometer at 293 K and 9.7 GHz. *Catalytic testings* were performed in a flow differential reactor at 453 K and atmospheric pressure of CO + $2H_2$ mixture. For removing impurities of O_2, H_2O, and carbonyls from syngas, it passed before going into the reactor through a U-tube with Mn^{2+}/SiO_2 and then through a trap cooled by liquid nitrogen. Products were analyzed gas-chromatographically, using a Poropak Q column for C_1–C_4 hydrocarbons, acetaldehyde, and alcohols and an OV-101/Firebrick column for C_1–C_8 hydrocarbons.

RESULTS

IR Spectra

The IR spectra of the samples at various stages of their preparation and after the catalytic reaction are given in Fig. 1. The spectra of the initial samples obtained on SiO_2 and TiO_2–SiO_2 supports showed fairly narrow bands similar to those in the spectrum of the $Co_2(CO)_8$ and $Co_4(CO)_{12}$ mixture (see example 1′ in Fig. 1B). On the contrary, only a broad poorly resolved band was observed in the spectrum after supporting $Co_2(CO)_8$ on TiH_x–SiO_2 (spectrum 1 in Fig. 1A).

The thermal treatment of the samples at 530 K resulted in disappearance of CO absorption bands, and the spectra were the same as those of the supports. After subsequent treatment of the catalysts by CO or after their testing in the CO + H_2 reaction, the band of adsorbed CO was clearly seen in the spectra only for the Co/TiH_x–SiO_2 sample (compare spectra 3 and 3′ in Fig. 1).

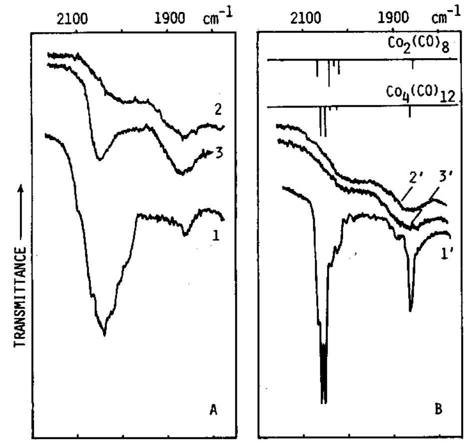


FIG. 1. IR spectra of samples prepared on TiH_x–SiO_2 (A) and TiO_2–SiO_2(III) (B) supports: 1,1′—after supporting $Co_2(CO)_8$; 2,2′—after thermal treatment under vacuum at 530 K; 3,3′—after CO hydrogenation followed by cooling and outgassing at 295 K.

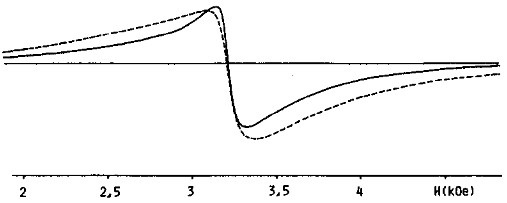


FIG. 2. ESR spectra of Co/TiO_2–SiO_2(III) catalyst prior to and after CO hydrogenation (dotted and solid line, respectively). The signal shape, but not the intensity, should be compared.

ESR Spectra

The thermal decomposition of Co carbonyl on SiO_2 and TiO_2–SiO_2 supports gave rise to a ferromagnetic resonance (FMR) signal in the spectra. The signal had a rather small width and demonstrated additional narrowing after CO hydrogenation (see example in Fig. 2). Its shape was practically not affected by adsorption/desorption of CO and H_2.

After pyrolysis of Co carbonyl on the TiH_x–SiO_2 support there was only the signal of Ti^{3+} ions in the ESR spectrum. The FMR signal was not detected even after additional heating of the catalyst at 670 K (under vacuum), but was observed for the sample used in the CO + H_2 reaction (Fig. 3).

Results of Magnetic Measurements

These results for pyrolyzed samples are presented in Fig. 4. All catalysts demonstrated superparamagnetic properties, so that the dependence of their magnetization (σ) on the strength of the magnetic field (H) and temperature (T) could be described by the Langevin equation

$$\sigma = \sigma_\infty \sum_i n_i \left(\operatorname{cth} \frac{v_i I_s H}{kT} - \frac{kT}{v_i I_s H} \right), \quad (2)$$

where σ_∞ is the magnetization at the saturation state, n_i the weight fraction of metallic particles with volume v_i, k the Boltzmann constant, and I_s the spontaneous magnetization which is equal to 1450 Oe for Co (*18*).

