

УДК 554.478.32

## Properties in CO Hydrogenation of the Nano-Catalysts Produced by Supporting Iron Carbonyls on SiO<sub>2</sub>

**Boris N. Kuznetsov<sup>a,c</sup>, Vladimir I. Kovalchuk<sup>b</sup>,  
Nadezhda M. Mikova<sup>c</sup>, Nikolai V. Chesnokov<sup>a,c,\*</sup>  
and Liliya V. Naimushina<sup>d</sup>**

<sup>a</sup> Siberian Federal University,

79 Svobodny, Krasnoyarsk, 660041 Russia

<sup>b</sup> Pittsburg University, PA 15261 USA

<sup>c</sup> Institute of Chemistry and Chemical Technology SB RAS,  
Akademgorodok, Krasnoyarsk, 660036 Russia

<sup>d</sup> Krasnoyarsk State Institute of Economics and Trade,  
2 L. Prushinskaya st., Krasnoyarsk, 660075 Russia<sup>1</sup>

Received 4.08.2008, received in revised form 22.09.2008, accepted 29.09.2008

*There have been studied the catalytic properties in the reaction of CO hydrogenation of nano-catalysts produced by supporting on silica the iron carbonyl compounds containing various numbers of metal atoms. It was determined that the catalytic activity of the supported carbonyls increases with the rise of the number of the metal atoms in their composition. Some of them have a very high selectivity in respect to the C<sub>2</sub>-C<sub>3</sub> olefins.*

*Keywords: nano-catalysts, preparation, iron carbonyls, silica, CO hydrogenation, products, olefins.*

### Introduction

For the past years, again there increases the interest in the catalytic synthesis of hydrocarbons from the synthesis gas (CO and H<sub>2</sub> mixture) produced from the carbon containing raw materials [1-6]. The most important task of the conducted research is creating selective catalysts of transforming the synthesis gas into the basic chemical products.

A high activity and a comparatively low cost of the supported iron catalysts is the reason why they are used in CO hydrogenation reaction [7-11]. There is the information that the supported iron

catalysts with nanosized metal particles possess a higher activity and selectivity in respect to olefins as compared to the massive catalysts [12]. The traditional methods of iron catalyst preparation are based on impregnating the oxide carrier with salts and their subsequent reduction to metal. Since the iron cations supported on the surface of the oxide carriers, are difficult to be reduced to a metal [13], it is necessary to use the high treatment temperatures, which does not allow to reach a high dispersion of the supported metal.

To make selective catalysts for hydrocarbons synthesis from the mixture of

\* Corresponding author E-mail address: [bnk@icct.ru](mailto:bnk@icct.ru)

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CO and H<sub>2</sub>, it is promising to use nanosized catalysts prepared by supporting metal carbonyls on the oxide carriers. The specifics of the composition of surface-active centers in these catalysts, may give them new catalytic properties in comparison with the traditional heterogeneous catalysts [14-16].

The supported catalysts prepared with using iron carbonyls, were studied in many papers [17-20]. Earlier the authors studied the mechanism of the thermochemical transformations of the supported on the silica iron carbonyls which contained from 1 to 6 metal atoms [21]. It was shown that during the process of supporting the carbonyls on the SiO<sub>2</sub> surface at room temperature, there takes place only their physical adsorption and the supported clusters do not undergo any chemical changes. There were determined the supported iron carbonyls thermal stability thresholds. It was established that for the supported iron carbonyls of Fe<sub>1</sub>-Fe<sub>3</sub>, practically the complete loss of the carbonyl ligands takes place at the temperatures of ≤425 K. The supported clusters with a higher number of metal atoms preserve in the indicated temperature range about two thirds of the carbonyl ligands coordinated with the Fe atoms. Their complete decarbonylation takes place after the heat treatment at 523 K. On the basis of the established regularities of the thermochemical transformations of the iron carbonyls on silica surface, there was carried out the selection of the conditions for their heat decomposition. They provide the formation of the metal particles with the size of 0.5 – 1.0 nm, which are distributed along the support surface rather uniformly. Such systems can be used as nanosized iron catalysts in different reactions.

In the present paper there were compared the catalytic properties in the reaction of the CO hydrogenation of the nano-catalysts prepared by supporting on the silica surface the iron carbonyls with different numbers of iron atoms.

