

Hydrocarbon synthesis from CO and H₂ on (Fe + Pt)/SiO₂ catalysts

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Received 14 February 1995; accepted 10 April 1995

Abstract

Catalytic and adsorption properties of (Pt + Fe)/SiO₂ catalysts prepared by coimpregnation of SiO₂ with FeCl₃ and H₂PtCl₆ aqueous solutions have been studied. According to the X-ray diffraction data, Fe–Pt particles of the size 5–36 nm and bcc or fcc crystal lattice are formed during the reduction of catalysts by flowing hydrogen. Bimetallic catalysts exhibit higher specific activity for the reaction of CO hydrogenation than do monometallic samples. The enhanced activity of Fe–Pt particles manifests itself mainly through increased formation of C₄₊ olefins. These observations suggest that the effect of Pt addition on the catalytic properties of silica-supported iron in CO hydrogenation is similar to the effect of potassium addition.

Keywords: Carbon monoxide; Hydrogenation; Iron; Platinum; Silica

1. Introduction

The unbroken interest in the study of iron-containing catalysts is certainly due to their application in the industrial synthesis of ammonia and the high activity of Fe in the synthesis of hydrocarbons from CO and H₂. The reduction of salt-derived supported catalysts to form iron in metallic state is known to require elevated temperature resulting in lower metal dispersion. Addition of a noble metal to supported Fe catalyst allows us to lower the temperature of reduction of iron cations, and as a consequence, to increase the metal dispersion. Moreover, the presence of iron can improve activity and selectivity of supported Pt, Ir, Pd catalysts towards methanol synthesis [1–

5] and Rh ones towards ethanol formation [6–8] during CO hydrogenation at elevated pressure. The above mentioned reasons have led to the intensive study of the state of components of iron–Group VIII noble metal supported catalysts [9–14].

However, catalytic properties of (Fe + Pt)/support systems for the CO + H₂ reaction have been the subject of a few papers dedicated to the study of the highly dispersed catalysts only [8,15]. Nevertheless, there is abundant evidence that the catalytic behavior of supported metallic catalysts in CO hydrogenation can depend on the size of metal particles [16–24]. Therefore, the objective of the research reported in this paper was to study the catalytic and adsorption properties of (Fe + Pt)/SiO₂ catalysts with low dispersion of supported metals.

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2. Experimental

Silica with specific surface area of $200 \text{ m}^2 \text{ g}^{-1}$ and granule size from 0.5 to 0.25 mm was used as support. The loadings of sodium and iron in the initial support were less than 0.01 wt.%. Prior to preparation of catalysts, SiO_2 was calcined in air at 870 K for 6 h to eliminate organic contaminants. To avoid overheating of support during the first moment of its contact with the impregnation solution, the silica was equilibrated with water at 298 K for 24 h followed by exposition in dynamic vacuum (10^{-4} Torr) overnight.

The catalysts were prepared by pore volume impregnation. The appropriate amount of SiO_2 was instantly added to a freshly prepared aqueous solution containing the necessary amounts of FeCl_3 and H_2PtCl_6 . Then the samples were dried at 380 K in the air for 5 h. Each of the concentrations of FeCl_3 and H_2PtCl_6 in the impregnation solutions was ≤ 0.25 M. The pH of 1 for the solution employed for the preparation of Fe/SiO_2 was provided by addition of hydrochloric acid. In other cases a distinctive value of pH was not maintained and it remained ≈ 1 due to the presence of H_2PtCl_6 . The metal loadings of the reduced catalysts were determined by X-ray fluorescence spectroscopy. The composition of catalysts is listed in Table 1.

Catalytic experiments were performed with a conventional fixed-bed differential reactor. Amount of catalyst charged in the reactor was 0.4–0.6 g. Prior to catalytic measurements, the sample was reduced for 3 h in flowing hydrogen at 820 K. The temperature was then lowered to 623 K and synthesis gas was introduced into the reactor. The reaction was allowed to proceed until steady-state conditions were reached (generally 5 h). During this initial period the activity of all catalysts decreased by 20 to 30%, and no dramatic changes in selectivity were observed. During catalytic measurements the total pressure was maintained at 0.1 MPa and an H_2/CO ratio of 1/1 was used. The space velocity was adjusted to maintain CO conversion below 1%. Product composition was determined by analysis with a gas chromatograph.

