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Formation of Iron Nanoparticles by Thermal Transformations of Iron Carbonyls on Silica Surface

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There have been determined some regularities of thermochemical transformations of supported on silica iron carbonyls containing from 1 to 6 metal atoms. There have been selected the conditions of iron carbonyls thermal decomposition which provides the formation of metallic particles having the size of 0,5 -1,0nm.

Keywords: iron carbonyls, silica, thermal transformations, nanoparticles.

Introduction

The nanoparticles of transition metals are finding an increasing application in producing the functional materials of various purposes. In particular, the systems on the basis of iron nanoparticles on solid supports present great interest for the industrial catalysis and electronics. To obtain metallic nanoparticles on the supports surface, various methods are used – from evaporation in vacuum to the thermal decomposition of the supported metalloorganic compounds [1, 2, 3]. For this purpose, it is possible to apply carbonyl iron clusters having a strictly given number of atoms and a metallic frame

structure. When being heated, the carbonyl groups are easily removed forming iron nanoparticles.

In the scientific literature, there is described the use of only a restricted number of iron carbonyls (mostly $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$) for supporting them to the oxide surface for the purpose of their further thermal decomposition to forming metallic particles [4-6]. Besides, there is no information about the influence of the initial iron carbonyls composition on the size of the metallic particles which are formed during their heat treatment. During the process of the thermal transformations of the iron carbonyls on the oxide supports, it is possible for them to chemically

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interact with the surface functional groups (for example, OH-groups), which leads to oxidizing metal atoms. One can expect that the reactivity of the supported iron carbonyls to the oxidation during the thermal treatment, will decrease as the number of metal atoms increases. And the size of the formed metal particles will depend on composition the initial carbonyl compound.

The aim of the given work is to carry out a systematic physical and chemical study of the peculiarities of forming iron nanoparticles during the thermal transformations of the iron carbonyls supported to the porous silica. The number of the atoms in the iron carbonyls varies from 1 to 6.

Experimental

The carbonyl compounds $[\text{TEA}][\text{HFe}(\text{CO})_4]$ [7], $\text{Fe}_2(\text{CO})_9$ [8], $[\text{TEA}]_2[\text{Fe}_2(\text{CO})_8]$ [7], $\text{Fe}_3(\text{CO})_{12}$ [9], $[\text{TEA}][\text{HFe}_3(\text{CO})_{11}]$ [8], $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]$ [10], $\text{Fe}_5\text{C}(\text{CO})_{15}$ [11], $[\text{TEA}]_2[\text{Fe}_5\text{C}(\text{CO})_{14}]$ [12], $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$ [12] ($\text{TEA} - (\text{C}_2\text{H}_5)_4\text{N}^+$), were synthesized according to the well-known methods.

As a carrier, there was used the silica dehydrated at 773 K (its specific surface was $250 \text{ m}^2/\text{g}$, the contents of Na and Fe were less than 0,01 mass %, the fraction was 0,5-0,25 mm).

The supporting of the carbonyls to the silica surface was carried out by impregnating SiO_2 with their solutions in acetone (for anion carbonyls), or in hexane (for neutral carbonyls). All the operations on synthesizing, supporting the clusters on SiO_2 , their transformations in various gaseous mediums were performed under the conditions excluding contact with air.

The thermal stability of the supported clusters was studied by using the method of IR spectroscopy (spectrometer "Specord – 75 IR") in the range of $1300\text{--}4000 \text{ cm}^{-1}$. For carrying out the studies, there was used a special vacuum cell having the windows from NaCl, which allowed to prepare samples, providing their high-temperature

treatment in various gaseous mediums as well as the spectra recording without contacting the air. In a typical experiment, the solid carrier was pressed to form plates ($8\text{--}10 \text{ mg}/\text{cm}^2$). Then it was fixed in the holder, put into the cell and trained in the vacuum at 873 K for an hour to remove the water. After that the plate was cooled to room temperature, and the cluster solution in the corresponding organic solvent was poured in. The excess of the solution was decanted. The solvent remaining in the carrier's pores, was removed by freezing with liquid nitrogen followed by the vacuum evaporation at 298 K to reaching the residual pressure of 10^{-5} torr.

The study of the transformations of the supported iron clusters at raised temperatures, was carried out by using the method of IR-spectroscopy, the thermoprogrammed decomposition and the electron microscopy of high resolution.

The thermoprogrammed decomposition of the supported iron carbonyls was performed in a flow-type installation by using a gas-chromatographic analysis of the products. The samples were put into a glass reaction vessel not contacting the air. The samples were blown off by helium at room temperature till the solvent traces disappeared. The decomposition of the supported carbonyls was carried out in the flow of the carrier gas (helium) in the conditions of the programmed temperature rise ($4\text{K}/\text{min.}$). The analysis of the decomposition products was accomplished by using the katharometer (CO , CO_2) and the flaming and ionizing detectors (hydrocarbons) on the columns filled with porapak-Q and Al_2O_3 . The quantitative interpretation was implemented according to the calibration obtained by measuring the area of the chromatographic peak CO_2 or CH_4 when introducing a strictly dosed adsorbate volume into the current of the carrier gas.

