



## Application of Mössbauer Spectroscopy to the Carbon Oxides Hydrogenation Reactions

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**Abstract.** Iron-based catalysts have favorable activity and selectivity properties for the CO and CO<sub>2</sub> hydrogenation reactions. Several Fe phases (oxides and carbides) can be present in these catalysts. The interaction of Fe with the other components of the catalyst (support, promoters) can affect the ease of reduction and also its transformation during the reactions. In this work, the relationship between catalytic behavior in the CO and CO<sub>2</sub> hydrogenation reactions and the Fe phase composition of fresh and reacted catalysts was studied. Two types of catalysts were tested: a laterite and the other one made of iron supported on alumina, both unpromoted and promoted with K and Mn. Only those Fe species which can be reduced-carburized, by means of a pretreatment or by an *in situ* transformation under the reaction, seem to be able to perform the CO or CO<sub>2</sub> hydrogenation. The reoxidation of the Fe carbide to magnetite was not associated to deactivation. The selectivity seems to be more affected by Fe species difficult to reduce than by magnetite produced by reoxidation.

**Key words:** Fischer–Tropsch synthesis, carbon dioxide hydrogenation, iron carbides, C<sub>2</sub>–C<sub>4</sub> hydrocarbons.

### 1. Introduction

The use of sources for fuels and chemicals alternative to oil (natural gas, carbon) is of great interest. The synthesis can be carried out by the indirect production of syngas (H<sub>2</sub> + CO) followed by its reaction (Fischer–Tropsch synthesis [1]). The CO<sub>2</sub> hydrogenation, on the other side, has attracted attention as an alternative to recycle into the atmosphere CO<sub>2</sub>, which is at the same time a cheap source of carbon. The CO<sub>x</sub> hydrogenation reactions have several features in common, Fe being an active component with favorable selectivity properties. In the CO<sub>2</sub> hydrogenation C<sub>2</sub>+ hydrocarbons seem to be produced by the hydrogenation of the CO formed as an intermediate [2–4].

K and Mn are frequently used as promoters for Fe in the CO<sub>x</sub> hydrogenation reactions [1, 3]. The changes of selectivity produced by K (less methane, more C<sub>2</sub>+ hydrocarbons and alkenes) are consistent with an increase in the C/H surface

ratio. An increase on the selectivity to C2–C4 alkenes is associated to the addition of Mn.

Iron does not remain as a metal during the CO [5] and the CO<sub>2</sub> [6] hydrogenation reactions, but it is transformed to carbide phases and also to magnetite by reoxidation. These same phases could appear when nonreduced catalysts are exposed to CO or syngas [7]. The Fe phases should also depend on metal-support interactions, which can make difficult the transformation into the metal state [8]. Many authors agree that carbide formation is necessary before the catalytic surface becomes active in Fischer–Tropsch synthesis [5, 7], however, there has been controversy about the Fe phases in the working catalyst and their role in the CO hydrogenation. The CO<sub>2</sub> hydrogenation reaction, on the other side, has been studied to a lesser extent. With the aim of contributing to elucidate the relationship between bulk Fe phases and the catalytic behavior in the carbon oxide hydrogenation reactions, we analyze the results obtained on the effect of the activation treatment, the addition of promoters (K, Mn), as well as, the preparation procedure of the catalyst. Two different types of catalysts, one based on a natural Fe material (laterite) and the other of Fe supported on alumina were used.

## 2. Experimental

The major components of the laterite were Al, Si and Ti, in addition to Fe. The laterite based catalysts were prepared by impregnation of the previously washed original laterite with K and Mn (carbonate and nitrate salts, respectively). The impregnated samples were dried and calcined at 723 K for 3 h. Fe and promoter contents were 22–25% and 4% (wt %), respectively. Fe/Al<sub>2</sub>O<sub>3</sub> based catalysts were prepared by impregnation of Fe (incipient wetness or excess of solution using nitrate as salt) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Fe and promoter contents as well as thermal treatments were similar to those for the laterite based catalysts.

Before reaction the calcined catalysts were submitted to a pretreatment with H<sub>2</sub> at 723 K during 16 h, followed by CO or syngas (H<sub>2</sub>/CO = 2) exposure at 423–573 K for 21 h. This treatment will be named here the standard pretreatment. Details about the catalytic tests were given elsewhere [9]. They were carried out with a fixed-bed reactor analyzing the effluent gases by gas chromatography.

