

## Hydrogenation of carbon oxides over Fe/Al<sub>2</sub>O<sub>3</sub> catalysts

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### Abstract

The behavior of unpromoted and K-promoted Fe/Al<sub>2</sub>O<sub>3</sub> catalysts in both, CO<sub>2</sub> and CO hydrogenation reactions at 553–563 K and 1.2 MPa was compared. To attain different degrees of interaction between Fe and the support, three different procedures were followed to prepare the catalysts: impregnation, precipitation and physical mixing of the support with Fe oxide obtained from citrate decomposition. Fe-phase composition of pretreated (reduction-carburization) and after reactions catalysts was analyzed by Mössbauer spectroscopy. Correlation between Fe phase composition of pretreated catalysts and product selectivity was evident. A lower proportion of carbided Fe in fresh catalysts led to higher methane selectivity and higher alkanes/alkenes and internal/terminal alkenes ratios for both reactions, CO<sub>2</sub> and CO hydrogenation. This relationship was observed independently of the reoxidation of carbide to magnetite, which took place during reactions for most catalysts. Lighter hydrocarbons were produced from CO<sub>2</sub> hydrogenation compared to CO hydrogenation. Higher selectivities to C<sub>2</sub>–C<sub>4</sub> alkenes were obtained from the first reaction through promotion with K. ©1999 Elsevier Science B.V. All rights reserved.

**Keywords:** CO hydrogenation; CO<sub>2</sub> hydrogenation; Iron catalysts; Potassium promotion; Alumina-supported catalysts; Hydrocarbon synthesis; Mössbauer spectroscopy

### 1. Introduction

Fe is an active component in the reactions of hydrogenation of carbon oxides. The use of this element as catalyst for Fischer–Tropsch (FT) synthesis has been extensively studied and documented ([1–3] and reference therein). CO<sub>2</sub> catalytic hydrogenation has recently drawn attention as an alternative for recycling this greenhouse-effect gas, which is also a cheap

source of carbon. The possibilities of Fe to produce C<sub>2</sub>+ hydrocarbons by CO<sub>2</sub> hydrogenation have been recognized [4–8]; other group VIII metals mainly produce methane. In this reaction CO is an intermediate product [4–5,9] and the dependence of selectivity upon conversion suggests that hydrocarbons are produced by hydrogenation of CO previously formed in a step of reverse water gas shift reaction (WGS). As a consequence, at increasing conversion the reacting CO<sub>2</sub> tends to be completely transformed into hydrocarbons. Something different occurs starting from CO and H<sub>2</sub>. In this case CO<sub>2</sub> produced together

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with hydrocarbons proceeds mainly from the secondary WGS reaction.

The promoter effect of K on Fe catalysts in CO hydrogenation is well known. The increase K produces in the C/H surface ratio [1–2] has been related to both a donation of electron density to Fe [2] as well as a local chemical interaction at the metal-promoter interface [10]. The promoting effect of K in the CO<sub>2</sub> hydrogenation has also been established [2,11–12]. It has been pointed out that H<sub>2</sub> chemisorption decreases and that of CO<sub>2</sub> increases. Due to its acidic character CO<sub>2</sub> could be adsorbed on the alkali [7].

The preparation of supported Fe catalysts can lead to metal–support interactions, which makes its transformation into the metal state difficult [13–14]. Activity in CO hydrogenation appears to correlate better with the extent of Fe reduction, a parameter related to the degree of metal–support interaction, rather than with dispersion, which is related to metal crystallite surface structure [1].

The aim of the present work was to get some insight into the not so well known CO<sub>2</sub> hydrogenation reaction. The relationship between Fe phase composition, which depends on metal–support interaction and catalytic behavior, was studied. A comparison between the two reactions was also made. To attain different degrees of interaction between Fe and alumina, three different preparation procedures were used: impregnation, precipitation in the presence of alumina, and physical mixing of the support with decomposed Fe citrate [15]. The behavior of these unpromoted and K-promoted catalysts in the CO<sub>2</sub> hydrogenation followed by the hydrogenation of CO was tested and bulk Fe phases of catalyst before and after the reactions were analyzed.