Temperature programmed desorption (TPD) of CO and H_2 was carried out to a stream of carrier gas followed by gas chromatography analysis of desorption products. The rate of sample heating was 14 K/min. Prior to the experiment, all catalysts were reduced in H_2 flow at 820 K for 3 h and cooled in carrier gas stream to the temperature of gas adsorption. CO adsorption was carried out at 313 K from a stream of CO + He gas mixture containing 3% CO. Hydrogen adsorption was conducted at 623 K followed by cooling to 313 K in

Table 1
Dispersion and phase composition of silica supported Fe, FePt and Pt catalysts after reduction at 820 K by flowing hydrogen

Catalyst ^a	Fe/Pt ^b	Particle size ^c , nm		Phase ^d	Relative content of the phase, %	Distortion of the interlayer distance, Δd_{200} (nm)
		X-ray ^d	ads. ^d			
2.0Fe	∞	30.0	36.0	α -Fe	100	± 0
3.5Fe + 0.5Pt	24.6	36.0	45.5	α -FePt	100	+0.00055
3.0Fe + 1.0Pt	10.4	23.0	25.0	α -FePt	100	+0.00063
2.0Fe + 2.0Pt	3.5	7.0	11.0	α -FePt	≈ 10	+0.00068
		7.5		γ -PtFe	≈ 90	-0.0035
1.0Fe + 3.0Pt	1.1	5.0	9.0	α -FePt	≈ 10	+0.00070
		7.5		γ -PtFe	≈ 90	-0.0054
2.0Pt	0	<3.0	3.0	Pt	100	± 0

^a Support- SiO_2 ; specific area, $200 \text{ m}^2 \text{ g}^{-1}$; metal loading is given in wt.%.

^b Atomic ratio.

^c Particle sizes are determined from broadening of X-ray lines and from CO TPD data (CO adsorption stoichiometry was assumed to be equal to 1).

^d α -FePt is FePt solid solution of α -Fe like structure, γ -PtFe is FePt solid solution of Pt like structure.

a hydrogen stream. Helium was used as carrier gas for CO, while argon was employed for hydrogen.

IR spectra of adsorbed CO were recorded with Carl-Zeiss-Jena Specord-75IR spectrometer equipped with vacuum cell, which allowed us to carry out high temperature treatments of samples inside and gas adsorption procedures without contact with atmospheric oxygen. For the IR study the catalyst samples were pressed into self-supporting wafers, with surface density 8–10 mg/cm².

X-ray powder patterns were recorded using DRON-4 diffractometer equipped with a receiving graphite monochromator to obtain monochromatic CuK α radiation and a scintillation detector.

The average size of particles in the reduced catalysts was determined from the broadening of [110], [111], [200], [220] and [211] X-ray lines, as described elsewhere [25] and from the amount of CO desorbed, determined in CO TPD experiments, taking CO adsorption stoichiometry, CO/Pt_s and CO/Fe_s, to be equal to 1. The coincidence of bulk and surface composition of bimetallic particles was supposed. In the latter case particle sizes were calculated assuming them to have spherical shape and average site densities for Pt and Fe of 8.4 and 9.4 Å²/atom, respectively [26].

3. Results and discussion

3.1. Preparation of catalysts

The pH value of an impregnation solution plays an important part during preparation of supported iron catalysts using Fe(III) salts as precursor. At the pH \cong 0 all Fe ions act as aquacomplexes poorly interacting with silica surface and capable of surface migration in the process of catalyst reduction. The dispersion of reduced catalysts is high enough in this case [27]. As the pH of the impregnation solution is increased, hydrolysis of Fe(III) ions occurs first accompanied by the formation of mononuclear hydroxycomplexes and then polynuclear

ones when the pH reaches the value of 2–3 [28]. At higher pH values even gels could be formed [28,29]. When deposited on the support surface, gels and polynuclear hydroxycomplexes yield low-dispersed catalyst upon reduction. Coimpregnation of silica with aqueous solution of FeCl₃ and H₂PtCl₆ of the pH \cong 1 allowed us to obtain (Fe + Pt)/SiO₂ catalysts containing bimetallic FePt particles of size 5–36 nm after reduction by flowing hydrogen at 820 K (see Table 1).