The size of the Co particles in the samples were calculated from the results of

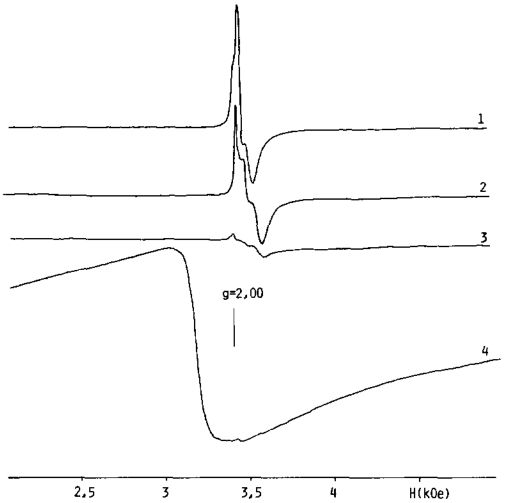


FIG. 3. ESR spectra of TiH_x–SiO_2 support (1) and the sample Co/TiH_x–SiO_2 (2–4). 2,3—After thermal treatment of the sample under vacuum at 530 K for 0.5 h (2) and at 670 K for 1 h (3); 4—after CO hydrogenation. Spectra 2 and 3 were recorded at a magnification of about 5 times greater.

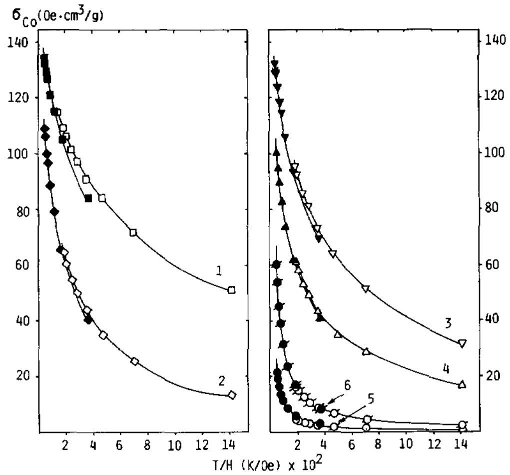


FIG. 4. Co magnetization after pyrolysis of supported carbonyl at 530 K for 0.5 h (1–5) and at 670 K for 1 h (6). Catalysts: 1—Co/SiO_2; 2—Co/TiO_2–SiO_2(II); 3—Co/TiO_2–SiO_2(I); 4—Co/TiO_2–SiO_2(III); 5,6—Co/TiH_x—SiO_2. The magnetic measurements were performed at 77 K (closed symbols) and 293 K (open symbols).

magnetic measurements in high-field (HF) and low-field (LF) areas by formulas

$$d_{\mathrm{HF}} = \left[\frac{6k}{\pi I_s}\left(1 - \frac{\sigma_{\mathrm{H,T}}}{\sigma_\infty} \cdot \frac{T}{H}\right)\right]^{1/3} \quad (3)$$

$$d_{\mathrm{LF}} = \left(\frac{18k}{\pi I_s} \cdot \frac{\sigma_{\mathrm{H,T}}}{\sigma_\infty} \cdot \frac{T}{H}\right)^{1/3} \quad (4)$$

is listed in Table 1. (The formulas are derived from HF and LF approximations of the Langevin equation, and the d values correspond to diameters of metal particles as if they adopt a spherical shape; see, e.g., Ref. (*18*).) The experimental $\sigma_{\mathrm{H,T}}$ points at $(T/H) = 0.51 \times 10^{-2}$ and 14.2×10^{-2} K/Oe were used for the HF and LF calculations, respectively. Except for the Co/TiH_x–SiO_2 sample, σ_∞ values were obtained by linear extrapolation of the magnetization to the point $(T/H) = 0$. The accuracy of the extrapolation depends on the sample, but in general may be estimated as ±10 Oe · cm³/g, which gives a possible error of ±2 Å for the calculated d_{HF} values and ±1 Å for d_{LF}. In the case of Co/TiH_x–SiO_2, σ_∞ was taken equal to 163 Oe · cm³/g (the value known for fully reduced metallic Co (*18*).