## 2. Experimental

### 2.1. Catalyst preparation

Catalysts were prepared using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Kentjen CK-300 (particle size <0.15 mm) as support and Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O as Fe source. The Fe(i)/Al<sub>2</sub>O<sub>3</sub> catalyst was obtained by incipient wetness impregnation, drying at 423 K for 2 h. The Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by continuous addition of NH<sub>4</sub>OH to the solution of the Fe salt until a final pH~6 was achieved;

alumina was added at pH~4, water was vaporized at 333 K for 16 h and the solid was dried. A precursor of Fe was also prepared from a solution of equimolar amounts of Fe nitrate and citric acid. The solvent was vaporized at 333 K for 16 h and the citrate was dried and decomposed at 673 K for 1.5 h in air flow (20 ml/(min g<sub>cat</sub>)) [15]. The Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst was obtained by physically mixing this precursor with alumina.

A K-promoted series was prepared by incipient wetness impregnation with K<sub>2</sub>CO<sub>3</sub>. Previously, Fe(i)- and Fe(p)/Al<sub>2</sub>O<sub>3</sub> samples were heated at 623 K to remove nitrate and water. The final calcination was performed at 733 K for 3 h in flowing air (20 ml/(min g<sub>cat</sub>)). The catalyst prepared from citrate was not submitted to further calcination after physical mixing with alumina or K impregnation.

### 2.2. Catalytic tests

Before reaction, catalysts were submitted to treatment with H<sub>2</sub> at 733 K (623 K for catalysts based on Fe(c)/Al<sub>2</sub>O<sub>3</sub>) during 16 h, followed by syngas exposure (H<sub>2</sub>/CO=2) at 433 K for 2 h and 573 K for 19 h. Catalytic tests were performed in a continuous flow system with a fixed-bed stainless steel reactor using ~2 g of catalyst. The reactions were carried out successively with the same catalyst load in the reactor. 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)). Both reactions were performed at 1.2 MPa, feed ratios H<sub>2</sub>/CO<sub>x</sub>=2, for 2 days on stream. Effluent gases were analyzed periodically by gas chromatography. Permanent gases (N<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub>) were analyzed on line with a Varian 3300 gas chromatograph equipped with a thermal conductivity detector using a Carbosieve SII packed column. C<sub>1</sub>–C<sub>7</sub> hydrocarbons were analyzed in a Chrompack CP 9001 chromatograph with a flame ionization detector and a WCOT Al<sub>2</sub>O<sub>3</sub>/KCl fused silica column. CO<sub>2</sub> and CO conversions were determined using nitrogen as an internal standard (5% in feed gas), and chromatograms were correlated through methane. Selectivities were obtained based on converted carbon. CO<sub>y</sub> free selectivities ( $y=1$  for H<sub>2</sub>+CO<sub>2</sub>,  $y=2$  for H<sub>2</sub>+CO) were determined as the ratio:selectivity to a hydrocarbon fraction / (1 – CO<sub>y</sub> selectivity). The percentage of selectivity to the C<sub>5</sub>+ fraction was obtained as

the difference between 100% and the percentage of selectivity to C1–C4 hydrocarbons.

### 2.3. Characterization

Chemical analysis of the catalysts was performed by atomic absorption and emission spectrophotometry (Varian Techtron AAG). The BET surface area was obtained using a Micromeritics Flowsorb II 2300 analyzer. Catalysts were examined by TEM-EDX using a Hitachi H-800 Electronic Microscope.

Catalysts were analyzed after pretreatment and reaction by  $^{57}\text{Fe}$  Mössbauer spectroscopy at room temperature using  $^{57}\text{Co}$  in a Pd matrix as the source. To minimize reoxidation by air exposure all catalyst samples (0.2 g) were rapidly placed on an aluminum holder and mixed with a fast dry epoxy after discharging the reactor. The sealed samples were subsequently analyzed. Spectra were fitted by means of a program of least squares.

## 3. Results and discussion

The Fe and K contents of the catalysts were 19–20% and 0.8–1.1%, respectively (Table 1). BET surface areas varied between 160 and 180  $\text{m}^2/\text{g}$ .

The presence of residual carbon due to an incomplete decomposition of citrate in the Fe(c) precursor is feasible [15]. The disappearing of the grayish tone of the solid (purple color) observed after calcination at 1073 K would be in agreement with this possibility. Residual carbon tends to concentrate at the surface layers of the solid [15].