The electron-microscopic studies of the Fe/SiO_2 systems were carried out by using the

electron microscope «EBM – 100B» having the limiting resolution on points 3 \AA . The samples were prepared under by means of mechanical grinding the ethanol followed by the ultrasound dispersion. The suspension was put on the carbon supports on copper grids. The electron-microscopic study was carried out in a light field mode at the accelerating voltage of 75 kV and the objective lens aperture of $6 \cdot 10^{-3}$ rad. according to the methods described in [13]. To exclude the influence of the carbon support on the contrast range of the picture, there were studied the sample parts which were in the holes of the carbon support. The microscope magnification made up $10^6 \pm 5\%$. The area-mean particle size was calculated from the differential granulometric composition diagrams of the particle distribution according to their size which was obtained by way of the statistical processing of the photomicrographies.

Results and discussion

During the supporting of carbonyls on SiO_2 surface at room temperature, only their physical adsorption occurs, and the carbonyl compounds may be washed off by the excess of the corresponding solvent in the initial form.

The results of the studies of the thermal stability in the H_2 atmosphere of the clusters $[\text{HFe}_3(\text{CO})_{11}]$ [TEA], $[\text{Fe}_4(\text{CO})_{13}]$ [TEA]₂, $[\text{Fe}_5\text{C}(\text{CO})_{14}]$ [TEA]₂, $\text{Fe}_5\text{C}(\text{CO})_{15}$ and $[\text{Fe}_6\text{C}(\text{CO})_{16}]$ [TEA]₂ supported on SiO_2 surface which was carried out by using the method IR spectroscopy, are given in Table 1. In the spectra of the supported compounds, there are only the most intensive absorption bands (a.b.) ν_{CO} of the carbonyl clusters. And there are not registered the bridge CO-groups and the high – frequency a.b. ν_{CO} , which are present in the IR spectra of the clusters in the solutions. Evidently it is caused by the insufficiently high clusters concentration on the carrier surface, because the indicated bands have relatively small intensities. It is noteworthy,

that the supporting of the clusters on the SiO_2 tablet placed in the IR-cell, was performed by the single – stage impregnation, and the cluster concentration on the carrier surface, was limited by its solubility.

The infra-red spectrum of the cluster $[\text{HFe}_3(\text{CO})_{11}]$ which is supported on SiO_2 , contains two a.b. ν_{CO} at 1980 and 2002 cm^{-1} . In the range of the supported $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ and $[\text{Fe}_5(\text{CO})_{14}]^{2-}$, there is present only one absorption band (at 1955 and 1965 cm^{-1}) respectively. These bands are a little displaced as compared to their position in the clusters spectra in the solutions. The treatment of the supported carbonyls by hydrogen for an hour at 373 K, leads to the complete disappearance of the mentioned a.b. ν_{CO} and appearing the intensive a.b. at 1635 cm^{-1} (Table 1). The low-frequency a.b. at 1635 cm^{-1} whose appearance is observed for all the studied clusters after their treatment in the hydrogen atmosphere at a temperature of ≥ 373 K, is considered to be the antisymmetric valence vibrations of CO_2 molecule adsorbed on the SiO_2 surface in accordance with [14].

In the spectrum of the neutral cluster $\text{Fe}_5\text{C}(\text{CO})_{15}$, supported on SiO_2 , there are a.b. ν_{CO} at 2050, 2098 cm^{-1} . There is also a greatly displaced, as compared to the spectrum in the solution, a.b. at 1973 cm^{-1} . After treatment the sample by hydrogen at 373 K, these absorption bands ν_{CO} disappear, but new a.b. appear at 1635 cm^{-1} (table 1).

In the carbonyl area of the cluster IR spectrum $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$, which is dissolved in acetonitrile, there are present a.b. at 1769 (weak), 1930 (arm), 1957 (arm), 1969 (very strong), 2029 (weak) cm^{-1} (table 1).