Catalysts were analyzed after pretreatment and reaction by <sup>57</sup>Fe Mössbauer spectroscopy at room temperature using <sup>57</sup>Co in a Pd matrix as the source. To minimize reoxidation by air exposure all catalyst samples (0.2 g) after treatment or reaction were immediately placed on an aluminum holder and mixed with a fast dry epoxy. The sealed samples were subsequently analyzed. Spectra were fitted by means of a least-squares fitting program.

### 3. Results and discussion

#### 3.1. EFFECT OF THE ACTIVATION TREATMENT (CATALYST: KMn/LATERITE, REACTION: H<sub>2</sub> + CO)

Three activation treatments were assayed [10]. Test 1 (Table I) was performed with the calcined catalyst. For Tests 2 and 3, the calcined catalyst was submitted to a treatment with H<sub>2</sub> followed by CO at increasing temperatures (Table I). According to the Mössbauer spectrum, the presence in the calcined catalyst of mixed oxide phases with different degrees of substitution by Al and Mn in the Fe oxide framework would be possible, since a broad sextet with a hyperfine magnetic field distribution (490–358 kG) was observed. No magnetic contributions were observed on the Mössbauer spectrum after the mild pretreatment for Test 2, which suggests an incipient transformation of the Fe oxide. Under the more severe reduction conditions for Test 3, that is after the standard pretreatment, 60% of the Fe oxide was transformed to Hägg carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>). The results for the reaction are shown on Table I, it can be observed that the calcined catalyst was reduced and carbided under syngas at reaction conditions. Moreover, the treatment conditions influenced the Fe phase composition. Milder reduction conditions favored the formation of hexagonal carbide (O-Fe<sub>2</sub>C, hyperfine magnetic field 167 kG), while the more severe led to the Hägg carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>: 220, 185 and 107 kG) [10]. These results agree with the greater thermodynamic stability of the last phase compared to hexagonal carbides. With respect to the catalytic behavior, a gradual increase in CO conversion was observed during 3 days on stream. The order of activity and also of the rate of activation was: Test 2 > Test 1 > Test 3 (Table I). However, the selectivity measured as the C<sub>2</sub>–C<sub>4</sub>/CH<sub>4</sub> ratio followed the opposite tendency. It was the more severe pretreatment (for Test 3), which gave rise to the best selectivity results. For this reason this pretreatment was chosen for the successive tests.

The tendency of the catalyst to be transformed by the syngas can depend on the calcination temperature [11]. Tests were performed with the KMn/Laterite calcined at 723 K and at 1223 K following the sequence: reaction-treatment with H<sub>2</sub> at 623 K-reaction-treatment with H<sub>2</sub> at 723 K-reaction. The tendency of the CO con-

Table I. Effect of the activation treatment on the KMn/laterite catalyst

Test	CO conversion (%)	C <sub>2</sub> –C <sub>4</sub> /CH <sub>4</sub>	Fe carbides <sup>c</sup> (%)	O-Fe <sub>2</sub> C/ $\chi$ -Fe <sub>5</sub> C <sub>2</sub>
1	57 <sup>a</sup>	2.2	58	0.5
2	67 <sup>b</sup>	1.7	39	1.4
3	51 <sup>a</sup>	3.5	69	0

<sup>a</sup>3 days on stream; <sup>b</sup>2 days on stream; <sup>c</sup>samples after reaction.

Pretreatments (samples calcined at 723 K for all tests): Test 2: H<sub>2</sub> at 608 K C 16 h and CO at 503 K 21 h, Test 3: H<sub>2</sub> at 723 K 16 h, CO at 423–573 K 21 h. Reaction conditions: 573 K, 1.1 MPa, SV = 5.0 l/g<sub>cat</sub>/h, H<sub>2</sub>/CO = 1.

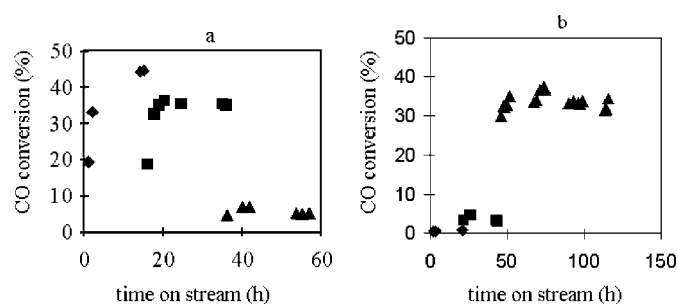


Figure 1. Effect of treatments with H<sub>2</sub> during the CO hydrogenation reaction with the KMn/laterite catalyst calcined at 723 K (a) and at 1223 K (b). ◆ Calcined catalyst, ■ H<sub>2</sub> treatment at 623 K, ▲ H<sub>2</sub> treatment at 723 K. Reaction conditions: 573 K, 1.2 MPa, H<sub>2</sub>/CO = 1, space velocity: (a) 7.5 l/g<sub>cat</sub>/h, (b) 2.1 l/g<sub>cat</sub>/h.

