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STABILIZATION OF VARIOUS CO + H_2 CATALYSTS, STUDIED BY IN SITU MÖSSBAUER SPECTROSCOPY

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The carbon formed during the reaction of CO + H_2 on iron catalysts plays an essential role in determining the catalytic activity, product selectivity and deactivation. Different forms of carbon can be distinguished in the reaction: (i) reactive or mobile carbon, already identified for iron and ruthenium catalysts; (ii) immobile carbon which is responsible for methane formation, and (iii) bulk, inactive carbide which makes the catalysts deactivated.

Various possibilities are available for stabilizing the catalytically active metallic component. One of the important factors is the particle size. The smaller the iron particle, the less amount of inactive carbon is formed. Other factors such as the type of support (e.g. zeolite) which maintains the iron in highly dispersed state, or the use of second metal or non-reducible promoter by which high dispersion of iron can be ensured and stabilized, favourably affect the activity and selectivity of the catalysts, as well. In the present paper examples are presented for the above mentioned cases.

1. Introduction

During CO hydrogenation over various catalysts the essential role of different carbide species has been intensively investigated. On this subject a review has been published for iron based catalysts [1]. Various carbide species have been identified in these studies. The ϵ and ϵ'-carbide (Fe_2C and $Fe_{2.2}C$, respectively) were suggested as surface carbide which are responsible for the reaction after CO dissociation [2]. A furter species was assigned as Häggs carbide which was assumed to decrease the activity of the catalyst [3]. The specific composition of the inactive carbide was established as $Fe_{20}C_9$ over unsupported iron [4]. Nevertheless, there was no argument about the existence of surface carbide which can be well distinguished from the inactive carbide [5].

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Several years ago we proposed a distinction among three types of carbon from in situ Mössbauer data obtained during CO + H_2 reaction. In the 570 K spectra of an Fe/SiO_2 sample a doublet was found with $\delta = 0.0$ mm s^{-1} and $\Delta = 0.41$ mm s^{-1}. For the assignment of this component a surface iron species coupled with reactive or mobile carbon was suggested since this doublet disappeared from the spectrum after disconnecting the reaction mixture [6]. Another argument for the existence of this component was found on the iron-ruthenium system on which the same doublet was observed during the reaction without formation of Häggs carbide in significant amount [7]. The second type of carbon species denoted as immobile carbon, was identified by kinetic evidences and this is the main source for methane formation. Finally, the third type of carbon is present in the bulk carbide phase, causing deactivation during the reaction. A reaction model has also been proposed with considering the different types of carbon [6].

On SiO_2 supported ruthenium similar species have been identified by Bell and associates [8–10] by temperature programmed surface reaction (TPSR) the carbon being either weakly bound and active in chain propagation or staying on the surface as alkyl species and not participating in the reaction. Bennett et al. concluded also on similar results from Mössbauer and transient mass spectroscopy measurements [11], and they also established a CO + H_2 reaction model [12].

In the present paper we wish to consider some of the factors by which formation of the inactive carbide being responsible for the deactivation processes, can influenced and thereby the catalyst activity can be maintained. Examples will be presented on how dispersion affects the inactive carbide formation either by using geometrical constrains for the iron particle formation, such as zeolite matrix, or alloying the iron by other metals such as rhenium. We also show the effect of promoters e.g. potassium and alumina on the particle size of iron. In these studies Mössbauer spectroscopy has been applied and is complemented by other methods.

2. Results and discussions

In our previous study [6] the disappearance of the doublet characterized by $\delta = 0.0$ mm s^{-1} and $\Delta = 0.41$ mm s^{-1} values was reported in the 570 K in situ Mössbauer spectra upon exchange the reaction mixture for vacuum. Further, additional kinetic experiments also showed that composition of the products changed and after CO disconnection; methane was the only hydrocarbon product left in the gas stream. This points to the absence of the reactive carbon participating in the chain propagation.

The detection of the reactive surface carbide on iron is very difficult sometimes, since during the catalytic reaction only a small fraction of the surface is active, while the overwhelming rest is covered by other reaction species. The further discussion is aimed therefore, to focus on stabilization of the small

Table 1
Relative amounts of various iron species in FeNaHX-zeolite sample after various treatments

Species	Treatments/T(K)				
	H_2/720	$CO+H_2$/570	$CO+H_2$/670	H_2/720 [a]	$CO+H_2$/670 [a]
Fe^{2+}_{oct}	50	95	79	97	90
Fe^{2+}_{tetr}	50	6	0	3	0
FeC	0	0	21	0	10

Note: [a] Treatment before hydrogenation in oxygen, for the others in air.

metallic particles on which formation of the inactive carbide phase causing deactivation, could be avoided.