After testing of Co/SiO_2 and Co/TiO_2–SiO_2 catalysts in CO hydrogenation, their magnetization was close to that of the initial catalysts treated by CO + H_2 mixture at room temperature (Fig. 5). On the other

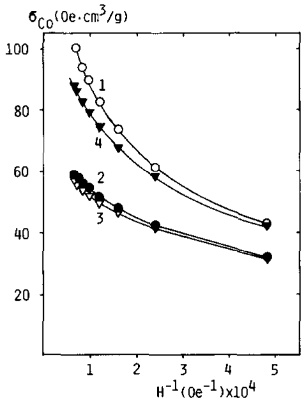


FIG. 5. Co magnetization for Co/TiO_2–SiO_2(III) after various treatments. 1—Initial pyrolyzed sample; 2—after treatment in CO + $2H_2$ flow (295 K, 1 h) followed by outgassing at 295 K; 3,4—after using in CO hydrogenation followed by cooling and outgassing at 295 K (3) and 520 K (4) for 5 min. The magnetic measurements were performed at 77 K.

TABLE 1

Properties of the Catalysts in CO Hydrogenation[a] at 453 K (CO : H_2 = 1 : 2)

Catalyst	Co (wt%)	Ti (wt%)	Size of Co particles		Activity[b]	α[c]	S^d_{alc}	$\left(\frac{\text{Ethanol}}{\text{Methanol}}\right)^e$
			d_{HF} (Å)	d_{LF} (Å)				
Co/SiO_2	0.9	0	22	30	4	0.72	5	1.2
Co/TiO_2–SiO_2(I)	1.2	1.2	19	25	5.5	0.71	5	1.5
Co/TiO_2–SiO_2(II)	0.8	2.7	17	20	4.5	0.67	10	2.5
Co/TiO_2–SiO_2(III)	1.1	1.1	17	22	4	0.65	10	2.5
Co/TiH_x–SiO_2	1.0	1.1	12[f]	12[f]	3	0.51	25	4

[a] Twenty hours after beginning of reaction.

[b] (mol CO/g Co/s) × 10^6.

[c] Probability of chain propagation for C_3–C_8 hydrocarbons.

[d] Selectivity of alcohol production (on carbon efficiency basis).

[e] Mole ratio; yield of ethanol is combined with that of acetaldehyde.

[f] After catalytic testing.

hand, the Co/TiH_x–SiO_2 catalyst demonstrated an enhanced magnetization (Fig. 6). In both cases the magnetization increased after removal (at least, partial) of adsorbed gases by means of a short-time outgassing of the catalysts at the temperature of their preparation.

Catalytic Properties of the Samples

The main organic products of CO hydrogenation were light hydrocarbons and alcohols. In what follows, only C_1–C_8 hydrocarbons and C_1, C_2 alcohols will be considered. They comprise not less than 70% of all hydrocarbons and oxygen-containing products, respectively, and are easy to be analyzed at any moment. Examples of hydrocarbon distribution vs. the number of carbon atoms are presented in Fig. 7.

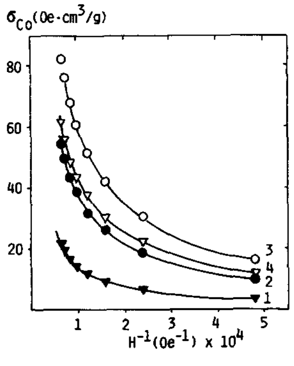


FIG. 6. Co magnetization for the catalyst Co/TiH_x–SiO_2 after various treatments. 1—Initial pyrolyzed sample; 2,3—after CO hydrogenation followed by cooling and outgassing at 295 K (2) and 520 (3) for 5 min; 4—after subsequent treatment of the samle (3) in CO + $2H_2$ flow for 1 h at 295 K and outgassing at 295 K. The magnetic measurements were performed at 77 K.

During the course of the reaction the activity of the catalysts in hydrocarbon synthesis decreased (the decrease was ~2 times to the end of the experiments). It was more pronounced for heavier products, so that the mole ratios M_{n+1}/M_n were decreasing with time (Fig. 7). In contrast, the yield of alcohols increased during the initial period of the reaction. (In the first 0.3–1.5 h alcohols were completely absent in the effluent gas.) All the changes mentioned proceeded mainly for the first 5–10 h of the experiments. The data for the properties of the catalysts at the stationary state are presented in Table 1.