Table II. Effect of the addition of K and Mn on the laterite based catalyst

Promoter	–	Mn	K	KMn
<i>Fe carbide</i> <sup>a</sup> (%)				
Pretreated	29 ( $\alpha$ -Fe = 8)	38 ( $\alpha$ -Fe = 10)	70	68
After reaction	48	55	46 (+11) <sup>b</sup>	74
CO conversion (%) <sup>c</sup>	<5 <sup>d</sup>	14 <sup>d</sup>	71	69
C2–C4/CH <sub>4</sub>	1.5	1.8	3.2	4.3
Alkenes in C2–C4 (%) <sup>e</sup>	–	69	82	89

<sup>a</sup> $\chi$ -Fe<sub>5</sub>C<sub>2</sub>; <sup>b</sup>46%  $\chi$ -Fe<sub>5</sub>C<sub>2</sub> and 11% O-Fe<sub>2</sub>C.

Pretreatment: calcination at 723 K, H<sub>2</sub> at 723 K 16 h, CO at 423–573 K 21 h. Reaction conditions: 1.2 MPa, H<sub>2</sub>/CO = 1, 563 K, variable space velocity.

<sup>c</sup>3 days on stream, SV = 1.2 l/g<sub>cat</sub>/h; <sup>d</sup>573 K, SV = 0.6 l/g<sub>cat</sub>/h; <sup>e</sup>at 60% CO conversion.

version for the tests was exactly opposite (Figure 1). For the catalyst calcined at the lower temperature, activation during the reaction occurred, which coincided with an increase on the proportion of carbided Fe, as stated above. The H<sub>2</sub> treatments produced a loss of activity. A decarburization–recarburization process could take place, together with an increase on particle size or sinterization. The calcination at 1223 K stabilized Fe for the reduction, as indicated by the lower Fe carbide proportion after this test compared with that for the catalyst calcined at 723 K (35 vs. 62% Hägg carbide). Syngas probably did not modify the catalyst calcined at the higher temperature. It was just the treatment with H<sub>2</sub> at 723 K, which led to a significant increase on activity, probably by the formation of more active phases (Figure 1).

3.2. EFFECT OF PROMOTERS (CATALYST: LATERITE, REACTION:  $H_2 + CO$ )

Catalytic tests and Mössbauer analysis of fresh pretreated (standard pretreatment) and reacted samples were performed for the unpromoted, K-, Mn- and KMn-promoted laterite catalysts [12]. Table II resumes the results, the Fe carbide proportions indicate that the addition of K accelerated remarkably the reduction–carburization of Fe in the laterite. This could be related with the effect of K on Fe catalysts which increase the adsorption and dissociation of CO. During reaction the reduction–carburization continued (Table II) for all catalysts except the K/laterite. The addition of K also produced very pronounced changes on the catalytic behavior, increasing activity, as well as, the C2–C4/CH<sub>4</sub> ratio and the selectivity to alkenes (Table II). The addition of Mn to the K promoted laterite increased additionally these parameters.

The KMn/laterite catalyst, however, showed a tendency to deactivate with the time on stream. The catalytic tests were performed at various space velocities, the initial and final ones were the same in order to check the stability (Figure 2). An increase on activity during the first 2 days on stream for both, K- and KMn/laterite catalysts was observed. The continuation of the reduction–carburization of Fe, as well as a simultaneous fragmentation of the particles by effect of the carburization [5] and also, changes in metal and promoters surface composition [8] could be involved. Activation on stream was then followed by deactivation in the case of the KMn/laterite catalyst (Figure 2a), carbon and high molecular weight hydrocarbons deposition, as well as, sinterization of the catalyst being possible causes. However, for the K/laterite catalyst (Figure 2b) instead of deactivation, an increase on activity was observed. This was also the only catalyst, which showed reoxidation, as well as, a change in the type of Fe carbide phases during reaction (Table II). In the syngas reaction the environment can change from reducing–carburizing at low conversions to oxidizing at high conversions (by the products H<sub>2</sub>O and CO<sub>2</sub>). A reoxidation of Hägg carbide to magnetite was feasible since high conversions were achieved (Figure 2). On the other hand, a direct transformation of Hägg to