After carbonyl supporting on SiO_2 surface at room temperature, one can observe a displacement of a.b. at 1969 and 2029 cm^{-1} to 1975 and 2036 cm^{-1} respectively. The holding of the sample $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}] / \text{SiO}_2$ in the hydrogen at the temperatures of 298 – 473 K leads to decreasing

Table 1. Absorption bands in the carbonyl area of dissolved and supported on SiO₂ iron carbonyl clusters

№	Sample	Treatment	Absorption bands ν_{CO} , cm ⁻¹
1	[TEA][HFe ₃ (CO) ₁₁] (a solution in the chlorine methylene)	-	1740 (bridge), 1933 (arm), 1953 (arm), 1981 (very strong), 2001 (strong), 2068 (mean)
	[TEA][HFe ₃ (CO) ₁₁] / SiO ₂	-	1980 (strong), 2002 (strong)
		H ₂ , 373 K, 1 hr	1635 (strong)
2	[TEA] ₂ [Fe ₄ (CO) ₁₃] (a solution in acetonitrile)	-	1615 (bridge, weak), 1896 (arm), 1949 (strong), 2021 (weak)
	[TEA] ₂ [Fe ₄ (CO) ₁₃] / SiO ₂	-	1955 (strong)
		H ₂ , 373 K, 1 hr	1635 (strong)
3	[TEA] ₂ [Fe ₅ C(CO) ₁₄] (a solution in acetonitrile)	-	1755 (bridge, weak) 1890 (arm), 1940 (arm), 1969 (very strong), 2027 (weak)
	[TEA] ₂ [Fe ₅ (CO) ₁₄] / SiO ₂	-	1965 (strong)
		H ₂ , 373 K, 1 hr	1635 (strong)
4	Fe ₅ C(CO) ₁₅ (a solution in cyclohexane)	-	1760 (very weak), 1991 (mean), 2012 (arm), 2031 (strong), 2050 (very strong), 2098 (weak)
	Fe ₅ C(CO) ₁₅ / SiO ₂	-	2050 (strong), 2098 (weak)
		H ₂ , 373 K, 1 hr	1635 (strong)
5	[TEA] ₂ [Fe ₆ C(CO) ₁₆] (a solution in acetonitrile)	-	1769 (bridge, weak), 1930 (arm), 1957 (arm), 1969 (very strong), 2029 (weak)
		-	1975 (very strong), 2036 (weak)
	[TEA] ₂ [Fe ₆ C(CO) ₁₆] / SiO ₂	H ₂ , 473 K, 1 hr	1635 (mean), 1975 (very strong), 2036 (strong)
		H ₂ , 523 K, 1 hr	1635 (mean)

the relative intensity of the absorption bands ν_{CO} . After treatment this sample by H₂ at 373 K, there appears an absorption band at 1635 cm⁻¹, whose intensity increases with the rise in temperature. The indicated a.b. disappears only after treatment the supported cluster by hydrogen at 523 K.

To get some additional information about the nature of the surface carbonyl iron compounds, there was carried out a study of the composition of the Fe carbonyls, extracted from the surface of the samples [Fe₆C(CO)₁₆][TEA]₂ / SiO₂ and [Fe₅C(CO)₁₄][TEA]₂ / SiO₂ heated in argon at various temperatures. The carbonyl clusters extracted from the carrier surface, were identified by comparing their IR spectra with the spectra of individual compounds and by using the data of the element analysis. It is determined that after being supported on SiO₂, the anion cluster [Fe₆C(CO)₁₆][TEA]₂ remains unchangeable. What testifies to

that is practically the complete correspondence between the IR spectra of the carbonyl compound extracted from the SiO₂ surface with acetonitrile (Fig. 1, curve 1) and the initial carbonyl carbide cluster (see Table 1) in the area of the valence vibrations of the carbonyl CO-groups.

The results of the studies of the behaviour of silica supported [Fe₆C(CO)₁₆][TEA]₂ during the thermolysis in the argon atmosphere, allowed to conclude that the supported cluster retained its initial composition after being heated at 423 K for two hours. The increase of the treatment duration to 4 hours leads to appearing alongside the main absorption band of the initial cluster at 1968 cm⁻¹, also the a.b. of small intensity at 2051, 2035, 2020 and 1990 cm⁻¹ (Fig. 1, curve 2). The latter can be referred to the neutral carbonyl iron compound, the identification of which is difficult due to its small quantities and not high stability.

When the treatment duration is 6 hours, on SiO_2 surface there is formed the cluster having the composition $[\text{Fe}_5\text{C}(\text{CO})_{14}][\text{TEA}]_2$, which was extracted with the yield to 30 % as calculated for the iron content (Fig. 1, curve 3). The discovered partial fragmentation of the octahedral carbide cluster $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ to the pentanuclear carbide carbonyl dianion $[\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$, agrees with the described in [12] the probable scheme of thermal transformation of the metal frame Fe_6C to Fe_5C :



As the temperature of heating the sample $[\text{Fe}_6\text{C}(\text{CO})_{16}][\text{TEA}]_2/\text{SiO}_2$ increases to 450 K, the number of the iron clusters extracted from the carrier's surface, decreases. After this thermal treatment, one can see a clearly marked arm at 1948 cm^{-1} which indicates the further progress of the chemical transformations of the supported carbonyl clusters (Fig. 1, curve 4). After treatment the sample $[\text{Fe}_6\text{C}(\text{CO})_{16}][\text{TEA}]_2/\text{SiO}_2$ in argon at a temperature of 473 K, there takes place the complete decarbonylating of the supported cluster, because in the IR spectrum of the acetonitrile extract, there are absent the a.b. of the valence vibrations of the CO groups.