3.2. X-ray diffraction

The reduction of (Fe + Pt)/SiO₂ catalysts led to the formation of FePt solid solutions on the silica surface (see Table 1). The samples with bimetallic particles containing up to 9 at.% platinum yielded only solid solutions with α -Fe lattice. This resulted in the increase of unit cell parameter of Fe crystal lattice ($\Delta\alpha = 2\Delta d_{200}$) by 0.0011–0.0013 nm. Solid solutions both with α -Fe lattice and that with Pt were formed at higher Pt mole fraction (22–47%). However, X-ray line intensities corresponding to the solid solution of α -Fe structure was much lower compared to those of solid solution of Pt lattice (see Table 1). With solid solutions of Pt lattice being formed, their unit cell parameter was decreased by 0.007–0.010 nm. No metal phase of iron has been found over the range of Fe/Pt ratios studied. However, it is known [15] that paramagnetic particles of iron have been detected by Mössbauer spectroscopy in the reduced high-dispersed (Fe + Pt)/ γ -Al₂O₃ catalyst with the atomic ratio of Fe/Pt = 10.

No data on surface composition of bimetallic particles have been obtained in the present research. However, the results reported in [26,34,35] suggest that it should be close to bulk composition, at least, in a reduction medium.

It is known [12,13,36] that more than a half of the total amount of iron of the high-dispersed (Pt + Fe)/SiO₂ catalysts is available in the form of Fe³⁺ ions even upon the reduction of samples at 770 K. Under these conditions Pt(IV) species are totally reduced to Pt metal. The comparison of composition of FePt bulk alloys and their unit cell

parameter [37–39] has shown that in the studied low-dispersed (Pt + Fe)/SiO₂ catalysts alloy particles should contain more than 90% of iron initially loaded to a catalyst. Thus, the extent of Fe reduction in these (Fe + Pt)/SiO₂ catalysts is higher than in the supported FePt catalysts of high dispersion. Irreducible iron ions should be bound with the surface of support through Si–O–Fe bonds. Surface iron ions could be either blocked by FePt particles since low-valent surface ions of metals could serve as centers of stabilization of supported metal particles [40], or belong to the alloy–support interface, as suggested elsewhere [12].

In Table 1 are listed X-ray diffraction and adsorption data which suggest that the sizes of metal particles determined from broadening of X-ray lines and from CO desorption data are fairly close. The size of supported metal particles is continuously increased following the increase of Fe content in Fe–Pt samples. For the catalyst with the highest Fe/Pt ratio (3.5% Fe + 0.5% Pt) the size of particles approaches that of the reduced monometallic 2.0% Fe/SiO₂ sample. The estimation of particle sizes of the studied catalysts along other faces of crystal lattice gave values equal to those of face (200). This result allows us to assume the symmetric shape of surface bimetallic particles.

3.3. IR spectroscopic and TPD data

Only one absorption band at 2085 cm⁻¹ was observed in IR spectrum of CO adsorbed on reduced Pt/SiO₂ catalyst with the metal particles size about 3.0 nm. There was a shift of the CO absorption band by 10–25 cm⁻¹ to lower wavenumbers as Pt surface coverage by adsorbed CO was reduced. This shift is usually interpreted either in the terms of dipolar interaction between adsorbed CO molecules [30] or in the terms of energy inhomogeneity of surface metal atoms [31]. Strong dependence of the heats of CO adsorption on supported Pt catalysts on the degree of CO surface coverage reported in [31] has led us to prefer the last reason for the above mentioned shift.

CO adsorption on reduced Fe–Pt catalysts was also accompanied by the appearance in the IR spectrum of one absorption band only at 2080 cm⁻¹ which was reasonably assigned to the linear mode of CO adsorbed on Pt atoms. IR bands of CO adsorbed on Fe atoms were ill-defined, probably due to low uptake.