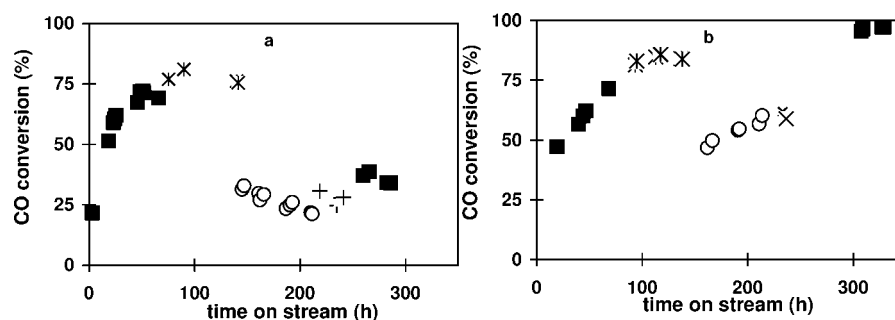


Figure 2. CO conversion as a function of the time on stream for the KMn/laterite (a) and K/laterite (b) catalysts at different space velocities. (■) 1.2, (✱) 0.9, (○) 2.5, (+) 1.8, (×) 3.8 l/h/g<sub>cat</sub>. Reaction conditions: 563 K, 1.2 MPa, H<sub>2</sub>/CO = 1.

hexagonal carbide is not consistent with the thermodynamic stability. However, since conversion was changed from high to low (Figure 2b) a process of reoxidation and recarburization should be possible.

The fact that the KMn/laterite catalyst did not reoxidize could be attributed to an effect of Mn stabilizing the Fe carbide phase. Results, which will be shown later corroborate this effect. It is worth to note that the reoxidation was not associated to deactivation. On the contrary, the catalyst which was not reoxidized, was deactivated. Differences in selectivity induced by the several Fe phases could give one possible explanation. The higher C/H surface ratio obtained with the KMn/laterite could favor deactivation by carbon deposition, while reoxidation in the K/laterite could help to the carbon elimination (by hydrogenation forming methane and even by steam gasification). Still another consideration to take into account is the transformation *in situ* to hexagonal carbide; as shown in the previous point, a higher activity can be associated to the presence of hexagonal compared to Hägg carbide.

### 3.3. COMPARISON OF THE REACTIONS (CATALYSTS: KMn/LATERITE AND FeKMn/Al<sub>2</sub>O<sub>3</sub>)

To compare the carbon oxides hydrogenation reactions, the KMn/laterite and a FeKMn/Al<sub>2</sub>O<sub>3</sub> catalyst were tested [4]. The behavior of the laterite based catalyst in the CO hydrogenation was shown above (Figure 2a). The alumina supported one showed a lower activity, and also a tendency to deactivation. An important degree of interaction between Fe and the other components of this catalyst (Al, Mn) was suggested by the small proportion of Fe carbide (29% Hägg carbide) achieved submitting this catalyst to the standard pretreatment.

In the hydrogenation of CO<sub>2</sub> a more stable behavior of the conversion with the time on stream for both catalysts was observed. Conversions were not higher than 30%. The *in situ* activation of the KMn/laterite catalyst was not favored during this reaction. The more oxidizing nature of the gas environment in CO<sub>2</sub> compared to CO hydrogenation could be involved in this result. Not only from the side of the reactants (CO<sub>2</sub> vs. CO), but also by the products (more H<sub>2</sub>O) the environment is more oxidizing for the CO<sub>2</sub> hydrogenation. Between both catalysts, the FeKMn/Al<sub>2</sub>O<sub>3</sub> one showed slightly higher conversions.

With the FeKMn/Al<sub>2</sub>O<sub>3</sub> catalyst a test of CO<sub>2</sub> hydrogenation was carried out in which, a mild reduction with H<sub>2</sub> (623 K for 3 h) was performed. Carbide or metallic Fe were practically absent in the fresh and after reaction catalyst samples. The CO<sub>2</sub> conversion for this test was 7% compared to 21% attained at the same reaction conditions on the catalyst submitted to the standard pretreatment (29% Fe carbide). This seems to indicate that, also to observe activity in the CO<sub>2</sub> hydrogenation reaction, the presence of Fe carbide is necessary.