TEM-EDX analysis showed a broad distribution of particle size for the impregnated (10–70 nm) and precipitated catalysts (5–40 nm), which could be related to the relatively high Fe content. On the other hand,

Table 1  
Chemical analysis and surface area of calcined catalysts

Sample	Fe (wt.%)	K (wt.%)	Fe/K(atomic)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )
$\text{Al}_2\text{O}_3$	–	–	–	215
Fe(i)/ $\text{Al}_2\text{O}_3$	–	–	–	170
Fe(i)K/ $\text{Al}_2\text{O}_3$	18.81	0.81	16.26	178
Fe(p)K/ $\text{Al}_2\text{O}_3$	18.93	0.78	16.99	167
Fe(c)	–	–	–	32
Fe(c)/ $\text{Al}_2\text{O}_3$	–	–	–	160
Fe(c)K/ $\text{Al}_2\text{O}_3$	20.44	1.10	13.01	–

a lower association between Fe and alumina was observed for the Fe(c)/ $\text{Al}_2\text{O}_3$  sample, as could be expected for this catalyst prepared by physical mixing.

### 3.1. Iron phase composition

Fe does not remain as a metal during CO [16–17] and  $\text{CO}_2$  [18] hydrogenation reactions, but it is transformed to carbide phases and also to magnetite by reoxidation. These same phases appear when non-reduced catalysts are exposed to CO or syngas [16,19–20]. Although there has been controversy about the role of the iron phases in FT synthesis, several authors agree that carbide formation is necessary before the catalytic surface becomes active [16–23]. The presence of carbide also seems to be required in order to achieve higher conversions of  $\text{CO}_2$  into hydrocarbons [9,11]. In the present case, catalysts were submitted to a reduction and carburization pretreatment. Mössbauer spectra of pretreated unpromoted catalysts are shown in Fig. 1, the

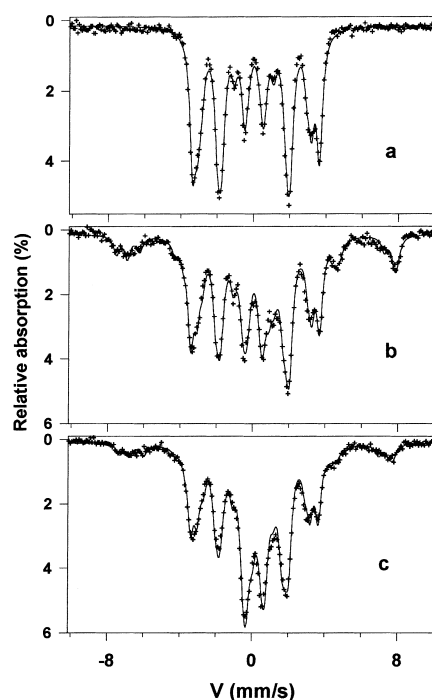


Fig. 1. Mössbauer spectra of unpromoted catalysts after pretreatment. (a) Fe(c)/ $\text{Al}_2\text{O}_3$ , (b) Fe(p)/ $\text{Al}_2\text{O}_3$ , (c) Fe(i)/ $\text{Al}_2\text{O}_3$ .