A possibility to stabilize small iron particles is to put a geometrical constrain for the growing metal crystallites. This is why NaHX-zeolite was used to prepare small iron ensembles [13]. In the faujasite framework the octahedral and tetrahedral positions occupied by Fe^{2+} ions (Fe^{2+}_{oct} and Fe^{2+}_{tetr}, respectively) can clearly by distinguished by their Mössbauer parameters [14]. The extraframework Fe^{2+}_{oct} ions prefer to occupy the hexagonal window positions, while the Fe^{2+}_{tetr} ions are located in the sodalite and supercages.

Typical relative intensity data obtained after different treatments of FeNaHX-zeolite samples [13] are presented in table 1. First, a very important feature is the hindered reduction of ion exchanged Fe^{3+} to metallic particles. Instead, Fe^{2+} is the prevailing species after reduction at 720 K sitting in different positions of the NaHX-zeolite matrix. After $CO + H_2$ reaction at 570 K the Fe^{2+}_{oct} remained unchanged while the amount of Fe^{2+}_{tetr} drastically decreased. This occurred since the iron species used for the reaction was consumed up from those located in tetrahedral position. Presumably Fe^{2+}_{oct} ions located in the more tight hexagonal prism are less accessible for the reactants. Here we should note that Fe^{2+}_{tetr} ions are not the active species in the reaction but are probably only the precursors to the active sites. As the data reveal, this process is more expressed at 670 K where all the iron species located in tetrahedral position have been used up and are converted to iron carbide.

In order to visualize the effect of zeolite matrix, here we can compare the data displayed in table 1 with those obtained on a 2 wt% Fe/SiO_2 catalyst after similar treatments [14,15]. In the latter sample after reduction in hydrogen at 720 K one can find iron in low, Fe^{2+}(L), and in high, Fe^{2+}(H), coordination states and in form of Fe^0 as well, in 28, 61 and 11 percent, respectively. The coordination sphere of the Fe^{2+} ions of low coordination is not completed, hence they are presumably located on the surface of the support, while the Fe^{2+}(H) ions possess completed coordination sphere either in the bulk or close to the surface; their Mössbauer parameters are well-distinguishable [15]. When the reduction temperature was increased to 870 K iron in Fe^0 was significantly risen and amounted for 87%. On the latter sample after the reaction in $CO + H_2$ at 530 K (at lower temperature than on FeNaHX/zeolite) all iron was converted into iron carbide. This unambiguously proves the stabilizing effect of a zeolite matrix for small particles.

The second possible modification of the iron is to prepare bimetallic particles in which alloys have not necessarily been formed yet. Illustrations for this instance are provided by a silica supported iron-rhenium system [16,17], or by alumina and silica supported iron-ruthenium combinations [18,19]. It has been proven previously that iron reduction even in presence of ruthenium is retarded [18] and this is attributed to the formation of FeO_xRuO_y-support interface. In the case of iron-rhenium at low reduction temperature (720 K) there is a slight increase of iron reduction (11 to 19% in Fe to FeRe, respectively) without changing the other Fe^{2+} species to a large extent [16]. However, reduction at 870 K makes the Mössbauer spectra of iron and iron-rhenium samples entirely different. While on pure iron magnetically split component is present in 86% measured at 300 K, on the FeRe sample the Fe^0 singlet is the dominating species amounting to 48%. Further evidence for stabilization of the high iron dispersion is provided by the Fe $2p_{3/2}$/Si 2p signal ratios determined by XPS for the reduced and impregnated catalysts [16]. The ratio is 0.23 for the pure iron sample, whereas it is 0.33 for the $FeRe/SiO_2$ catalyst, i.e. the rhenium containing samples is sintered to lesser extent during reduction.

The effect of rhenium is the most pronounced when the Fe and FeRe samples reduced at 870 K, are compared after $CO + H_2$ reaction carried out at 530 K [17]. While on pure iron all iron is transferred into Häggs carbide characterized by the hyperfine splitting of 21, 17.7 and 9.3 T, the carbide formation is not detectable in the rhenium containing iron sample. This clearly lends evidence that carbide formation during the catalytic reaction is strongly suppressed on the FeRu sample.

Here we must emphasize that not only alloy formation can be regarded as the effect of rhenium on the iron particles, but also non-easily reducible rhenium oxide surface layer interfacing metal particles to the support, exists which raises a barrier against the migration of small iron particles.

A third possibility for stabilizing small iron particles is the use of additives. The most frequently used promoter is potassium [20], but its effect is still not understood in every detail. In some cases an increase was found in the strength of CO chemisorption. The general and accepted feature is the suppressed formation of saturated hydrocarbons, however.