### 3.4. EFFECT OF PROMOTERS IN THE CO<sub>2</sub> HYDROGENATION (Fe/Al<sub>2</sub>O<sub>3</sub>)

The addition of K or Mn did not produced great changes in the CO<sub>2</sub> conversion (slightly lower than 30%) [13]. It seems to be a characteristic of the CO<sub>2</sub> hydrogenation reaction that the sensitivity of the conversion to changes on different parameters (space velocity [4], addition of promoters [13], preparation procedure [9]) is small, at least at CO<sub>2</sub> conversions relatively high (20–30%). This could be related to an inhibition effect of the water produced, which makes less perceptible the changes in activity.

Tendencies in CO<sub>2</sub> hydrogenation were similar to that shown above for the CO reaction. The addition of K produced the more pronounced effect on selectivity, which was consistent with an increase on the C/H surface ratio. Moreover, K tended to accelerate slightly the reduction–carburization of Fe during the pretreatment, while Mn stabilized Fe carbide for reoxidation (Table III).

Results in Figure 3 show the evolution of the CO<sub>2</sub> conversion and the bulk Fe phases for the FeK/Al<sub>2</sub>O<sub>3</sub> catalyst. Although a gradual reoxidation of bulk Fe carbide to magnetite took place, CO<sub>2</sub> conversion remained constant with the time on stream. According to the available experimental results a participation of magnetite in the CO<sub>2</sub> transformation could not be discarded. Possible differences between bulk and surface Fe phases must also be taken into account.

### 3.5. EFFECT OF THE PREPARATION PROCEDURE (FeK/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub> + CO<sub>x</sub>)

To attain different degrees of interaction between Fe and alumina, three different preparation procedures were used [9]: impregnation (incipient wetness, Fe(i)/Al<sub>2</sub>O<sub>3</sub> catalyst), precipitation in the presence of alumina (Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalyst) and physical mixing of the support with decomposed Fe citrate (Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst). A K promoted series was also prepared. The Fe and K contents of the catalysts were close to 20% and 1% (wt %), respectively [9].

Before reaction, catalysts were submitted to the standard pretreatment. For the catalysts Fe(c)/Al<sub>2</sub>O<sub>3</sub> the temperature for the step with H<sub>2</sub> was 623 K instead of 723 K. The reactions were carried out successively, first CO<sub>2</sub> hydrogenation (563 K, 1.2 l/(g<sub>cat</sub>·h)) and then CO hydrogenation (553 K, 1.2 and 2.4 l/(g<sub>cat</sub>·h)).

Table III. Effect of promoters on the Fe carbide proportion (%) for the Fe/Al<sub>2</sub>O<sub>3</sub> catalyst

Promoter	–	Mn	K
Pretreated <sup>a</sup>	53	54	60
After H <sub>2</sub> + CO <sub>2</sub> <sup>b</sup>	28	43	31

<sup>a</sup>Calcined at 723 K, H<sub>2</sub> at 723 K 16 h, syngas (H<sub>2</sub>/CO = 2) at 423–573 K 21 h.

<sup>b</sup>Reaction conditions: 1.2 MPa, H<sub>2</sub>/CO<sub>2</sub> = 2.2, 563 K, 0.6 l/g<sub>cat</sub>/h, 2 days on stream.

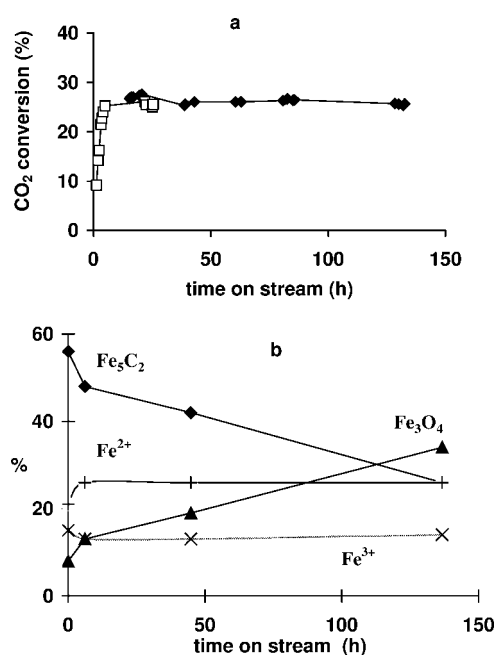


Figure 3. Conversion of CO<sub>2</sub> (a) and Fe phase composition (b) as a function of the time on stream for the FeK/Al<sub>2</sub>O<sub>3</sub> catalyst. Reaction conditions: H<sub>2</sub>/CO<sub>2</sub> = 2, 563 K, 0.6 l/g<sub>cat</sub>/h.