Table 2  
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> pretreated (Fig. 1a)	0.24	0.20	0.11	217	43.0	Fe <sub>5</sub> C <sub>2</sub>
	0.19	0.20	0.02	195	26.5	Fe <sub>5</sub> C <sub>2</sub>
	0.19	0.20	0.02	181	13.8	Fe <sub>5</sub> C <sub>2</sub>
	0.19	0.20	0.04	116	16.7	Fe <sub>5</sub> C <sub>2</sub>
Fe(p)/Al <sub>2</sub> O <sub>3</sub> pretreated (Fig. 1b)	0.22	0.20	0.13	221	26.2	Fe <sub>5</sub> C <sub>2</sub>
	0.22	0.20	0.03	197	18.3	Fe <sub>5</sub> C <sub>2</sub>
	0.22	0.20	0.10	181	9.1	Fe <sub>5</sub> C <sub>2</sub>
	0.22	0.20	0.04	120	13.4	Fe <sub>5</sub> C <sub>2</sub>
	0.27	0.20	0	476	5.7	Fe <sub>3</sub> O <sub>4</sub>
	0.64	0.20	0	461	7.0	Fe <sub>3</sub> O <sub>4</sub>
	0.64	0.20	0	419	4.7	Fe <sub>3</sub> O <sub>4</sub>
	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> pretreated (Fig. 1c)	0.22	0.20	0.13	219	20.6	Fe <sub>5</sub> C <sub>2</sub>
	0.22	0.20	0.03	194	17.0	Fe <sub>5</sub> C <sub>2</sub>
	0.22	0.20	0.10	174	8.0	Fe <sub>5</sub> C <sub>2</sub>
	0.22	0.20	0.04	120	13.0	Fe <sub>5</sub> C <sub>2</sub>
	0.27	0.20	0	462	3.0	Fe <sub>3</sub> O <sub>4</sub>
	0.64	0.20	0	452	3.7	Fe <sub>3</sub> O <sub>4</sub>
	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> after H <sub>2</sub> +CO (Fig. 4)	0.23	0.20	0.11	220	11.5	Fe <sub>5</sub> C <sub>2</sub>
	0.20	0.20	0.01	186	11.0	Fe <sub>5</sub> C <sub>2</sub>
	0.20	0.20	0.05	112	6.7	Fe <sub>5</sub> C <sub>2</sub>
	0.28	0.20	0	494	26.9	Fe <sub>3</sub> O <sub>4</sub>
	0.66	0.20	0	463	43.9	Fe <sub>3</sub> O <sub>4</sub>

<sup>a</sup> Isomer shift.

<sup>b</sup> Half width at medium height.

<sup>c</sup> Quadrupole splitting.

<sup>d</sup> Hyperfine field.

respective Mössbauer parameters are presented in Table 2. The carbide phase detected was the Hägg carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>), which involves three different sites of Fe (hyperfine fields ~120, 180 and 220 kG). Fitting to the experimental spectrum was better when a fourth contribution with a hyperfine field close to 195 kG was used. A study presently carried out seems to indicate that this component is not the result of another Fe carbide phase.

Preparation procedure led to differences in the degree of Fe transformation achieved with the pretreatment, Fig. 2a summarizes the phase composition. For the sake of clearness we will distinguish in the text, carbided Fe and the Fe which was present in the oxide phases referred as non-carbided Fe. For both series, unpromoted and K-promoted, the Fe(c)/Al<sub>2</sub>O<sub>3</sub>

catalyst showed the highest proportion of carbided Fe (>90% of Hägg carbide), even when pretreatment conditions were milder than for the other catalysts. The first step with H<sub>2</sub> instead of being carried out at 733 K, it was performed at 623 K, which should be enough to achieve a complete reduction of the Fe(c) precursor [15]. The lowest carbided Fe proportion (~60%) was observed on the Fe(i)/Al<sub>2</sub>O<sub>3</sub> catalyst. The partial transformation of Fe, as well as, stabilization of the (II) oxidation state during the reduction process could be attributed to the support effect [13–14]. Concerning the Fe<sup>3+</sup> paramagnetic contributions they could be either in the form of superparamagnetic small oxide particles or embedded in the alumina support. The isomer shift value (Table 2) is not consistent with the presence of small carbide particles.

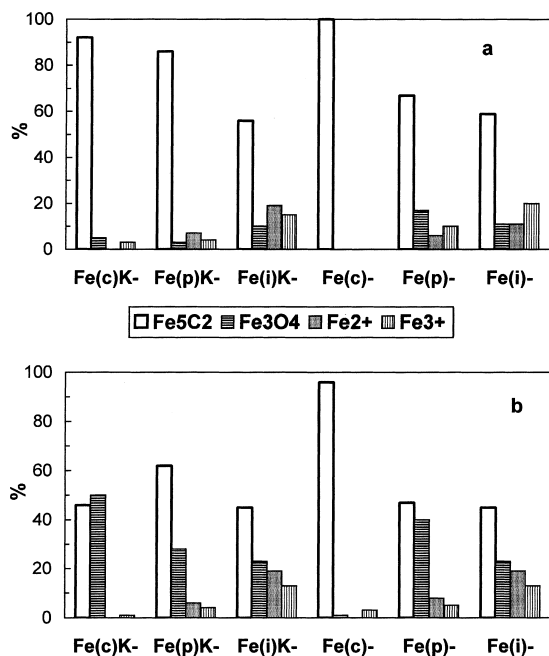


Fig. 2. Composition of Fe phases for unpromoted and K-promoted catalysts, pretreated (a) and after CO<sub>2</sub> hydrogenation (b).