## Experimental

The catalysts were prepared by supporting on the silica the carbonyl iron compounds [TEA][HFe(CO)<sub>4</sub>], Fe<sub>2</sub>(CO)<sub>9</sub>, [TEA]<sub>2</sub>[Fe<sub>2</sub>(CO)<sub>8</sub>], Fe<sub>3</sub>(CO)<sub>12</sub>, [TEA][HFe<sub>3</sub>(CO)<sub>11</sub>], [TEA]<sub>2</sub>[Fe<sub>4</sub>(CO)<sub>13</sub>], Fe<sub>5</sub>C(CO)<sub>15</sub>, [TEA]<sub>2</sub>[Fe<sub>5</sub>C(CO)<sub>14</sub>], [TEA]<sub>2</sub>[Fe<sub>6</sub>C(CO)<sub>16</sub>] (TEA – (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>). The characteristics of the used compounds and the ways of the catalysts preparation are described in [21].

The kinetics of the CO hydrogenation reaction was studied in the flow-type catalytic installation under the pressure of the reaction mixture of 0.1 MPa, the ratio of H<sub>2</sub> : CO=1, the volume speed of 200-1000 h<sup>-1</sup> in the temperature range of 298-623 K. To carry out the research, there was used a glass quartz reactor with a catalyst fixed bed. The degree of the CO conversion did not exceed 0.5%. This allows to calculate the reaction rate without considering the concentration gradient on the catalyst bed. The catalyst sample (0.2-1.0g) was charged in the counterflow of the inert gas. On reaching the given temperature, there was measured the dynamics of changing the catalytic activity for 5-10 hours. Then a higher temperature was set. The applied anion iron clusters having tetraethylammonium as a counterion, which were not subjected to the preliminary reduction, were blown off with helium with each rise in temperature. It was carried out till the complete disappearance of the cation decomposition products. Then there was measured their catalytic activity. The measuring time of 5-10 hours was sufficient to reach the catalyst fixed activity. The analysis of the initial mixture and the reaction products, was carried out chromatographically (katharometer and FID) using the columns filled with the zeolite of NaX and Al<sub>2</sub>O<sub>3</sub>.

## Results and Discussion

Table 1 and Fig. 1-2 demonstrate the influence of the temperature on the catalytic properties in the CO hydrogenation reaction of the supported

Table 1. The catalytic properties in the reaction of CO hydrogenation iron carbonyls supported on SiO<sub>2</sub>