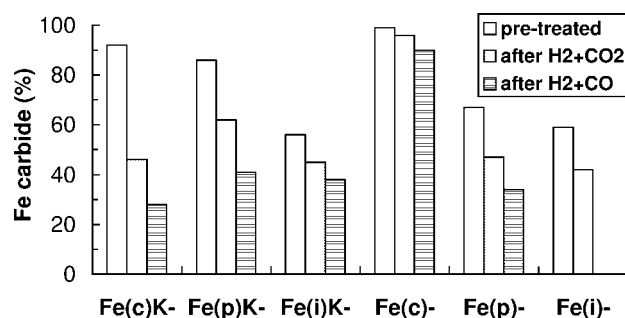


Figure 4. Effect of the preparation procedure on the proportion of Fe carbide for the Fe/Al<sub>2</sub>O<sub>3</sub> catalysts pretreated and after CO<sub>2</sub> and CO hydrogenation.

Both reactions were performed at 1.2 MPa, feed ratios H<sub>2</sub>/CO<sub>x</sub> = 2, for two days on stream each one.

Figure 4 shows the Fe carbide percentage of the fresh pretreated catalysts, as well as, of the samples after each reaction. To illustrate the Mössbauer results obtained the spectra of some of the catalysts samples are shown in Figure 5 and their adjusted parameters are given in Table IV. The carbide phase observed is very similar to the Hägg carbide being here fitted with four hyperfine field components: 219 ± 2 (~2), (195 ± 2, 181 ± 5) (~2) and 117 ± 5 (~1), the hyperfine fields are in kG, in parentheses are their area weights grouped in three parts like for



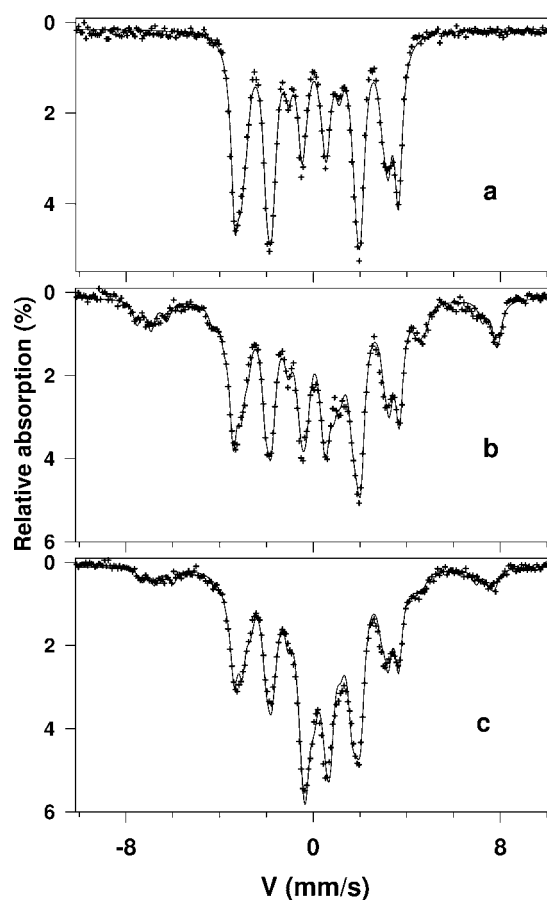


Figure 5. Mössbauer spectra of unpromoted catalysts after pretreatment: (a) Fe(c)/Al<sub>2</sub>O<sub>3</sub>, (b) Fe(p)/Al<sub>2</sub>O<sub>3</sub>, (c) Fe(i)/Al<sub>2</sub>O<sub>3</sub>.

the Hägg carbide. It will be shown elsewhere that this Fe carbide evolves with the time on stream to one which is the classical Hägg carbide, that can be fitted with 3 components:  $\sim 220$  (2), 180 (2) and 120 kG (1). This can be observed in the spectrum shown in Figure 6 corresponding to a reacted catalyst. The Fe carbide proportion for the fresh catalysts decreases in the order Fe(c)/Al<sub>2</sub>O<sub>3</sub> > Fe(p)/Al<sub>2</sub>O<sub>3</sub> > Fe(i)/Al<sub>2</sub>O<sub>3</sub>, for both the K promoted and the unpromoted series (Figure 4). This is the order expected considering the possibility of metal-support interactions. The addition of K gave rise once again to an increase in the Fe carbide proportion (Figure 4), in this case only for the Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalyst. For the impregnated one the metal-support interaction could be stronger and the K added was not able to accelerate the transformation.