When heating the cluster $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$ supported on SiO_2 , in the atmosphere of a synthesis gas at 423 K for 2 hours, one could not observe any substantial changes in the IR spectrum which indicates that the initial cluster composition was retained. The longer heating (6 hours) of this sample under the given conditions, leads to forming some amount (about 7 %) of the carbonyl compound, whose IR spectrum in the area of the valence vibrations of CO is similar to the range of the neutral carbide cluster $\text{Fe}_5\text{C}(\text{CO})_{15}$. The reason for forming the uncharged Fe_5C cluster on the surface of the dehydrated silica, may be the oxidation of the cluster Fe_6C and Fe_5C – dianions of which such oxidizing transformations in solutions are quite typical. So, the neutral $\text{Fe}_5\text{C}(\text{CO})_{15}$ was obtained

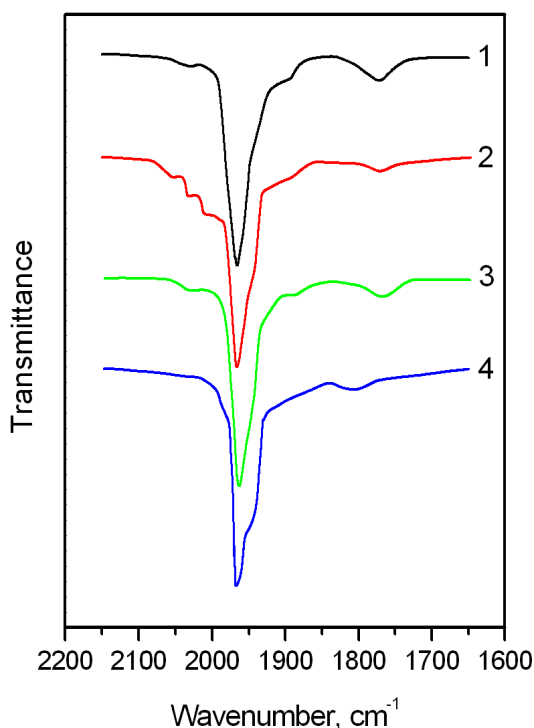


Fig. 1. The IR spectra of the acetonitrile solution of the cluster $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$ extracted from the SiO_2 surface (1), and also of the solutions, obtained by extracting the sample $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]/\text{SiO}_2$ by acetonitrile, after its being heated in the argon atmosphere at temperature of 423 K for 4 hr. (2), at 423 K for 6 hours (3), at 448 K for 6 hours (4)

by oxidizing $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ with the salts Ce^{4+} , Fe^{3+} or the concentrated H_2SO_4 [11]. The same result is achieved when $[\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$ is oxidized with the salt Ce^{4+} in the acid medium [12]. In our case, the oxidizer nature is not determined. But one can suppose that as the latter, there may be the surface OH-groups of SiO_2 .

Based on the obtained data, one can come to the conclusion, that the iron carbonyls with the nuclearity from 1 to 4, have a not high threshold of thermal stability. Already at 373 K, one can observe their practically complete decarbonylating. The clusters with 5-6 iron atoms, containing a carbide carbon atom, are characterized by a higher thermal stability.

The obtained results testify to the fact that despite the structural changes of the cluster frame

and the corresponding carbonyl surrounding, the included carbon atom is preserved inside the metallopolyhedron up to the full destruction of the surface molecular clusters raising their thermal stability.

In Fig. 2-4 and in Table 2, there are given the results of studying the thermoprogrammed decomposition (TPD) of the iron carbonyl compounds supported on SiO_2 . The products of their thermal degradation in the flow of the inert gas, are CO , CO_2 , saturated and unsaturated hydrocarbons $\text{C}_1 - \text{C}_6$. With some exceptions, the material balance on carbon is tabulated satisfactorily (Table 2). It is noteworthy, that among the products of the clusters thermolysis, on the surface of SiO_2 , there may also be hydrogen formed, probably, during the oxidation of iron atoms with the surface hydroxyl groups, or as a result of the conversion of water gas.

The emission of hydrogen was observed earlier during the decomposition of $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ [15]. During the thermal decomposition of the charged carbonyl iron clusters, in addition to ethylene, there may also be formed ethylamines and ammonia. In the given work, no attempts were made to register hydrogen, alkylamines or ammonia. It is also necessary to note that the formation of ethylamines during the thermal programmed decomposition of the supported clusters can be thought of only in the experiments where there was an unsatisfactory balance on the carbon, that is for the samples $[\text{TEA}][\text{HFe}(\text{CO})_4]/\text{SiO}_2$, $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]/\text{SiO}_2$ and $[\text{TEA}]_2[\text{Fe}_5\text{C}(\text{CO})_{14}]/\text{SiO}_2$.