The properties shown in Table 1 were not significantly affected by the flow rate of the gas mixture (2000–10,000 cm³/g cat./h), and the difference of the catalysts in these properties was maintained. The flow rate had, however, considerable influence on the ratio of saturated and unsaturated compound

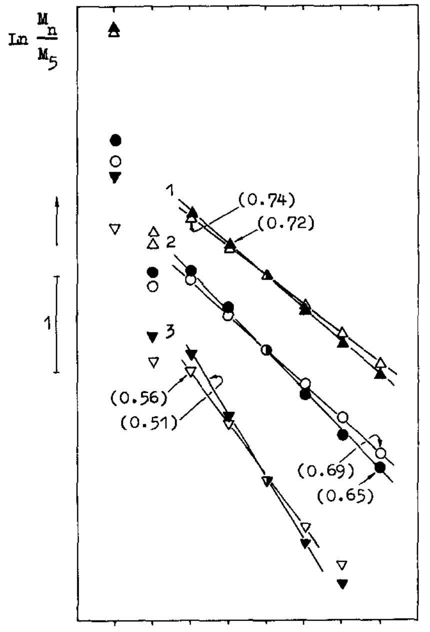


FIG. 7. CO hydrogenation ($CO:H_2 = 1:2$) at 453 K. Examples of the distribution of the obtained hydrocarbons vs the number of carbon atoms. The ratio of molar yields $\alpha = M_{n+1}/M_n$ in the area of C_3–C_8 products is given near the curves in parentheses. Open symbols correspond to the time of less than 40 min after the beginning of the reaction, closed symbols correspond to 400 min and above. Catalysts: 1—Co/SiO_2; 2—Co/TiO_2–SiO_2(II); 3—Co/TiH_x–SiO_2.

in the product mixture. Upon increasing the flow rate, an increase of the relative yield of olefins, primarily of α-olefins, was observed. It was also the case for aldehydes, though their fraction remained low in the experimental conditions, e.g., the C_2H_4O/C_2H_5OH ratio was within 0.05–0.2.

Air-Susceptibility of the Samples

All samples studied had a very oxophilic character and hence extreme care was necessary in using them. When contact of pyrolyzed catalysts with air was deliberately allowed, it resulted in an immediate change of color (from grey-brown to light grey), disappearance of the FMR signal and a sharp drop in magnetization (more than one order of magnitude). When initial samples were pretreated for recording IR spectra in air, CO stretching bands were not seen in the spectra.

DISCUSSION

1. The Effect of Titanium Ions on the State of Supported Cobalt

The samples before thermal treatment. Dehydrated silica was reported (*10, 19*) to be incapable of adsorbing Co carbonyl irreversibly. When supported by the impregnation technique, $Co_2(CO)_8$ transformed partly to $Co_4(CO)_{12}$, due to a higher stability of the Co_4 cluster at a low CO pressure. The Co carbonyls were in the state of a physical adsorption on the support and could be easily washed off by a solvent. Only a weak interaction with SiO_2 was noted for $Co_4(CO)_{12}$ and $CH_3Co_3(CO)_9$ in Refs. (*20, 21*). On the other hand, Al_2O_3, MgO, TiO_2, and ZrO_2 were capable of irreversibly adsorbing $Co_2(CO)_8$, apparently due to the presence of basic hydroxyl groups and/or Lewis acid centers on their surface (*10, 19*). Simultaneously, some new carbonly species were formed on Al_2O_3 and MgO surfaces (*19, 20*).

The results of the present study show that the modification of SiO_2 by Ti ions results in a more strong interaction of the support with Co carbonyls, the effect being most pronounced for the TiH_x–SiO_2 support. This latter support is capable of adsorbing the largest amount of $Co_2(CO)_8$ from solution, and the IR spectrum of the sample obtained differs essentially from that of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ in solution (Fig. 1).

Probably, some Ti ions in TiO_2–SiO_2 supports have properties of a Lewis acid and are capable of holding the carbonyl complex via coordination of carbonyl oxygen. Two factors may be responsible for the stronger carbonyl–support interaction in the case of TiH_x–SiO_2 support. First, reactions with the participation of Ti–H bond might be involved. Second, steric hindrances for the interaction are minimal in the case of anchored hydride complexes of

Ti. (Note that silica with Ti ions screened by bulky benzyl substituents was inert to adsorption of $Co_2(CO)_8$.) Additional investigations are needed, however, for a detailed description of the state of supported carbonyls in the samples. In particular, data on the interaction of carbonyl compounds and hydride complexes in solution would be useful.