The catalyst Fe(p)/Al<sub>2</sub>O<sub>3</sub> showed an intermediate transformation between that of Fe(c)- and Fe(i)/Al<sub>2</sub>O<sub>3</sub> catalysts (Fig. 2a). The reduction to  $\alpha$ -Fe of a Fe/Al<sub>2</sub>O<sub>3</sub> catalyst can be significantly delayed when prepared by precipitation in comparison with physical mixing [14]. Moreover, results in Fig. 2a seem to indicate that in this case the support effect was higher for the impregnated catalyst than for the precipitated one. The reduction-carburization of the Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalyst was affected by the presence of K. Carburization of metallic Fe is accelerated by this promoter [11,24]. When starting from the catalyst in oxide state, the addition of K can also favor Fe transformation [25]. This could be related to the effect of K to favor CO adsorption on Fe, CO being a reducing and carburizing agent. The results could be explained on the basis that Fe was easily reduced and carburized when physically mixed with the alumina. This was the case of the Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst. Interaction between Fe and the support was stronger for the catalyst prepared by precipitation and the addition of K accelerated the transformation. For the impregnated catalyst the metal–support interactions were even stronger and K was not able to accelerate the transformation.

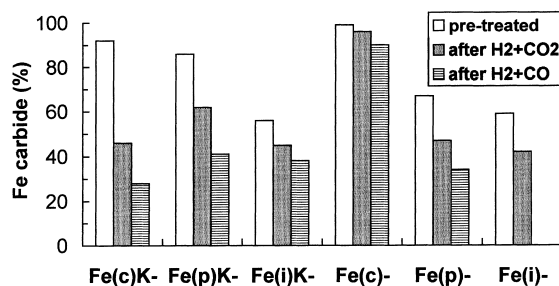


Fig. 3. Proportion of Fe carbide for the catalysts pretreated and after CO<sub>2</sub> and CO hydrogenation.

The exposure of the catalysts to the environment of the two reactions, H<sub>2</sub> + CO<sub>2</sub> (Fig. 2b) followed by H<sub>2</sub> + CO, led to a progressive reoxidation of the carbide to magnetite, which could be attributed to water formed in this reactions (Fig. 3). Only the unpromoted Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst deviated from this trend, its carbided Fe proportion remained  $\geq 90\%$ . The likely presence of residual carbon and a less intimate contact between Fe and alumina for this catalyst could give rise to a more hydrophobic surface, thus retarding reoxidation. However, K addition reversed this behavior and the promoted Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst showed the greater reoxidation extent in the promoted series (Fig. 4, Table 1). The presence of K could increase affinity or water adsorption ability, thus favoring carbide reoxidation.

### 3.2. Catalytic behavior

#### 3.2.1. CO<sub>2</sub> hydrogenation

**3.2.1.1. Activity.** CO<sub>2</sub> conversion was 21–26% after 2 days on stream. The similarity in CO<sub>2</sub> conversion for all catalysts could be attributed to several factors. The

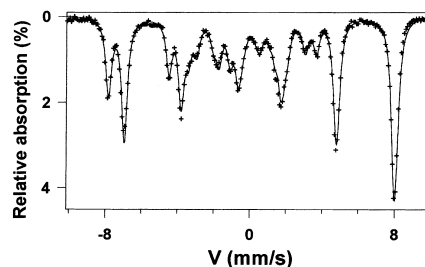
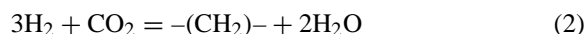
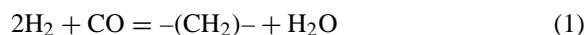


Fig. 4. Mössbauer spectrum of the Fe(c)K/Al<sub>2</sub>O<sub>3</sub> catalyst after hydrogenation of carbon oxides.