As shown before, during both reactions reoxidation of carbide (Figure 4) to magnetite take place (Figure 6 and Table IV), except for the unpromoted Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst, whose Fe carbide proportion remained  $\geq 90\%$ . The presence of residual

Table IV. Mössbauer parameters for Fe/Al<sub>2</sub>O<sub>3</sub> catalysts

Catalyst	IS <sup>a</sup> (mm/s)	HWMH <sup>b</sup> (mm/s)	QS <sup>c</sup> (mm/s)	H <sup>d</sup> (kG)	Area (%)	Species
Fe(c)/Al <sub>2</sub> O <sub>3</sub>	0.24	0.20	0.11	217	43.0	Fe <sub>5</sub> C <sub>2</sub>
pretreated	0.19	0.20	0.02	195	26.5	“
(Figure 5a)	0.19	0.20	0.02	181	13.8	“
	0.19	0.20	0.04	116	16.7	“
Fe(p)/Al <sub>2</sub> O <sub>3</sub>	0.22	0.20	0.13	221	26.2	Fe <sub>5</sub> C <sub>2</sub>
pretreated	0.22	0.20	0.03	197	18.3	“
(Figure 5b)	0.22	0.20	0.10	181	9.1	“
	0.22	0.20	0.04	120	13.4	“
	0.27	0.20	0	476	5.7	Fe <sub>3</sub> O <sub>4</sub>
	0.64	0.20	0	461	7.0	“
	0.64	0.20	0	419	4.7	“
	1.24	0.25	1.24	–	6.2	Fe <sup>2+</sup>
	0.43	0.25	1.21	–	9.5	Fe <sup>3+</sup>
Fe(i)/Al <sub>2</sub> O <sub>3</sub>	0.22	0.20	0.13	219	20.6	Fe <sub>5</sub> C <sub>2</sub>
pretreated	0.22	0.20	0.03	194	17.0	“
(Figure 5c)	0.22	0.20	0.10	174	8.0	“
	0.22	0.20	0.04	120	13.0	“
	0.27	0.20	0	462	3.0	Fe <sub>3</sub> O <sub>4</sub>
	0.64	0.20	0	452	3.7	“
	0.64	0.20	0	403	3.5	Fe <sub>3</sub> O <sub>4</sub>
	1.01	0.25	1.64	–	11.2	Fe <sup>2+</sup>
	0.34	0.25	1.06	–	20.1	Fe <sup>3+</sup>
Fe(c)K/Al <sub>2</sub> O <sub>3</sub>	0.23	0.20	0.11	220	11.5	Fe <sub>5</sub> C <sub>2</sub>
after	0.20	0.20	0.01	186	11.0	“
H <sub>2</sub> + CO	0.20	0.20	0.05	112	6.7	“
(Figure 6)	0.28	0.20	0	494	26.9	Fe <sub>3</sub> O <sub>4</sub>
	0.66	0.20	0	463	43.9	“

<sup>a</sup>Isomer shift; <sup>b</sup>Half width at medium height; <sup>c</sup>Quadrupole splitting; <sup>d</sup>Hyperfine field.

carbon produced by an incomplete decomposition of the Fe citrate [9] and a less intimate contact between Fe and alumina for this catalyst could give rise to a more hydrophobic surface, thus retarding reoxidation. The addition of K increased notoriously the reoxidation tendency of this catalyst.

Similar CO<sub>2</sub> conversions (21–26%) after two days on stream were observed for all catalysts, as commented in the previous point. The CO conversions were also similar for the catalysts (close to 100 or 80% depending on the space velocity),

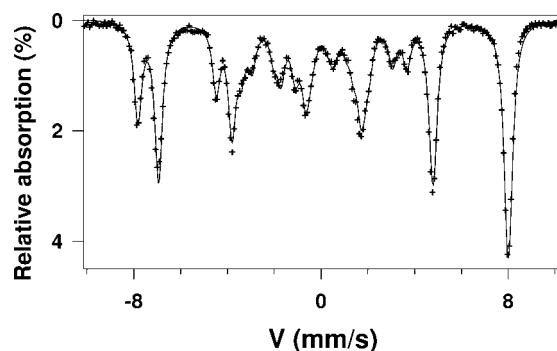


Figure 6. Mössbauer spectrum of the Fe(c)K/Al<sub>2</sub>O<sub>3</sub> catalyst after hydrogenation of carbon oxides.