Pyrolyzed samples. A high magnetization of Co/SiO_2 and Co/TiO_2–SiO_2 catalysts, the FMR signal in their ESR spectra, and absence of CO absorption bands in the IR spectra indicate that the thermal treatment leads to complete decomposition of supported Co carbonyl with formation of particles of metallic Co. A considerable dependence of magnetization on T/H ratio and a narrow FMR signal are known to be the characteristics of small, superparamagnetic metal particles (*18, 22*). Thus, the data presented in Figs. 2 and 4 show the size of Co particles formed to be rather small. The high dispersion of the supported metal is confirmed by the fairly strong influence of CO/H_2 adsorption on catalyst magnetization (Fig. 5). Co/SiO_2 and Co/TiO_2–SiO_2 catalysts have, therefore, the typical properties of samples prepared by fast pyrolysis of Co carbonyl on oxide supports (*10, 23*).

The calculations of the average size of Co particles in the catalysts (Table 1) show that the size decreases when silica is modified by Ti ions. (Some disagreement between d_{HF} and d_{LF} values for a catalyst is explained by the size nonuniformity of Co particles. Because $d_{\mathrm{HF}} \sim (\bar{v}_i)^{1/3}$, but $d_{\mathrm{LF}} \sim (\overline{v_i^2}/\bar{v}_i)^{1/3}$, where $\bar{v}_i$ and $\overline{v_i^2}$ are, respectively, the average and average square volume of a particle, the larger metal particles influence d_{LF} more strongly.) This fact is in agreement with the data of our previous work (*10*). The use of the supports capable of adsorbing $Co_2(CO)_8$ from solution resulted in the formation of smaller Co particles by thermal decomposition of the carbonyl. The effect was found even if the main part of the carbonyl was in the state of physical adsorption, having been supported by the impregnation technique (as was the case for the samples based on TiO_2–SiO_2 supports). This phenomenon may be explained by production of a greater number of metal nuclei serving as centers of carbonyl decomposition, when there were carbonyl species strongly bound with support.

We have to note, however, that a comparison of the size of Co particles in different samples needs caution. The difference between d_{HF} values for the Co/SiO_2 and Co/TiO_2–SiO_2 catalysts is comparable with the possible error in their determination. Only a comparison of d_{LF} values allows one to claim that larger Co crystallites are formed on unmodified silica.

Thus, the effect of Ti ions in Co/TiO_2–SiO_2 catalysts on the size of Co particles may be considered to be quite small. It is much more pronounced for the Co/TiH_x–SiO_2 sample. The extremely low magnetization of this catalyst and absence of an FMR signal (Figs. 3 and 4) indicate the formation of the very small Co particles which do not show ferromagnetic properties. (The calculation by formula 4, when using the parameters appropriate to ferromagnetic Co, leads to a d_{LF} value equal to 8.5 Å).

Interestingly, the properties of the Co/TiH_x–SiO_2 catalyst differ substantially even from those for samples based on pure TiO_2. A sample of 2.2% Co/TiO_2 prepared by adsorption of $Co_2(CO)_8$ and then pyrolyzed at 530 K demonstrated an FMR signal and there were Co particles of 17–23 Å in size (d_{HF}-d_{LF} values); an intensive sintering of Co was observed on additional treatment of the sample at 690 K (*10*). By contrast, for Co/TiH_x–SiO_2 catalyst the FMR signal is absent after treatment both at 530 and 670 K (Fig. 3). The magnetization of the catalyst treated at 670 K is indeed enhanced (so Co sintering presumably occurs), but is still very low (Fig. 4).

This difference between TiO_2 and TiH_x–SiO_2 as supports may be accounted for by the ability of the low-valent Ti ions of the latter support to form a direct and strong bond with Co atoms. The high stability of the metal to sintering was earlier explained in such a manner in the case of other anchored low-valent ions and supported metals (*12*).

Due to the strong metal–support interaction, raft-like Co particles seem very likely to be formed on TiH_x–SiO_2 support. In such a case, there are the strong influence of the support on the electronic properties of Co and the high anisotropy of the metal particle shape. These two factors may be supplementary reasons for unusual magnetic properties of the sample. In particular, an increase of magnetic anisotropy leads to the broadening of the FMR signal (*24*), and, in principle, this signal may become unobservable. Besides that, the raft-like shape of particles may contribute to a sharp decrease of interatomic interaction, which takes placed for sufficiently small particles and results in the disappearance of ferromagnetic properties.