Supported carbonyl	Temp, K	Total activity*	Selectivity,wt %					
			CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub> *	C <sub>4</sub> <sup>+</sup>
1	2	3	4	5	6	7	8	9
[TEA][HFe(CO) <sub>4</sub> ]	373	1.69·10 <sup>-6</sup>	>99	–	–	–	–	–
	423	1.57·10 <sup>-5</sup>	12	88	–	–	–	–
	473	2.21·10 <sup>-5</sup>	5	95	–	–	–	–
	523	1.22·10 <sup>-4</sup>	6	78	12	4	–	–
	573	5.07·10 <sup>-4</sup>	2	62	30	<1	<1	5
	623	7.30·10 <sup>-4</sup>	9	41	18	13	1	18
Fe <sub>2</sub> (CO) <sub>9</sub>	523	1.79·10 <sup>-6</sup>	>99	–	–	–	–	–
	573	2.61·10 <sup>-5</sup>	36	35	–	29	–	–
	623	1.48·10 <sup>-4</sup>	33	31	7	–	23	6
[TEA] <sub>2</sub> [Fe <sub>2</sub> (CO) <sub>8</sub> ]	423	2.78·10 <sup>-6</sup>	–	3	97	–	–	–
	473	1.30·10 <sup>-5</sup>	>99	–	–	–	–	–
	523	6.0·10 <sup>-5</sup>	17	83	–	–	–	–
	573	2.01·10 <sup>-4</sup>	46	24	7	21	2	–
	623	1.81·10 <sup>-3</sup>	33	38	12	16	1	–
Fe <sub>3</sub> (CO) <sub>12</sub> /SiO <sub>2</sub>	373	1.04·10 <sup>-5</sup>	traces	–	–	99.5	–	–
	423	1.06·10 <sup>-5</sup>	traces	–	–	99.5	–	–
	473	4.59·10 <sup>-5</sup>	9	32	–	59	–	–
	523	4.56·10 <sup>-4</sup>	15	62	–	23	–	–
	573	4.86·10 <sup>-3</sup>	40	32	5	19	1	3
	623	8.61·10 <sup>-3</sup>	40	32	4	18	1	5
[TEA][HFe <sub>3</sub> (CO) <sub>11</sub> ]	373	2.32·10 <sup>-6</sup>	76	24	–	–	–	–
	423	1.19·10 <sup>-6</sup>	>99	–	–	–	–	–
	473	7.5·10 <sup>-6</sup>	64	29	–	7	–	–
	523	9.6·10 <sup>-6</sup>	12	17	–	71	–	–
	573	1.38·10 <sup>-4</sup>	42	14	–	43	<1	<1
	623	5.4·10 <sup>-4</sup>	34	17	–	46	<1	2.5
[TEA] <sub>2</sub> [Fe <sub>4</sub> (CO) <sub>13</sub> ]	373	2.18·10 <sup>-5</sup>	28	72	–	–	–	–
	423	2.66·10 <sup>-5</sup>	1	99	–	–	–	–
	473	5.24·10 <sup>-4</sup>	–	99	1	–	–	–
	523	9.32·10 <sup>-4</sup>	–	73	27	–	–	–
	573	1.52·10 <sup>-3</sup>	20	44	22	12	–	–
	623	6.04·10 <sup>-3</sup>	15	45	22	12	2	4
Fe <sub>5</sub> C(CO) <sub>15</sub>	373	5.55·10 <sup>-5</sup>	2	–	–	98	–	–
	423	2.4·10 <sup>-5</sup>	traces	2	–	98	–	–
	473	6.21·10 <sup>-5</sup>	–	35	–	65	–	–
	523	2.6·10 <sup>-4</sup>	45	30	–	25	–	–
	573	4.99·10 <sup>-4</sup>	29	28	8	29	–	6
	623	7.05·10 <sup>-3</sup>	13	11	7	16	3	50

Table 1

1	2	3	4	5	6	7	8	9
[TEA] <sub>2</sub> [Fe <sub>5</sub> C(CO) <sub>14</sub> ]	373	1.27·10 <sup>-6</sup>	–	99	–	1	–	–
	423	5.15·10 <sup>-4</sup>	1	99	–	–	–	–
	473	1.02·10 <sup>-3</sup>	23	58	12	4	3	–
	523	1.33·10 <sup>-3</sup>	38	26	5	22	4	5
	573	1.46·10 <sup>-3</sup>	33	36	6	22	1	2
	623	7.65·10 <sup>-3</sup>	64	22	5	8	–	<1
[TEA] <sub>2</sub> [Fe <sub>6</sub> C(CO) <sub>16</sub> ]	373	1.67·10 <sup>-4</sup>	31	49	20	–	–	–
	423	2.93·10 <sup>-4</sup>	–	100	–	–	–	–
	473	6.36·10 <sup>-4</sup>	11	80	9	–	–	–
	523	4.30·10 <sup>-3</sup>	43	32	8	14	2	1
	573	1.10·10 <sup>-2</sup>	29	29	15	21	2	4
	623	8.94·10 <sup>-3</sup>	34	33	14	15	2	2

\*CO mole (cluster mole)<sup>-1</sup>· c<sup>-1</sup>

iron carbonyls. Practically all iron carbonyls start to show the catalytic activity already at a temperature of 373 K (with the exception of the inactive at moderate temperatures, Fe<sub>2</sub>(CO)<sub>9</sub>).