The curves of the CO emission during the thermal programmed decomposition of iron carbonyls, confirm the conclusion made on the basis of the IR spectroscopy data about the comparatively not high stability of the Fe carbonyl clusters on the surface of SiO_2 . In Fig. 2 there is given the composition of the products emitting during the thermoprogrammed decomposition of

the uncharged clusters $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}_5\text{C}(\text{CO})_{15}$ supported on SiO_2 . On the graphic dependence of the amount of the emitted products on temperature, there are two maxima of CO emission, which differ in their intensity. For $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$, the first maximum at the temperature of 363 K, corresponds to the emission of approximately 9,5 moles of CO per mole of the initial cluster, the second, at 423 K – 0,6 moles of CO . In the temperature range 393–533 K, there was registered the CO_2 emission in the amount of about 0,8 mole. On the curve of the thermoprogrammed decomposition of the sample $\text{Fe}_5\text{C}(\text{CO})_{15}/\text{SiO}_2$, one can observe two maxima – at 348 K and at 423 K. The first maximum corresponds with emitting of about 1,7–1,8 moles of CO / cluster mole, the second one corresponds with the emission of about 3 moles of CO / cluster mole. In the temperature range 348–373 K, there is observed the emission of about 3,5 moles of CO_2 / mole of cluster. So, with the rise in the temperature of the thermoprogrammed decomposition to 373 K, the supported cluster $\text{Fe}_3(\text{CO})_{12}$ loses, on the average, more than a third of the initial quantity of the CO molecules coordinated with iron.

It is discovered that for the supported iron carbonyls of low nuclearity $\text{Fe}_1\text{--Fe}_3$ practically the complete loss of carbonyl ligands takes place at the temperatures of ≤ 423 K. The four-nuclei cluster $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]$ loses in this temperature range, approximately half of the coordinated CO -groups. The supported clusters of high nuclearity $\text{Fe}_5\text{--Fe}_6$ in the indicated temperature range, retain about two thirds of the CO molecules coordinated with the atoms of Fe (Fig. 2-4).

On the curve of the CO emission, during the thermoprogrammed decomposition of the cluster $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]$ supported on SiO_2 , there are present two maxima (Fig. 4B). One of them (390 K) corresponds to the emission of ~ 2 moles of CO / mole of cluster. And as distinct from the other clusters in this temperature range, practically no emission of any other decomposition products

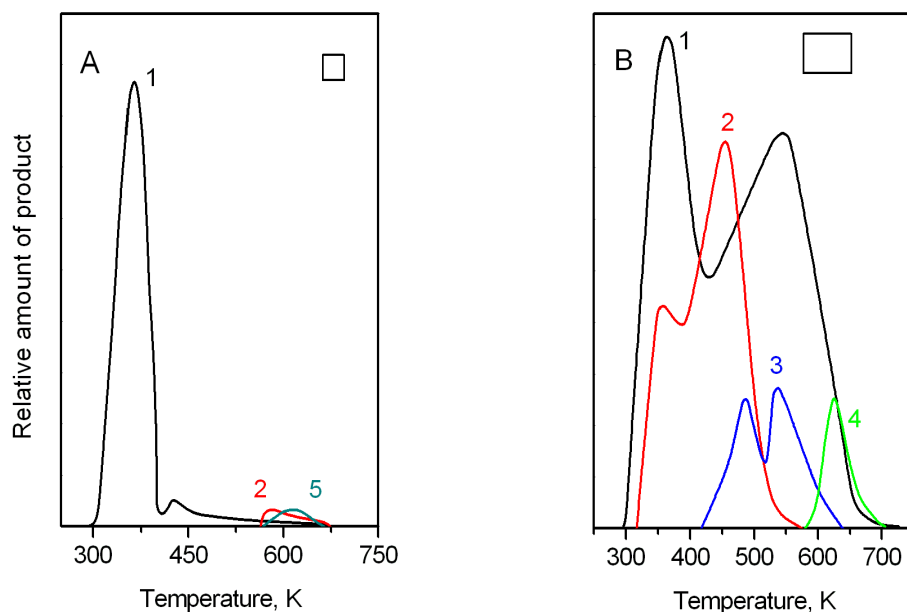


Fig. 2. The composition of the thermoprogrammed destruction products $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ (A), $\text{Fe}_5\text{C}(\text{CO})_{15}/\text{SiO}_2$ (B): 1 – CO; 2 – CO_2 ; 3 – C_2H_4 ; 4 – C_2H_6 ; 5 – C_3H_6
 □ – is the area corresponding to $5 \cdot 10^{-1}$ moles of the product