The CO desorption spectra for monometallic 2.0% Pt/SiO₂, 2.0% Fe/SiO₂ and bimetallic FePt samples are shown in Fig. 1A. The CO TPD spectrum from 2.0% Fe/SiO₂ catalyst consists of one peak located at 370 K while the spectrum for 2.0% Pt/SiO₂ catalyst has two peaks situated at 390 and 670 K, the high-temperature peak being much more intense. In addition, the shapes of CO TPD spectra for 2.0% Pt/SiO₂ sample and 0.38% Pt/ γ -Al₂O₃ catalysts studied in [31] are very close. Since energy inhomogeneity of surface Pt atoms in Pt/ γ -Al₂O₃ has been established elsewhere [31], the same energy inhomogeneity of Pt on silica could be assumed. Taking into account this fact and the IR spectroscopy data, the presence of two peaks in the CO TPD spectrum might be referred to CO desorption from centers with essentially different heats of CO adsorption rather than CO adsorption in two modes, e.g. in linear and bridging ones. The TPD spectra for CO desorption from bimetallic (Fe + Pt)/SiO₂ catalysts contain two peaks too. The major peak occurs at 380 K for all the catalysts. The peak of smaller magnitude is located between 600 K and 670 K depending on the catalyst composition. The smaller the fraction of platinum in the bimetallic catalyst, the smaller is the area of the high-temperature peak (Fig. 1A).

Following [15], we have chosen CO adsorption to represent the fraction of surface metal atoms in the catalysts since CO is more strongly adsorbed than H₂ and covers most of the metal surface [32,33]. Correct choice of the stoichiometry of CO adsorption on Pt and Fe is a rather complicated problem, especially for bimetallic particles. But the close agreement in particle sizes determined from X-ray and adsorption data (see Table 1) justifies the choice of stoichiometric ratios, CO/Pt_s and CO/Fe_s, to be equal to 1.

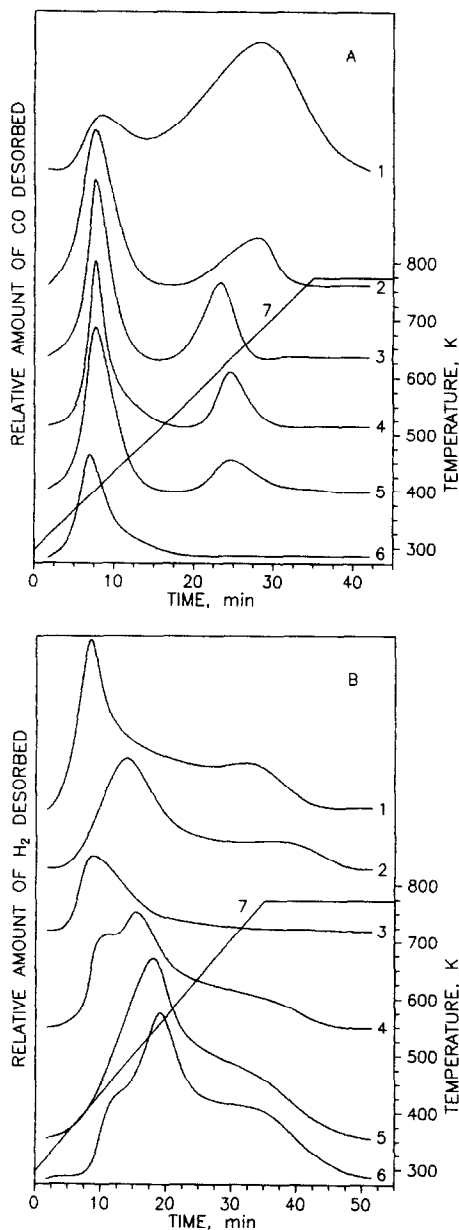


Fig. 1. CO TPD (A) and H₂ TPD (B) spectra of reduced 2.0% Pt/SiO₂ (1); (1.0% Fe + 3.0% Pt)/SiO₂ (2); (2.0% Fe + 2.0% Pt)/SiO₂ (3); (3.0% Fe + 1.0% Pt)/SiO₂ (4); (3.5% Fe + 0.5% Pt)/SiO₂ (5); 2.0% Fe/SiO₂ (6) catalysts. Curve 7 – catalyst temperature vs time.