In principle, the unique properties of the Co/TiH_x–SiO_2 sample might also be explained by complete oxidation of supported Co. However, this is unlikely. Oxidation by atmospheric oxygen was completely prevented by using an all-glass technique for catalyst preparation. As for possible oxidation via interaction with surface hydroxyl groups, it is less probable than for the other catalysts studies. Some, if not all, Si–OH groups disappeared on reaction with tetrabenzyltitanium, but Ti–OH groups could not form. If, nevertheless, there is a large fraction of oxidized Co in Co/TiH_x–SiO_2, it would increase on raising the temperature of thermal treatment of the sample, and further decrease of magnetization should be expected. However, on the contrary, an increase of magnetization is observed with the temperature rise (compare curves 5 and 6 in Fig. 4).

Catalysts after CO + H_2 reaction. The magnetic measurements bear witness that the size of Co particles in Co/TiO_2–SiO_2 catalysts did not change significantly under the conditions of CO hydrogenation. The decreased magnetization of the samples used in the reaction and then outgassed at room temperature can be accounted for by the presence of adsorbed reactants and products on the metal surface. The narrowing of the FMR signal after the reaction (Fig. 2) may reflect the change of the shape of metal particles. Presumably, the shape became more spherical. Earlier (*10*), this phenomenon was also observed and thought to be typical for small Co particles.

In the case of the Co/TiH_x–SiO_2 sample more considerable changes of the state of supported metal seem to occur. After being used in the reaction, the catalyst demonstrates an increased magnetization and produces a FMR signal in the ESR spectrum (Figs. 3 and 6). At the highest magnetic field used in our experiments the magnetization reaches 80 Oe · cm^3/g (curve 3 for outgassed sample in Fig. 6). This value is somewhat smaller as compared with the other catalysts (Fig. 4), but there is a stronger dependence of σ on magnetic field in the former case. It allows one to conclude that in both cases σ_∞ values will be comparable. (For TiH_x–SiO_2, a nonlinear dependence of σ on T/H is typical for all magnetic fields applied, which prevents a direct extrapolation of σ to the saturation state.) Under the reaction conditions, Co particles in Co/TiH_x–SiO_2 presumably adopted a three-dimensional shape. An increase of the number of Co atoms in them is also not excluded.

It may be noted that the magnetization of the Co/TiH_x–SiO_2 sample after catalytic testing is higher than that after thermal treatment in vacuum at 670 K (compare curve 3 in Fig. 6 and curve 6 in Fig. 4). Besides that, only in the first case is the FMR signal observed, although the CO + H_2 reaction was carried out at much lower temperature. These results may be explained by rupture of the Co–Ti bond under the action of water produced in CO hydrogenation. As a result of the oxidation of Ti ions, their state became the same as that for TiO_2–SiO_2 supports and, consequently, the state of supported Co in all the catalysts became similar.

At the same time, the increase of the size of the Co particles in the Co/TiH_x–SiO_2 sample is limited and there are still the smallest metal particles in this catalyst (Table 1). Some uncertainty in σ_∞ value for Co/TiH_x–SiO_2 (due to the nonlinear dependence of σ on T/H) and, thus, in d values, does not play an essential role. Here, σ_∞ was taken equal to 163 Oe · cm^3/g as for fully reduced Co. When taking the experimental σ points at $(T/H) = 0.51 \times 10^{-2}$ and 0.65×10^{-2} K/Oe and using *linear* extrapolation of σ to the saturation state, $\sigma_\infty \approx 140$ Oe · cm^3/g is obtained. If even this undoubtedly underestimated σ_∞ value was used for the calculations, both d values would increase up to 13 Å only.

The presence of very small Co particles in the Co/TiH_x–SiO_2 catalyst agrees with the observation of a rather intense band of adsorbed CO near 2050 cm^{-1} in spectrum 3 in Fig. 1A, whereas the bands of adsorbed CO could not be seen in the case of the other catalysts. An increase of Co dispersion is known to be accompanied by an increase of stoichiometry of CO adsorption on the surface atoms; at an appropriate size, multiple adsorption occurs (CO/Co > 1) (*25a*). The intensity and position of the bands in the IR spectrum may differ from those for CO adsorbed on large crystallites (usually the bands between 2100 and 2050 cm^{-1} predominate in spectra of CO adsorbed on supported Co (*25b*)). Rather intense bands near 2040–2030 cm^{-1} were earlier observed in the spectrum of Co/Al_2O_3 catalyst used in the CO + H_2 reaction and containing Co particles with average size of 11–12 Å (*10*).