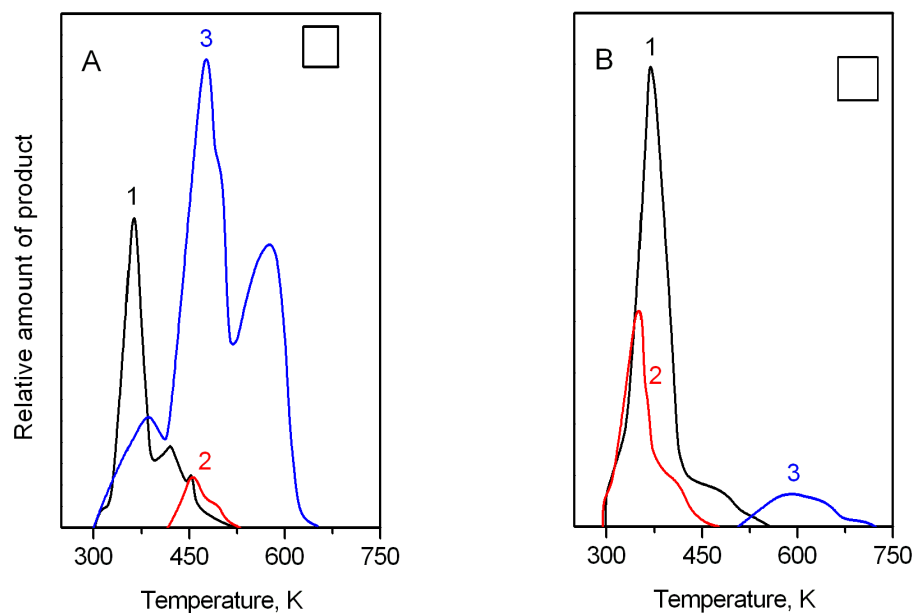


Fig. 3. The composition of the thermoprogrammed destruction products $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ (A), $\text{Fe}_5\text{C}(\text{CO})_{15}/\text{SiO}_2$ (B): 1 – CO; 2 – CO_2 ; 3 – C_2H_4 ; 4 – C_2H_6 ; 5 – C_3H_6
 □ – is the area corresponding to $5 \cdot 10^{-1}$ moles of the product

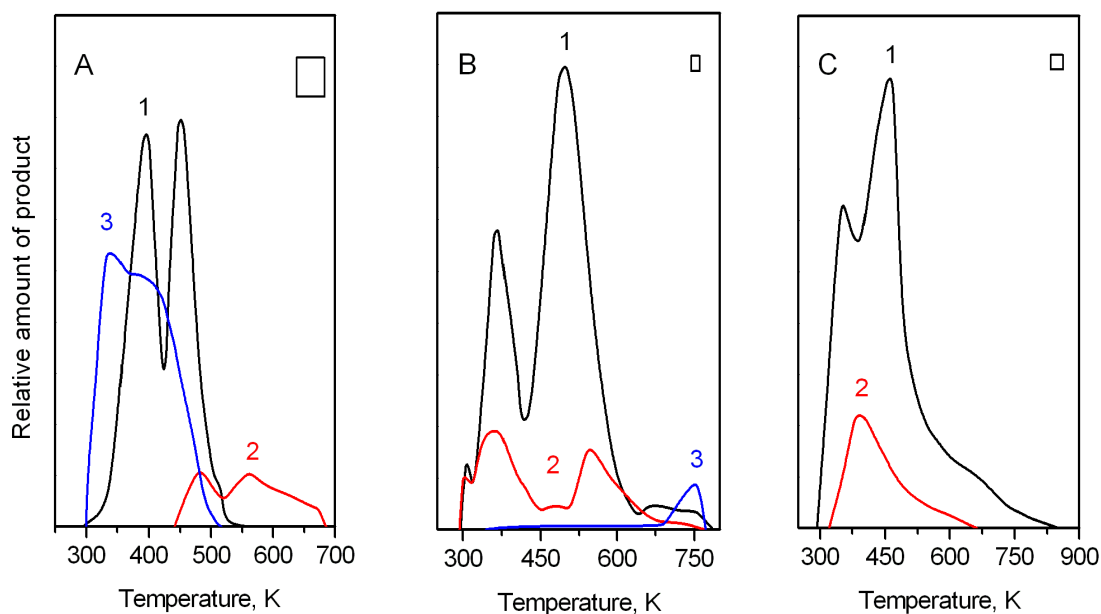


Fig. 4. The composition of the thermoprogrammed destruction products: $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]/\text{SiO}_2$ (A), $[\text{TEA}]_2[\text{Fe}_5\text{C}(\text{CO})_{15}]/\text{SiO}_2$ (B), $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]/\text{SiO}_2$ (C): 1 – CO; 2 – CO_2 ; 3 – CH_4
 □ – is the area corresponding to $1 \cdot 10^{-1}$ mole

Table 2. The composition of the termoprogrammed destruction products of the iron carbonyls with various nuclearity (mole of carbon / mole of cluster), supported on the silica.