The TPD spectra for H₂ desorption from 2.0% Pt/SiO₂, 2.0% Fe/SiO₂ and (Fe + Pt)/SiO₂ catalysts are shown in Fig. 1B. The spectrum of H₂ TPD from Pt/SiO₂ catalyst has two maxima. The first one, of higher intensity, is located at 390 K, the second, substantially smaller in magnitude, at

750 K. The major peak for H₂ desorption from 2.0% Fe/SiO₂ is located at 540 K. This peak is accompanied by low-temperature shoulder at 430 K and broad ill-resolved peak between 730 and 770 K. With an exception of (2.0% Fe + 2.0% Pt)/SiO₂ the shape of the spectra for H₂ desorption from (Fe + Pt)/SiO₂ catalysts suggests the presence of all adstates for H₂ adsorption which are present for monometallic Pt and Fe catalysts. The major peak for H₂ desorption from (Fe + Pt)/SiO₂ catalysts is shifted to lower temperatures with increase of Pt amount in (Fe + Pt)/SiO₂ catalysts (see Fig. 1B). This suggests that the energy of H₂ interaction with the metal surface decreases with Pt content increasing in the bimetallic particles. These observations might be due to an interaction between Fe and Pt atoms in reduced catalysts.

3.4. Activity measurements

Specific activity of bimetallic samples in the reaction of CO hydrogenation was significantly higher compared to that of monometallic Fe and Pt catalysts. The phenomenon of non-additive changes of catalytic activity of bimetallic Fe–Pt catalysts is illustrated in Fig. 2 and Table 2. The turnover frequency of supported Pt is 7 times higher than that of Fe. The addition of 4 at.% of platinum to the supported iron catalyst results in

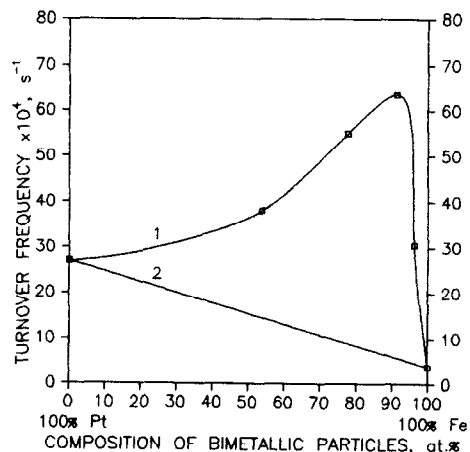


Fig. 2. Specific activity of FePt catalysts in CO hydrogenation vs. catalyst composition. 1 – experimental curve, 2 – dependence on additive.

Table 2

Catalytic properties of silica supported Fe, FePt and Pt catalysts in the CO + H₂ reaction at 623 K

Catalyst	TOF × 10 ⁴ s ⁻¹	Selectivity, wt. %							
		C ₁	C ₂	C ₃	C ₄₊	C ₂ ⁻	C ₃ ⁻	C ₄ ⁻	C ₅₊ ⁻
2.0Fe	4	17	9	1	9	18	20	7	19
3.5Fe + 0.5Pt	31	17	6	1	1	16	20	9	30
3.0Fe + 1.0Pt	64	14	5	2	3	13	22	11	30
2.0Fe + 2.0Pt	55	30	12	2	1	8	20	10	17
1.0Fe + 3.0Pt	38	21	15	5	2	7	21	12	17
2.0Pt	27	92	8	-	-	-	-	-	-

the sharp increase of specific catalytic activity. As the content of platinum is increased, the specific activity of the Fe–Pt catalysts passes via maximum. The highest activity is observed for Fe–Pt sample with Pt mole fraction about 10%. It should be noted that Pt catalyzes formation of paraffins with methane prevailing (92 wt.%) and Fe catalyst produces a high amount of olefins (up to 64 wt.%, Table 2).