On the temperature dependences of the activity of catalysts [TEA][HFe(CO)<sub>4</sub>]/SiO<sub>2</sub>, [TEA]<sub>2</sub>[Fe<sub>2</sub>(CO)<sub>8</sub>]/SiO<sub>2</sub>, [TEA]<sub>2</sub>[Fe<sub>4</sub>(CO)<sub>13</sub>]/SiO<sub>2</sub>, Fe<sub>5</sub>C(CO)<sub>15</sub>/SiO<sub>2</sub>, [TEA]<sub>2</sub>[Fe<sub>5</sub>C(CO)<sub>14</sub>]/SiO<sub>2</sub>, [TEA]<sub>2</sub>[Fe<sub>6</sub>C(CO)<sub>16</sub>]/SiO<sub>2</sub>, one can observe an approximately linear increase of the catalytic activity with the temperature rise from 323 to 623 K (Fig. 1). The apparent activation energy of the reaction of CO hydrogenation varies for the supported carbonyl catalysts in the range of 19-31 kJ/mole. Besides the tendency being towards decreasing the reaction activation energy when passing from the supported carbonyls with the low number of iron atoms (Fe<sub>1</sub>-Fe<sub>4</sub>) to the higher ones (Fe<sub>5</sub>-Fe<sub>6</sub>) is observed. In case of the supported trinuclear iron clusters Fe<sub>3</sub>(CO)<sub>12</sub> and [TEA][HFe<sub>3</sub>(CO)<sub>11</sub>], the dependence of the logarithm of the CO hydrogenation reaction rate on the reverse temperature, is not of a linear character (Fig. 1, curves 6, 7). One can observe the increase of the apparent activation energy with the rise of the reaction temperature from 323 K to 623 K.

Comparing the data on the catalytic activity with the earlier obtained results on studying the thermal stability of the iron carbonyls supported on the silica [21], allows to make a supposition that the observed variations of the catalytic properties with the rise of the reaction temperature, are connected with changing the nature of the surface catalytically active centers in the studied nano-catalysts. With the rise in temperature, the iron carbonyls supported on the silica surface, lose part of the CO groups. At higher temperatures, the formation of iron nano-particles takes place.

It is known from the literature [22], that in the case of supported iron catalysts, prepared by impregnating SiO<sub>2</sub> with the water solution of Fe(NO<sub>3</sub>)<sub>3</sub>, the activation energy of the CO hydrogenation reaction depends on the duration of reducing the supported iron. For the catalyst reduced by hydrogen at 723 K for 1hr, activation energy makes up 37 kJ/mole and it increases to 118 kJ/mole with the rise of the duration of reducing the catalyst to 16 hours.

The increase of the specific catalytic activity of the supported iron carbonyls with the rise in the number of the metal atoms from 1 to 6 in its composition was found (Fig. 2). This effect develops especially considerably at moderate