2. *The Regularities in the Properties of the Samples in CO + H_2 Reaction*

One can see that the catalytic behavior of the samples studied is, in general, similar to that of the traditional Co systems (*26, 27*) and of the catalysts obtained by pyrolysis of supported $Co_2(CO)_8$ and studied earlier (*10, 17*). Thus the Schulz–Flory distribution is valid for C_3^+ hydrocarbons (Fig. 7). Primary hydrocarbon products of the reaction are α-olefins which undergo subsequent isomerization and hydrogenation. Therefore, their relative yield is reduced at a low flow rate of the gas mixture. Apparently, primary C_2^+ oxygen-containing products are also unsaturated compounds, namely aldehydes, but alcohols are formed via their hydrogenation. On the other hand, the distribution both of hydrocarbons and of oxygen-containing products vs the number of carbon atoms was not essentially affected by the flow rate of the gas mixture. Hence, the secondary transformation of the primary products, which changes this distribution, can proceed here only to a small extent.

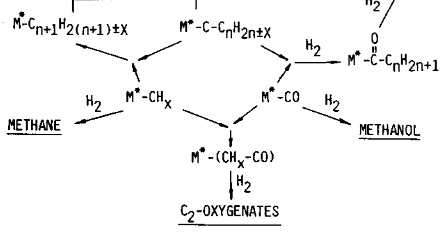
In particular, a considerable amount of ethanol cannot be obtained by homologation reaction of methanol. To verify this opinion, special experiments with addition of methanol into the gas mixture were performed. Only a short-time increase of ethanol yield was observed. The increase is obviously explained by the ease of removal of previously formed ethanol from the catalyst under such conditions. The addition of water was reported earlier to give the same effect (*19*). The retention of oxygen-containing products on the surface of the support explains also the gradual rise of the alcohol yield for the initial period of the reaction (*19, 28*).

It has been reported (*10, 11, 29, 30*) that the decrease of Co particle size (upon decreasing the metal loading on support) results in a decrease of the specific activity of Co and in an increase of the fraction of light products in hydrocarbon synthesis from CO and H_2. Some other metals demonstrated a similar behavior (see (*10, 29*) and references therein). This is also seen from the data presented in Table 1. In relation to the average size of Co particles, the catalysts may be arranged as Co/SiO_2 > Co/TiO_2–SiO_2 > TiH_x-SiO_2. (Because of some error that might arise in the determination of d values, the relative disposition of the Co/TiO_2–SiO_2 (I, II, III) samples is not clear.) In the same order is observed a decrease of the α value determining the average molecular mass of hydrocarbon products. Co/TiH_x–SiO_2 catalyst, although being most dispersed, has the lowest activity per 1 g of Co.

The most interesting result of the present work is the existence of a close relation between the catalytic properties in hydrocarbon and alcohol syntheses (production of oxygen-containing products was not studied earlier in detail). One can see from Table 1 that the decrease of the probability of chain propagation in hydrocarbon synthesis is accompanied by an increase of the relative yield of alcohols and the fraction of ethanol in them.

In the light of present-day knowledge of the mechanism of CO hydrogenation on heterogeneous Ni, Ru, and Co catalysts (see, e.g., Refs. (*31–33*), the formation of the various products may be described by Scheme 1. This scheme includes reactions of three kinds of surface carbon species, namely (1) carbon monoxide adsorbed in a molecular form $(CO)_s$; (2) $(CH_x)_s$ species formed by dissociative CO adsorption followed by incomplete hydrogenation of surface carbon; and (3) growing hydrocarbon chains $(C_nH_{2n\pm x})_s$.

It is reasonable to suppose that diminishing the size of metal particles leads to an increase of the surface concentration of $(CO)_s$ groups (as happens with CO adsorption at low temperature) and makes dissociative CO adsorption more difficult. Note that some CO species stable in hydrogen at the reaction temperature were observed on a highly dispersed Ru (*34*). This causes a decrease in the rate of hydrocarbon formation, including the rate of chain growth proceeding via the interaction of $(CH_x)_s$ and $(C_nH_{2n\pm x})_s$ fragments.