effect of the support could not be very pronounced due to the relatively high Fe loading. An inhibiting effect of water could also be mentioned. Although the CO<sub>2</sub> conversion at thermodynamic equilibrium is close to 50% [26], it seems difficult to achieve CO<sub>2</sub> conversions higher than 30% under the reaction conditions employed. A previous work using Fe catalysts promoted with K and Mn showed that a great decrease on space velocity gave rise only to a small increase on CO<sub>2</sub> conversion [9]. The results from Lee et al [5] also showed this tendency. Water produced during reaction could have an inhibiting effect, which limits increase in conversion. This effect has been previously reported for CO hydrogenation with Fe catalysts [2,27] and could play an important role in CO<sub>2</sub> hydrogenation, where higher proportions of water are formed. According to the stoichiometry for hydrocarbon formation:



the amount of water is twofold in CO<sub>2</sub> as compared to CO hydrogenation. The difference in the amount of water produced for a same conversion in both reactions is even higher if the contribution of WGS reaction for CO hydrogenation is taken into account. Since great changes in space velocities are required to obtain moderated differences in CO<sub>2</sub> conversion, the differences of activity between catalysts would be also less perceptible.

The observed similarity in conversions could also be related to a dependence between activity and proportion of carbided Fe, however, some deviations from this statement were found. As a consequence of the reoxidation of the catalyst during reaction the differences in the percentage of carbided Fe of most catalysts decreased (Fig. 2b and Fig. 3). According to this criterion the unpromoted Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst should show the highest activity, since this was the only one that was practically not reoxidized. However, CO<sub>2</sub> conversion was not higher on this catalyst. Differences between surface and bulk Fe phases could be invoked. The surface having similar composition for all catalysts and bulk reoxidation being more difficult in the case of unpromoted Fe(c)/Al<sub>2</sub>O<sub>3</sub>. But also, a certain participation of the magnetite produced by reoxidation in CO<sub>2</sub> transformation can not be ruled out, which

implies that reoxidation of the catalysts did not produce great changes in activity. As previously mentioned, the formation of carbided Fe seems to be necessary to observe activity, but the nature of the active phase(s) at the surface during reaction is still not clear, even for the more extensively studied CO hydrogenation reaction. Surface techniques such as XPS have shown limitations to establish this point [16,19].

**3.2.1.2. Selectivity.** Selectivity to CO was 7–12% and CO free selectivities to the different hydrocarbon fractions were also similar for all catalysts (Fig. 5). However, methane selectivity showed a defined tendency, and the order, Fe(c)– < Fe(p)– < Fe(i)/Al<sub>2</sub>O<sub>3</sub> was observed for both, unpromoted and K-promoted series. The decrease in methane selectivity and the increase in C5+ fraction produced by addition of K can be also observed in Fig. 5.

Alkenes proportion in the C2–C4 fraction was higher for Fe(c)/Al<sub>2</sub>O<sub>3</sub> than for Fe(i)/Al<sub>2</sub>O<sub>3</sub> catalyst for both series, with and without K (Fig. 6). The location of the Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalyst within the sequence depended on the presence of K. Thus, the precipitated catalyst showed the lower alkenes selectivity among unpromoted catalysts, but K addition approached its behavior to that shown by Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst. The internal/terminal alkenes ratio in the C4 (Table 3) and C5 fractions showed exactly the inverse order to that obtained for alkenes in the C2–C4 hydrocarbons (Fig. 6).

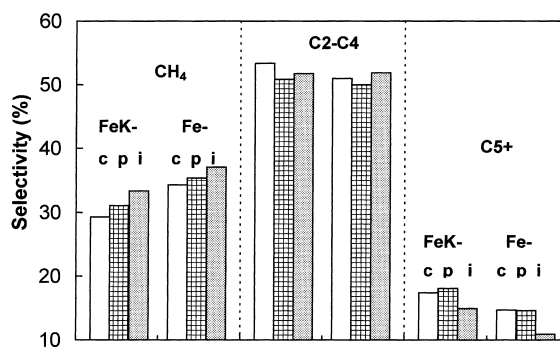


Fig. 5. CO free selectivities for unpromoted and K-promoted catalysts in the CO<sub>2</sub> hydrogenation reaction (H<sub>2</sub>/CO<sub>2</sub> = 2, 563 K, 1.2 MPa, 1.2 l/(g<sub>cat</sub> h), 2 days on stream).