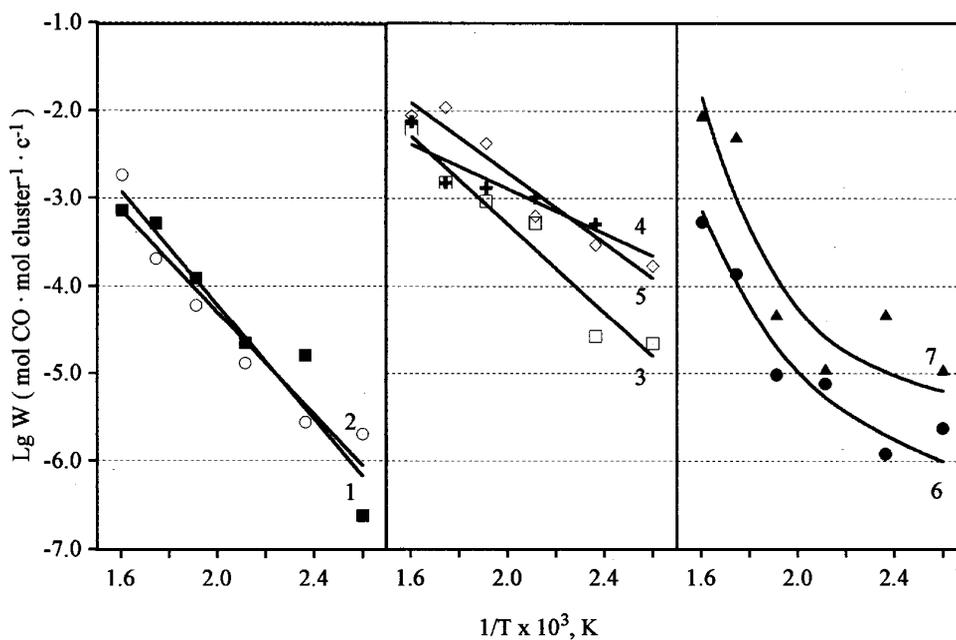


Fig. 1. The temperature dependences of the catalytic activity of the catalysts [TEA][HFe(CO)<sub>4</sub>]/SiO<sub>2</sub> (1); [TEA]<sub>2</sub>[Fe<sub>2</sub>(CO)<sub>8</sub>]/SiO<sub>2</sub> (2); [TEA]<sub>2</sub>[Fe<sub>4</sub>(CO)<sub>13</sub>]/SiO<sub>2</sub> (3); [TEA]<sub>2</sub>[Fe<sub>5</sub>C(CO)<sub>15</sub>]/SiO<sub>2</sub> (4); [TEA]<sub>2</sub>[Fe<sub>6</sub>C(CO)<sub>16</sub>]/SiO<sub>2</sub> (5); Fe<sub>3</sub>(CO)<sub>12</sub>/SiO<sub>2</sub> (6); [TEA][HFe<sub>3</sub>(CO)<sub>11</sub>]/SiO<sub>2</sub> (7) in the reaction of CO hydrogenation

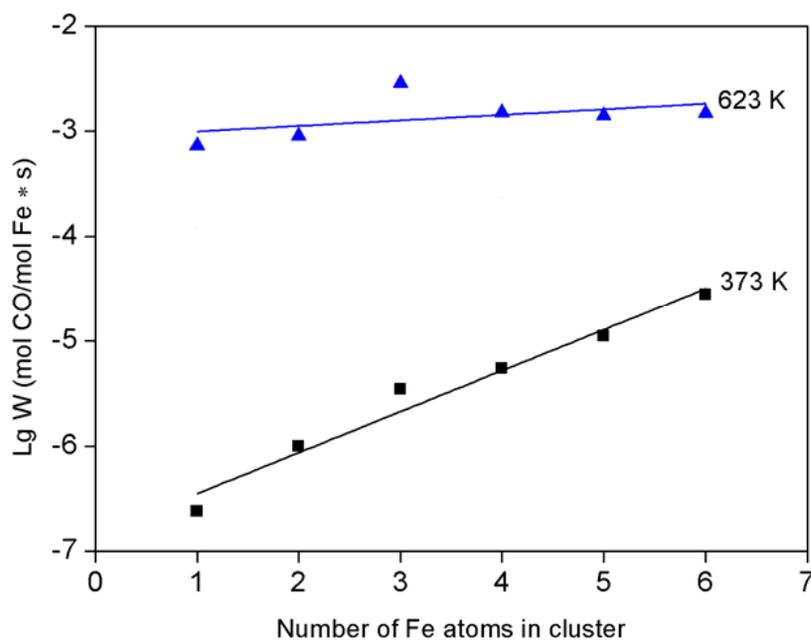


Fig. 2. The influence of the number of the metal atoms in the iron supported carbonyls on the rate of CO hydrogenation reaction

reaction temperatures, in particular at 373 K. As it was shown earlier [21], at this temperature, only the partial decarbonylation of the supported carbonyls may take place. This allows to suppose that the surface carbonyl or subcarbonyl iron compounds are catalytically active centers of the reactions of CO hydrogenation at moderate temperatures.

The distribution of the hydrocarbon products of CO hydrogenation on supported iron carbonyls differs greatly from the traditional Shultz-Flory distribution especially at the moderate reaction temperature (Table 1). The products composition changes when the reaction temperature varies. As a rule, the selectivity of forming individual hydrocarbons is the highest at the moderate temperatures of CO hydrogenation (373-423 K), and it decreases with the rise of the reaction temperature to 523-623 K (Table 1).

In case of the supported carbonyls with a low number of iron atoms the prevailing product of the CO hydrogenation at some local temperatures (373 K for  $[\text{TEA}][\text{HFe}(\text{CO})_4]/\text{SiO}_2$ , 473 K for  $[\text{TEA}]_2[\text{Fe}_2(\text{CO})_8]/\text{SiO}_2$  and 523 K for  $\text{Fe}_2(\text{CO})_9/\text{SiO}_2$ ) is methane. Catalyst  $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$  develops in the temperature range 373-423 K, a unique high selectivity as regards propylene (over 99%), which decreases at higher temperatures. The main product of the CO hydrogenation reaction on the supported tetranuclear cluster  $[\text{TEA}]_2[\text{Fe}_4(\text{CO})_{13}]$ , is ethylene. In the temperature range of 423-473 K the selectivity of this catalyst as regards ethylene, makes up 99 wt %.