Sample	The decomposition products of the supported clusters								
	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4^+	Σ
$[\text{TEA}]_2[\text{Fe}(\text{CO})_4\text{H}]/\text{SiO}_2$	2,3	0,1	4,5	< 0,1	< 0,1	-	0,8	1,5	9,3
$[\text{TEA}]_2[\text{Fe}_2(\text{CO})_8\text{H}]/\text{SiO}_2$	2,8	0,9	0,2	1,4	12,4	-	< 0,1	1,6	19,3
$\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$	10,0	0,8	-	-	-	-	1,0	-	11,8
$[\text{TEA}][\text{HFe}_3(\text{CO})_{11}]/\text{SiO}_2$	4,1	1,8	2,0	0,3	0,2	1,1	1,3	7,2	18,0
$[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]/\text{SiO}_2$	4,5	0,7	4,5	3,9	3,0	< 0,1	3,5	4,9	25,1
$\text{Fe}_5\text{C}(\text{CO})_{15}/\text{SiO}_2$	4,9	7,2	< 0,1	1,2	2,5	-	-	-	15,8
$[\text{TEA}]_2[\text{Fe}_5\text{C}(\text{CO})_{14}]/\text{SiO}_2$	12,5	2,3	1,3	1,2	1,2	-	0,1	7,1	25,7
$[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]/\text{SiO}_2$	13,0	2,4	0,3	2,0	3,7	1,0	1,5	8,5	32,4

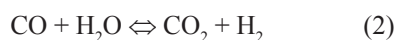
TEA – is tetraethylammonium

takes place. It is not excluded that under these conditions, there occurs the transformation of cluster $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$ into $\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$, described above in the scheme 1. And the unstable fragment $\{\text{Fe}(\text{CO})_2\}$ is decomposed or oxidized by the surface carbonyl groups with the emission of two molecules of CO per each molecule of the initial cluster.

The temperature ranges of the emission of both CO and CO_2 as well as the intensities of the corresponding peaks on the curves of the thermoprogrammed decomposition, differ greatly for the supported anion iron carbonyls of various composition. And it is difficult to reveal any regularities when analyzing the obtained data (Fig. 3-4).

During the thermoprogrammed decomposition of the supported clusters $[\text{Fe}_2\text{C}(\text{CO})_8]^{2-}$, $[\text{Fe}_5\text{C}(\text{CO})_{14}]^{2-}$ and $[\text{Fe}_6\text{C}(\text{CO})_{16}]^{2-}$, the emission of CO_2 starts practically with room temperature. For the supported clusters $[\text{HFe}(\text{CO})_4]^-$ and $[\text{Fe}_4(\text{CO})_{13}]^{2-}$, the emission of CO_2 is observed only at temperatures of ≥ 420 K. In case of the supported cluster $[\text{HFe}_3(\text{CO})_{11}]^-$ on the curve of the CO_2 emission, one can observe two maxima – at 330 K (corresponding to 0,6 mole of CO_2 per mole of the initial cluster), and at 643 K (1, 2 moles per mole of the initial cluster).

The formation of CO_2 may happen, for example, in the way of the reaction of converting CO with steam



also, as a result of the disproportionation of carbon monoxide (Buduar reaction):



Since the Buduar reaction is carried out only at higher temperatures, the most probable route of the CO_2 formation during the thermoprogrammed decomposition of the supported carbonyls (at least in the range of moderate temperatures), is the

reaction of CO conversion. What testifies to the fact that this supposition is true is the information concerning the catalysis of the reaction of converting CO with steam using iron carbonyls in solutions [15].

The thermoprogrammed decomposition of the neutral clusters $\text{Fe}_3(\text{CO})_{12}$ and $\text{Fe}_5\text{C}(\text{CO})_{15}$ taking place on the SiO_2 surface, leads to the formation, alongside the carbon oxides of propylene (in case of a three-nuclei cluster), of a mixture of ethane and ethylene for the pentanuclei carbonyl, when there are tracing amounts of methane (Table 2). Let us note that propylene is formed during the hydrogenation of CO on the supported catalysts obtained with using the carbonyl $\text{Fe}_3(\text{CO})_{12}$ [15]. As regards methane, it is most likely the product of hydrogenating the coordinated CO, as the hydrogenolysis or the cracking of hydrocarbons C_{2+} on iron occurs only at the temperatures ≥ 573 K [16].

Besides the reaction of converting CO with steam, the source of hydrogen may also be the surface hydroxyl groups, since it is known, that the iron-containing carbonyl clusters, supported on SiO_2 , may be oxidized with them forming hydrogen already at room temperature [17, 18].