The effect of potassium largely depends on the system to be investigated. Thus, in cases of silica supported iron and iron rhenium formation of metallic particles are hindered by potassium at moderate temperature reductions as was revealed by Mössbauer spectroscopy studies carried out on 2 wt% K + 2 wt% Fe/SiO_2 samples [16]. Similar results are reported for potassium promoted 15 wt% Fe/SiO_2 systems; and the retarded reducibility was not accompanied with any change of the size of iron particles [21].

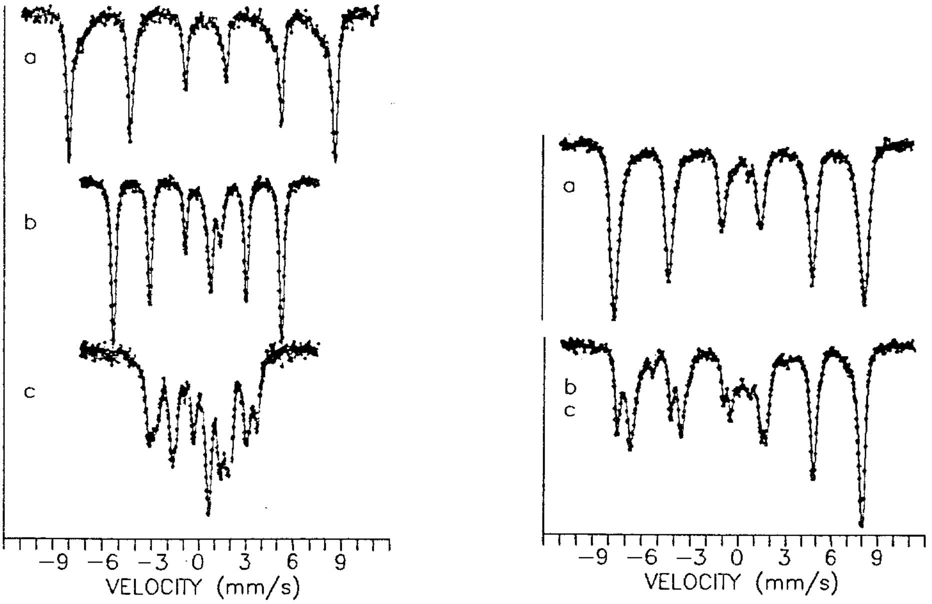

Fig. 1. 300 K Mössbauer spectra measured on 10 wt% Fe/MgO (A) and 10 wt% Fe/MgO with 1 wt% Al (B). Spectra were obtained after calcination at 720 K, (a); after reduction at 700 K in H_2 for 5 h, (b); and after $CO + H_2$ reaction at 520 K for 17 h, (c); respectively.

Considering the Mössbauer data obtained on the potassium promoted 2 wt% Fe/SiO_2 systems, an explanation can be suggested for the hinderance of the reduction of Fe^{2+} ions. Namely, significant differences were revealed in the coordination state of the surface ions in the 570 K in situ spectra [17]; the quadrupole splitting values were significantly smaller for the Fe^{2+}(L) ions in the samples containing potassium. From this observation it can be proposed that formation of K^+-Fe^{2+} pairs on the surface of the support plays essential role in retarding the reducibility.

The third example that we are presenting here is the effect of alumina in the Fe/MgO system. This system provides also a convincing illustration for avoiding the inactive carbide formation by addition of a promoter. In fig. 1a the 300 K Mössbauer spectra of 10 wt% Fe on MgO are presented after calcination, reduction in hydrogen for 5 h at 700 K and after $CO + H_2$ reaction for 17 h at 530 K, respectively. The catalyst behaves in a classical way: large iron oxide particles are reduced to α-iron which is converted into Häggs carbide after $CO + H_2$ reaction for 17 h at 530 K. On the other hand, when the same catalyst is promoted by 1 wt% Al_2O_3, after reduction no zerovalent iron can be detected at all, only magnetite (Fe_3O_4) is formed. After the subsequent 17 h treatment in $CO + H_2$ at 530 K no iron carbide is found, the spectrum hardly changes, although the catalytic activity is retained on the sample [22]. This is again indicative of stabilization of small particles generating active sites for dissociation of CO without forming inactive bulk carbide phase.

3. Conclusions

It has been established that presence of small metallic particles is prerequisite for the formation of reactive or mobile carbon which ensure the active sites in CO hydrogenation.

Different possibilities are available for stabilizing the small metallic particles:
(i) geometrical constrain to confine the growth of large particles using e.g. zeolites;
(ii) using a second metallic component which might either be active in the catalytic reaction itself, or, at least, contains non-easily-reducible components;
(iii) Addition of ionic promoters which are non reducible, but are also able to stabilize small metallic particles.

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