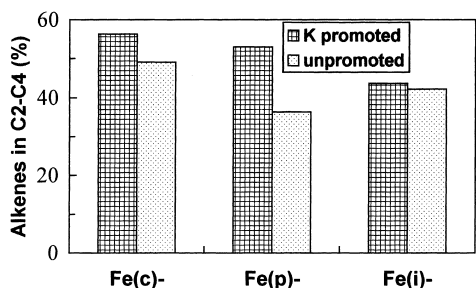


Fig. 6. Alkenes in the C2–C4 fraction for CO<sub>2</sub> hydrogenation. (563 K, 1.2 MPa, 1.2 l/(g<sub>cat</sub> h), H<sub>2</sub>/CO<sub>2</sub> = 2, 2 days on stream).

Table 3  
(*cis*-+*trans*-2-)/1-butenes for CO<sub>2</sub> hydrogenation

Catalyst	1 day on stream	2 days on stream
Fe(i)/Al <sub>2</sub> O <sub>3</sub>	1.79	2.00
Fe(i)K/Al <sub>2</sub> O <sub>3</sub>	1.28 <sup>a</sup>	1.92
Fe(p)/Al <sub>2</sub> O <sub>3</sub>	2.74	3.19
Fe(p)K/Al <sub>2</sub> O <sub>3</sub>	1.03	1.2
Fe(c)/Al <sub>2</sub> O <sub>3</sub>	1.35	1.19
Fe(c)K/Al <sub>2</sub> O <sub>3</sub>	0.74	1.07

<sup>a</sup> 3 h on stream.

Selectivity results can be well correlated with the degree of transformation achieved by the reduction–carburization pretreatment. A higher proportion of carbided Fe on the starting catalyst led to lower methane selectivity, alkanes/alkenes and internal/terminal alkene ratios (Fig. 7). Terminal or 1-alkenes are primary products in CO hydrogenation, which can undergo secondary reactions such as hydrogenation and double-bond isomerization. Both reactions are favored by an increase in H<sub>2</sub> partial pressure, and the parallelism between them has been associated with the participation of a common intermediate [23]. The trends on selectivity obtained in this case are consistent with a lower C/H ratio at the catalytic surface in the presence of higher proportions of non-carbided Fe. In CO hydrogenation this behavior has been related to the higher acidity of an oxide surface [28]. A deviation on the parameters related to secondary reactions of alkenes was obtained for the unpromoted Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 7). These reactions should depend on both, the hydrogenation activity and also on the ability of the catalyst to activate alkenes. Probably, not only the proportion, but also the nature of

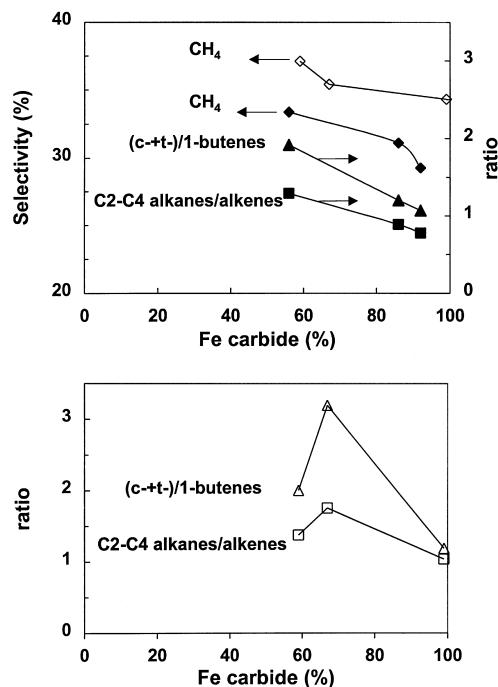


Fig. 7. Selectivity parameters in CO<sub>2</sub> hydrogenation as a function of the Fe carbide proportion in fresh pretreated catalysts. Open symbols: unpromoted catalysts, Closed symbols: K-promoted catalysts. (563 K, 1.2 MPa, 1.2 l/(g<sub>cat</sub> h), H<sub>2</sub>/CO<sub>2</sub> = 2, 2 days on stream).

the non-carbided Fe could play a role. Figs. 1, 2 and Table 2 show some differences in the non-carbided Fe species of the Fe(p) and Fe(i)/Al<sub>2</sub>O<sub>3</sub> pretreated catalysts, i.e. on the relative proportion of magnetite, Fe<sup>3+</sup> and Fe<sup>2+</sup> species.