On the  $\text{Fe}_5\text{C}(\text{CO})_{15}/\text{SiO}_2$  catalyst one can observe the highly selective formation of propylene (>99 wt %) at the temperatures of 373-423 K (Table 1). As distinguished from the supported neutral cluster of  $\text{Fe}_5\text{C}(\text{CO})_{15}$ , the anion cluster of  $[\text{TEA}]_2[\text{Fe}_5\text{C}(\text{CO})_{14}]$  catalyzes the ethylene formation in the temperature range of 373-473 K (Table 1). Only the ethylene is formed on the  $[\text{TEA}]_2[\text{Fe}_6\text{C}(\text{CO})_{16}]/\text{SiO}_2$  catalyst at temperature 423 K.

The increase of the reaction temperature, as well as the use of the reducing treatment of the catalyst with hydrogen or  $\text{CO}+\text{H}_2$  mixture at the temperatures of 423-573 K, leads to forming the nano-sized iron particles on the carrier surface [21]. The catalytic properties of these nanoparticles differ from the properties of the surface iron carbonyl or subcarbonyl compounds. In the narrow temperature ranges, some of them possess a unique high selectivity in  $\text{C}_2\text{-C}_3$  hydrocarbon synthesis.

As it follows from the data given in Table 2, concerning the catalytic properties of the reduced catalysts in the CO hydrogenation reaction, one can observe a sharp increase in the methane yield. The distribution of the reaction products in a number of cases, corresponds to the Shultz-Flory equation [23], that is it is similar to the observed for traditional catalysts of the Fisher-Tropsch process. The only exception is the  $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$  catalyst. Its treatment with hydrogen does not lead to the substantial changes in the catalytic properties. Like in the case of the non-treated catalyst it ensures the selective propylene formation at 473 K. Also one can observe the sufficiently high propylene contents in the reaction products (67-77 wt % at 423-573 K) for the reduced  $[\text{TEA}][\text{HFe}(\text{CO})_4]/\text{SiO}_2$  catalyst.

So, the studies of the catalytic properties of the  $\text{SiO}_2$  supported carbonyls with different number of iron atoms show that in contrast to traditional Fe-catalysts they display a unique selectivity in respect to the individual hydrocarbons, as a rule, in the reaction temperature range of 373-473 K.

The literature data show that during heating the iron carbonyls supported on  $\text{SiO}_2$ , there takes place the oxidation of a definite portion of the metal atoms with the carrier hydroxyl groups already at room temperatures [24]. It is testified for example, by the emission of the molecular hydrogen during thermal decomposition of the carbonyl  $\text{Fe}_3(\text{CO})_{12}$  supported on the silica

Table 2. The catalytic properties in the CO hydrogenation reaction of the reduced catalysts prepared by supporting iron carbonyls on SiO<sub>2</sub>