It should be emphasized that the turnover frequency of all studied Fe–Pt catalysts exceeded that of 2.0% Fe/SiO₂ sample. This enhanced activity manifests itself mainly through increased formation of C₂–C₈ hydrocarbons rather than increased yield of methane to be expected in the case of additive catalytic action of Fe and Pt. The selectivity of bimetallic catalysts with mole fraction of Pt up to 9% towards olefins is higher than that of silica-supported Fe catalysts and makes up 75–76 wt.% (see Table 2). One could also observe higher amount of C₅₊ hydrocarbons produced over Fe–Pt catalysts compared to those of Fe. The distribution of all hydrocarbons followed Schultz–Flory kinetics for polymerization/polycondensation processes proceeding with constant rates of chain propagation and rupture, as shown in Fig. 3, where chain propagation probabilities (α) estimated from the slopes of the lines drawn through the data, are also presented. For all bimetallic catalysts α is higher than that for Fe/SiO₂ sample (Fig. 3). It is interesting to note that catalysts of different composition containing alloy particles of the same crystal structure have, in fact, the same α values.

Thus, the effect of Pt addition on the catalytic properties of silica-supported Fe in CO hydrogenation resembles the effect of potassium addition to iron catalysts [41]: promoted catalysts have enhanced specific activity and the product distribution is shifted to higher molecular weights. Electron state of iron in potassium promoted catalysts is considered to be altered by the transfer of electrons from the potassium oxide to the metal [42]. Hence, one could expect increasing of electron density on the Fe atoms to be accompanied by electron transfer to the adsorbed CO molecules. This should increase the Fe–C bond strength and decrease the C–O bond strength facilitating hydrogenation of the adsorbed CO species and increasing the reaction rate, considering the mechanism of CO hydrogenation proposed by Anderson

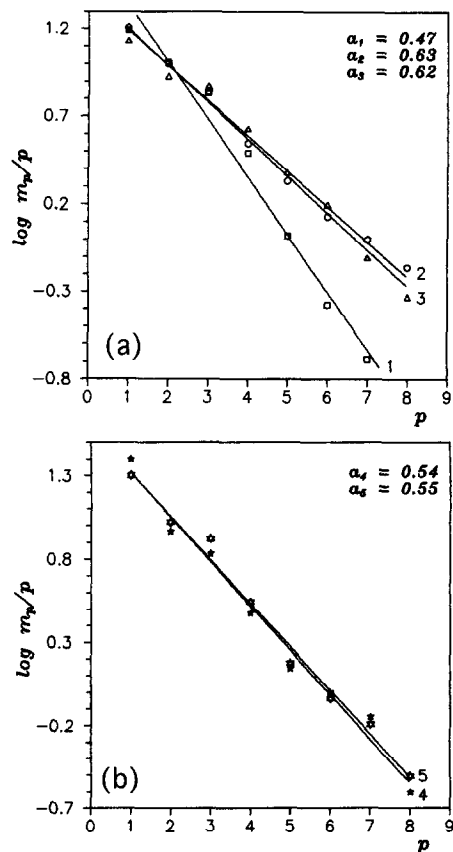


Fig. 3. Schultz–Flory plots for the 2.0% Fe/SiO₂ (1), (3.5% Fe + 0.5% Pt)/SiO₂ (2), (3.0% Fe + 1.0% Pt)/SiO₂ (3), (2.0% Fe + 2.0% Pt)/SiO₂ (4) and (1.0% Fe + 3.0% Pt)/SiO₂ (5) catalysts. m_p is the weight fraction of a hydrocarbon with p carbon atoms in the chain.

[41]. The greater amount of hydrocarbons of higher molecular weight should be due to stronger Fe–C bonds. The average residence time of surface intermediates (hydroxymethyl or carbene complexes) increases, thereby increasing the probability of chain growth.