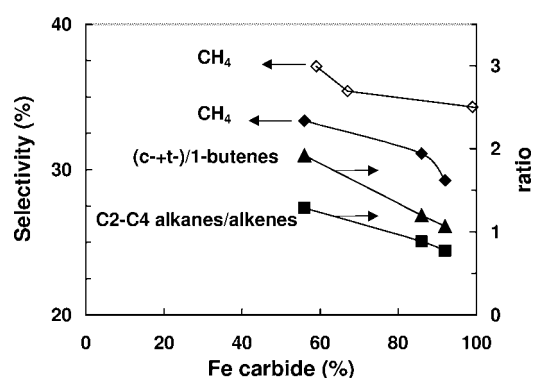


Figure 7. Selectivity parameters for the CO<sub>2</sub> hydrogenation as a function of the Fe carbide proportion in the fresh pretreated catalysts. Open symbols: unpromoted Fe/Al<sub>2</sub>O<sub>3</sub> catalysts, closed symbols: K-promoted catalysts. Reaction conditions: 563 K, 1.2 MPa, 1.2 l/g<sub>cat</sub>·h, H<sub>2</sub>/CO<sub>2</sub> = 2, 2 days on stream.

if conversions are close to thermodynamic equilibrium, differences between catalysts should be less evident. Considering the tendency of most catalysts to bulk reoxidation, the existence of a high proportion of magnetite at the surface during both carbon oxides reactions at high conversions seems probable. Thus once again, direct participation of magnetite in the transformation of reactant gases cannot be discarded.

The small but consistent differences in selectivity obtained could be related to the Fe phase composition of pretreated catalysts. As Figure 7 shows for the CO<sub>2</sub> hydrogenation reaction, higher proportions of non carbide Fe in the fresh catalyst gave rise to more methane, alkanes and internal alkenes formation, which could be associated to higher H/C surface ratios. This behavior has been correlated with the higher acidity of an oxide compared to a carbide surface [14]. Alkanes and internal alkenes are formed by secondary hydrogenation and double bond isomerization of the primary products 1-alkenes. The slight increase on the

(cis+trans-2-)/1-butenes ratio obtained between the first and the second day on stream [9] could be consequence of the progressive reoxidation of the Fe carbide.

Selectivity of the different catalysts correlated well with the Fe carbide Fe proportion in the fresh sample (Figure 7), but not with that present after reaction, which was similar for the most catalysts (Figure 4). The results suggest that Fe species that could not be reduced (magnetite formed by partial reduction, Fe<sup>3+</sup> and Fe<sup>2+</sup> species) led to higher H/C surface ratios than magnetite produced by reoxidation. The properties (e.g., acidity, particle size or exposed surface) of these Fe phases could be different. Mössbauer spectra showed the expected hyperfine fields in the case of the magnetite obtained from reoxidation (Figure 6, Table IV). However, broader lines and lower hyperfine fields were obtained for that produced by incomplete reduction in pretreatment (Figures 5b and 5c, Table IV). These last features have been associated to a higher dispersion and/or to the presence of Al ions in the lattice of Fe<sub>3</sub>O<sub>4</sub> spinel [8]. The presence of Al in the magnetite lattice seems to be less probable for the phase produced by reoxidation, since the starting carbide is formed from metallic Fe.

For the CO hydrogenation reaction, which was carried out following the CO<sub>2</sub> hydrogenation, the tendencies were similar.

#### 4. Conclusions

To observe activity in the CO<sub>x</sub> hydrogenation reactions with Fe based catalysts the formation of Fe carbide seems necessary, either by an activation pretreatment or by an in situ transformation during the reaction. Those Fe species, which by the interaction with the other constituents of the catalyst cannot be transformed to the metallic state and then to Fe carbide seem to have a more indirect role, participating in secondary reactions of the products.

A direct relation between the reoxidation of the Fe carbide to magnetite and the deactivation was not evident, on the contrary, deactivation was observed with the Hägg carbide phase stabilized respect to reoxidation. Differences in selectivities induced by the Fe species could be one of the explanations. A lower proportion of methane and of products of secondary reactions of alkenes were observed in the presence of the Hägg carbide phase compared to hexagonal Fe carbide and magnetite or Fe oxide species. The Fe oxide species not transformed to Fe carbide seemed to have a greater influence on selectivity inducing higher H/C ratios than the magnetite produced by Fe carbide reoxidation during the reaction.

The addition of K can modify the Fe transformation during the pretreatment and the reaction. The reduction-carburization of Fe during the activation treatment can be accelerated by this promoter. On the other side, the reoxidation of Fe carbide to magnetite was favored in the presence of K, while the addition of Mn retarded the Hägg carbide reoxidation during reaction.

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