In case of charged clusters, the source of hydrocarbons $\text{C}_2\text{-C}_6$ may be a tetraethyl ammonium ion. So, the formation of the hydrocarbons C_{2+} during the thermoprogrammed decomposition of the anion clusters, was not discussed.

To measure the size of the iron particles formed on the SiO_2 surface, during the thermal treatment of the supported iron carbonyls, there was used the method of transmitting electron microscopy of high resolution. The electron microscopic study of the samples $[\text{TEA}]_2[\text{HFe}(\text{CO})_4]/\text{SiO}_2$, $[\text{TEA}]_2[\text{Fe}_2(\text{CO})_8]/\text{SiO}_2$, $\text{Fe}_3(\text{CO})_{12}$, $[\text{TEA}][\text{HFe}_3(\text{CO})_{11}]/\text{SiO}_2$, $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]/\text{SiO}_2$, treated with the synthesis gas at the temperatures 423-623 K, showed that the iron particles size on the carrier surface, does

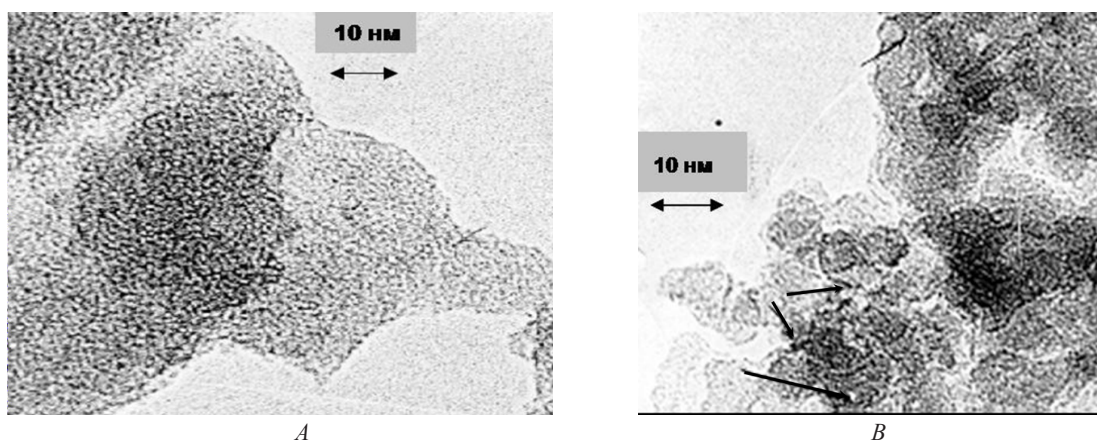


Fig. 5. The electron microscopic pictures of the sample $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]/\text{SiO}_2$ treated with the mixture of CO and H_2 at 523 K (A) and the sample $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]/\text{SiO}_2$ treated with H_2 at 623 K (B)

not exceed 2 nm. So, in the electron microscopic picture of the sample $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]/\text{SiO}_2$, treated with the synthesis gas at 523 K, one can clearly see homogeneous metallic particles of the size 1-2 nm and a small number of two-dimensional particles having a somewhat large size (Fig. 5 A).

A higher dispersity is typical of the thermally treated samples $\text{Fe}_5\text{C}(\text{CO})_{15}/\text{SiO}_2$, $[\text{TEA}]_2[\text{Fe}_5\text{C}(\text{CO})_{14}]/\text{SiO}_2$, $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]/\text{SiO}_2$. For example, in the electron microscopic pictures of the reduced sample $[\text{Fe}_6\text{C}(\text{CO})_{16}]^2-/ \text{SiO}_2$, which was thermally treated at 623 K, there are present the particles having the size of the order of 0,5 nm, which is close to the size of the Fe_6 cluster frame (Fig. 1 B). These data confirm the conclusion about the stabilizing influence of the carbide atom of the carbon, included into the metal frame of carbonyl clusters.

For comparison, let us note, that according to the data of the work [15], the size of the metallic particles, obtained by the thermal decomposition

in the hydrogen of the cluster $\text{Fe}_3(\text{CO})_{12}$ supported on SiO_2 , made up 1,4 nm, whereas according to the data of [19], it made up 14 nm. The smallest particles (0,5 nm) were obtained by the thermal decomposition in the vacuum at 310 K of the cluster $\text{Fe}_3(\text{CO})_{12}$ which was supported on Al_2O_3 [6].

So, on the basis of the determined regularities of the thermochemical transformations of the iron carbonyls supported on silica, differing in the number of the metal atoms, there has been carried out the selection of conditions of their thermodestruction, with supply the formation of the metallic particles having the size from 0,5 to 1,0 nm. They are distributed in a rather homogeneous way along the surface of the support.

These systems may be used as functional nanomaterials and as model catalysts when studying the effects of the size in the catalysis with iron nanoparticles.

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