Thus, we assume that the transfer of electrons from platinum to iron takes place in (Fe + Pt)/SiO₂ catalysts studied. However, the suppressed catalytic activity of iron in (Fe + Pt)/ γ -Al₂O₃ catalysts was found elsewhere [15]. On the basis of positive isomer shift (the measure of s-electron density on the atoms of absorber [43]) for iron in the Mössbauer spectra compared to that of bulk iron, this suppressed activity was attributed to the electron deficiency of Fe atoms because of their interaction with more electronegative platinum [15]. Negative isomer shift has been observed in [44] for ¹⁹⁵Pt nuclei of FePt bulk alloys in Mössbauer spectrum, which supports the conclusion of the previous paper. Meanwhile, iron in Fe–Pt alloys has a larger electron density than in bulk Fe due to the enhanced overlapping of the d-bands [45] resulting in a larger screening of the s-electrons. The last leads to the increased value of isomer shift for ⁵⁷Fe in Mössbauer spectra.

It has been found [46] that the absorption band corresponding to multicenter mode of CO adsorption on Pt is shifted to higher wavenumbers for (Fe + Pt)/SiO₂ catalysts in comparison with Pt/SiO₂ one. The shift value makes up almost 100 cm⁻¹ for PtFe catalyst containing 71 at.% Fe. It might be caused by decreased electron density on Pt atoms.

Nevertheless, the suppressed activity of iron in (Fe + Pt)/ γ -Al₂O₃ reported in [15] could be also caused by its interaction with surface Fe³⁺ ions, which are always present in the reduced (Fe + Pt)/support catalysts [12,13,15], resulting in electron deficiency of metallic iron. A contribution from the interaction between FePt particles and surface Fe³⁺ ions should become less with the growth of size of supported bimetallic particles (because of the decrease in the Fe³⁺/Fe⁰ ratio). Hence, for sufficiently large FePt particles the phenomenon of electron transfer from Pt to Fe

caused by overlapping of their d-bands could have a determining effect on their catalytic properties.

One more reason for higher catalytic activity of FePt catalysts compared to those of monometallic Fe and Pt samples could be connected with surface concentration of H atoms which may be essentially different in Fe/SiO₂ and (Fe + Pt)/SiO₂ catalysts. It is well known that platinum atoms promote fast and dissociative adsorption of H₂ [47]. Then hydrogen atoms could be spilled over from Pt to Fe, thereby increasing the rate of hydrogenation of intermediate species, assuming Fe atoms provide the hydrocarbon chain growth. The extremum on the dependence of specific catalytic activity of catalysts studied on Fe/Pt ratio may be due to a best compromise between the concentration of Fe and Pt on the surface of FePt particles for the catalyst with Fe/Pt ratio equal to 10.4 (Fig. 2). A decrease of surface concentration of platinum should lead to a shortage of active hydrogen atoms resulting in the lower specific activity. However, decreasing the surface concentration of iron reduces a number of sites for hydrocarbon chain growth with the same result. Nevertheless, the nature of synergistic behaviour of low-dispersed (Fe + Pt)/SiO₂ catalysts in CO + H₂ reaction needs further investigation.

4. Conclusion

Silica was coimpregnated by FeCl₃ and H₂PtCl₆ aqueous solutions to produce (Fe + Pt)/SiO₂ catalysts with Fe/Pt atomic ratio within 24.6–1.1. The reduction of the catalysts by flowing hydrogen at 820 K yielded alloy FePt particles having bcc or fcc crystal lattice and of the average size from 5 to 36 nm. The adsorption and catalytic properties of bimetallic samples were significantly different from those of Pt and Fe catalysts. With the increasing of Pt amount in (Fe + Pt)/SiO₂ catalysts the major peak for H₂ TPD from (Fe + Pt)/SiO₂ catalysts was shifted to low temperature side. The area of the high-temperature peak in the CO desorption spectra for bimetallic catalysts decreased with the decrease of the mole

fraction of Pt in the bimetallic particles. The (Fe + Pt)/SiO₂ catalysts have exhibited superior specific activity for CO hydrogenation, and the shift in selectivity to higher molecular weight hydrocarbons in comparison with monometallic Fe and Pt samples was observed. The enhanced activity of Fe–Pt particles manifests itself mainly through increased formation of C₄₊ olefins. These observations suggest that the effect of Pt addition on the catalytic properties of silica-supported Fe in CO hydrogenation is similar to the effect of potassium addition to iron.

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