SCHEME 1

On the other hand, while increasing the concentration of $(CO)_s$ species, there is an increase of the probability of the formation of oxygen-containing compounds which become the only products in the case of homogeneous catalysts. Thus when using the catalytic system "$Co_2(CO)_8$/organic solvent," mainly C_1-oxygenates, glycols, and their derivatives were obtained from CO and H_2; C_2^+ alcohols were not the primary products, and hydrocarbons could be detected only if part of the carbonyl decomposed to produce a metallic precipitate (*35*). Because there are both $(CO)_s$ and $(CH_x)_s$ fragments on the surface of metal crystallites, C_2-oxygenates may be obtained with a high selectivity at suitable dispersion of metal.

It is always difficult in the case of supported catalysts to conclude whether there is a true crystallite size effect or whether a support effect determines the difference of catalytic properties for samples with different metal dispersion (*36, 37*). The variation of the size of metal particles does cause changes in the structural and electronic properties of the metal. However, these changes may also arise from the more intimate contact of smaller metal particles with the support.

With this uncertainty in mind we believe, however, that the crystallite size effect predominates or, at least, plays an important role in our case. There is an increased number of metal atoms in smaller particles, which have high coordinative unsaturation and are capable of binding several CO molecules. Molecular metal clusters can be regarded as an extreme case, e.g., $Co_4(CO)_{12}$, where the CO/metal ratio turns out to be much more than unity. (Note that the support effect is eliminated in the latter case.)

Perhaps the effect of the support on the electronic state of metallic particles is of importance for the initial Co/TiH_x–SiO_2 sample, where the state of the Ti ions is unusual and a very strong Co–support interaction takes place. This may explain the behavior of this catalyst during CO + H_2 reaction. Although considerable changes of the state of Co occurred here, dramatic changes of catalytic properties were not observed. (Analysis for C_1–C_4 hydrocarbons and alcohols was first performed 10–15 min after the loading of catalysts into the reactor; the first point for C_1–C_8 hydrocarbons was obtained after ~40 min. Only somewhat more pronounced deactivation of the Co/TiH_x–SiO_2 catalyst when going to the steady-state conditions was noticed.) It might be the case that increasing Co particle size was compensated (with respect to the catalytic properties) by weaking the electronic influence of support on supported Co.

Finally, it is expedient to analyze the possibility of the specific promotion effect of Ti ions in alcohol formation, due to changing the electronic properties of small Co crystallites or via direct participation of these ions in the synthesis as active centers for CO activation. Strong influence of the chemical nature of the support on the properties of metal in alcohol production is well known for the Rh system (see, e.g., (*38, 39*) and references therein). In particular, modification of silica by Ti ions resulted in great enhancement of selectivity of Rh/SiO_2 catalysts in ethanol formation (*39*). However, there is only a slight difference between the catalytic properties of Co/SiO_2 and Co/TiO_2–SiO_2(I) catalysts (Table 1). The same is true for Co/TiO_2–SiO_2(II) and Co/TiO_2–SiO_2(III) samples, though they differ considerably in Ti loading. It gives support for a mainly indirect effect of Ti ions in our case, i.e., at the expense of the decrease of Co particle size.

CONCLUSIONS

The results of the present study show that the introduction of Ti ions to silica surface may serve as a method to decrease the size of metal particles obtained by pyrolysis of supported Co carbonyl. The state of the surface ions plays an important role. The interaction of carbonyl with support is the strongest and the metal particles obtained have the smallest size, if there are hydride complexes of a low-valent Ti on the surface.

The interaction of Co with the support weakens during CO + H_2 reaction. Co particles adopt a more regular shape and very small ones seem to grow in size.

Our data confirm the previously noted decrease of the specific activity of Co in the Fischer–Tropsch synthesis and rise of the fraction of light hydrocarbon products, as Co dispersion increases. The other specific feature of small Co particles proved to be an increased yield of alcohols, especially of ethanol. Thus, with respect to the properties in CO hydrogenation, highly dispersed Co catalysts may be regarded as intermediates between heterogeneous Co catalysts with a low Co dispersion (which are used for the production of heavy hydrocarbons) and homogenous catalysts (which demonstrate activity in the formation of light oxygen-containing compounds).

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