Supported carbonyl	Preliminary reducing treatment	Temp., K	Total activity*	Selectivity, wt %					
				CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> <sup>+</sup>
[TEA][HFe(CO) <sub>4</sub> ]	523 K, CO+H <sub>2</sub> , 1.5 h	373	7.43·10 <sup>-7</sup>	99	–	–	1	–	–
		423	2.75·10 <sup>-6</sup>	33	–	–	67	–	–
		473	4.01·10 <sup>-5</sup>	43	1	–	56	–	–
		523	9.24·10 <sup>-5</sup>	7	16	–	77	–	–
		573	4.24·10 <sup>-4</sup>	1	24	–	68	–	7
[TEA][HFe <sub>3</sub> (CO) <sub>11</sub> ]	573 K, H <sub>2</sub> , 1.5 h	423	6.0·10 <sup>-8</sup>	100	–	–	–	–	–
		473	3.9·10 <sup>-6</sup>	76	–	–	24	–	–
		523	3.3·10 <sup>-5</sup>	75	3	–	22	–	–
		573	2.37·10 <sup>-4</sup>	54	6	–	38	<1	1
		623	4.2·10 <sup>-4</sup>	53	4	–	33	<1	10
Fe <sub>3</sub> (CO) <sub>12</sub>	423 K, H <sub>2</sub> , 1.5 h	373	1.17·10 <sup>-5</sup>	71	24	5	<1	–	–
		423	6.36·10 <sup>-5</sup>	9	–	5	55	–	31
		473	6.69·10 <sup>-5</sup>	–	–	–	100	–	–
		523	3.72·10 <sup>-3</sup>	28	22	7	26	2	15
		573	4.02·10 <sup>-3</sup>	29	24	3	22	<1	21
		623	8.49·10 <sup>-3</sup>	34	28	3	17	<1	16
[TEA] <sub>2</sub> [Fe <sub>4</sub> (CO) <sub>13</sub> ]	423 K, H <sub>2</sub> , 1.5 h	423	6.8·10 <sup>-5</sup>	67	33	–	–	–	–
		473	4.44·10 <sup>-4</sup>	57	25	7	6	4	1
		523	4.68·10 <sup>-4</sup>	57	34	3.5	5	–	–
		573	1.02·10 <sup>-3</sup>	34	39	10	15	2	<1
		623	1.34·10 <sup>-3</sup>	29	36	17	13	2	3
[TEA][Fe <sub>5</sub> C(CO) <sub>14</sub> ]	423 K, H <sub>2</sub> , 1.5 h	473	2.71·10 <sup>-3</sup>	40	16	4	21	2	17
		523	1.17·10 <sup>-2</sup>	26	17	7	19	1	30
		573	1.41·10 <sup>-2</sup>	32	19	8	20	1	20
		623	1.42·10 <sup>-2</sup>	47	26	6	13	1	7

\*CO mole (cluster mole)<sup>-1</sup> c<sup>-1</sup>

surface [25]. The formation of iron ions during the thermal decomposition of the supported Fe<sub>3</sub>(CO)<sub>12</sub> cluster is also confirmed by the data of the Mössbauer spectroscopy [26]. The concentration of the surface OH–groups of the silica, will determine the portion of the iron ions fixed with the carrier surface by chemical bonds. These fixed ions are very difficult to be reduced by hydrogen. It is known [24, 27], that even in the bimetallic catalysts Fe–Rh, Fe–Pt, treated at the high temperature with hydrogen, a considerable part of the iron is in the oxidized state, in spite of

the fact that Pt and Rh can promote reducing the iron at the expense of the dissociative adsorption of H<sub>2</sub> and the subsequent spillover of the hydrogen atoms to the iron ions.

Since the products of the CO hydrogenation reaction on the supported iron carbonyls are chiefly the hydrocarbons C<sub>1</sub>–C<sub>3</sub>, it is possible to conclude that the reaction does not take place in the polymerization way, which is considered in [23]. Within the framework of this mechanism, there takes place the polymerization of the carbenic intermediates on the metallic surface.

However, on the nano-particles, consisting of the low number of the metal atoms, the realization of the indicated mechanism can be made difficult.

The high selectivity of the  $[\text{TEA}]_2[\text{Fe}_2(\text{CO})_8]/\text{SiO}_2$  catalyst on the  $\text{C}_2$ -products, allows to suppose that in this case the CO hydrogenation reaction may run on the active centres consisting of the two metal atoms situated close to each other. The high selectivity in respect to ethylene, of the catalyst  $[\text{HFe}(\text{CO})_4]/\text{SiO}_2$  does not contradict to the aforesaid, because it is known [19], that the mononuclear carbonyls on the surface of the oxide carriers even at moderate temperatures, are able to be transformed into the polynuclear carbonyl clusters. It is not excluded that the hydrocarbons  $\text{C}_2$  and  $\text{C}_3$  may be formed on the same active centres, since it is shown for the catalyst  $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$  that ethylene is the precursor of the

propylene [25]. The change of the selectivity at the higher reaction temperatures (523-623 K) for all catalysts based on supported iron carbonyls, is likely to be connected with destroying the cluster metallic skeleton as a result of the temperature stimulated dissociation/association processes of the surface carbonyl particles.

The observed increase of the specific activity of the  $\text{SiO}_2$  supported iron carbonyls with the growth of the number of the metal atoms in their composition (Fig. 2), may be explained either by the influence of the so called structural factor (for example, increasing the number of the required active centres), or by the effect of weakening the electron-acceptor action of the oxide carrier on the supported iron carbonyls with raising the size of the supported iron carbonyls.

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