Selectivity results correlated well with the carbided Fe proportion in the fresh catalyst, but not with that present after reaction. The unpromoted and K-promoted Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalysts corroborate this observation. In spite of its opposite reoxidation behavior (Fig. 3), they seemed to involve the highest C/H ratio in each series. Further, the K-promoted Fe(c) and Fe(i)/Al<sub>2</sub>O<sub>3</sub> catalysts with the greatest differences in selectivities in the series, showed the same carbided Fe proportion after reaction. This indicates that selectivity was more affected by the Fe phase composition of the fresh catalyst, consequence of the interaction with the support, than by reoxidation. Magnetite produced by carbide reoxidation during reaction seemed to play a different role to that of

non-carbided Fe species present in the fresh catalyst (magnetite produced by partial reduction,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  species). The properties (such as acidity, particle size or exposed surface) of these Fe phases compared to that of magnetite coming from reoxidation could be different. It is worth mentioning that Mössbauer spectra showed the expected hyperfine fields for magnetite obtained from reoxidation (Fig. 4, Table 2). However, broader lines and lower hyperfine fields were obtained for that produced by incomplete reduction in pretreatment (Fig. 1b and c, Table 2). These last features have been associated to a higher dispersion and/or to the presence of Al ions in the lattice of  $\text{Fe}_3\text{O}_4$  spinel [14]. 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 [29–30].

Results of the (*cis*-+*trans*-2-)/1-butenes ratio (Table 3) are consistent with a different participation for magnetite produced by reoxidation compared to non-carbided Fe present on fresh catalysts. The slight increase in this ratio between the first and second day on stream for each catalyst could be the result of a progressive reoxidation. However, although the carbided Fe proportion for the most catalysts was similar after 2 days on stream, the (*cis*-+*trans*-2-)/1-butenes ratio correlated well with the carbided Fe proportion in the fresh catalyst. This suggests that magnetite produced by reoxidation favored secondary reactions in a lesser extent than non-carbided Fe, which could not be reduced by the pretreatment. The unpromoted  $\text{Fe}(\text{c})/\text{Al}_2\text{O}_3$  catalyst again showed a behavior different from that of the rest of the catalysts. Between the first and the second day on stream the 2-/1-butenes ratio underwent a slight decrease instead of an increase, maybe related to the resistance of the catalyst to reoxidation.

The relationship between non-carbided Fe proportion on fresh catalyst and selectivity also explains the greater inhibition of secondary reactions (Fig. 6, Table 3) produced by addition of K over the  $\text{Fe}(\text{p})/\text{Al}_2\text{O}_3$  in comparison with other catalysts. For the former, besides the probable modification of the catalytic properties, K addition increased the Fe transformation during pretreatment (Fig. 2a). Differences in the K content could not explain this result, on the contrary, the Fe/K ratio was slightly higher for the  $\text{Fe}(\text{p})/\text{Al}_2\text{O}_3$  catalyst (Table 1).

### 3.2.2. CO hydrogenation

After hydrogenation of  $\text{CO}_2$  the catalysts were tested in CO hydrogenation. Activity was higher for the last reaction. At a temperature 10 K lower (553 K) and at the same space velocity (1.2 l/(g<sub>cat</sub> h)) CO conversions were close to 100%. Conversion decreased to near 80% by increasing twice the space velocity. Moreover, as observed in  $\text{CO}_2$  hydrogenation, conversions were similar independently of the preparation method and of the presence of K on the catalyst. Only the  $\text{Fe}(\text{p})/\text{Al}_2\text{O}_3$  catalyst deviated from this tendency, showing a lower CO conversion (between 60% and 50% instead of 80%), as well as a decreasing tendency during the 2 days on stream, which could be a consequence of deactivation for this catalyst. In principle, due to the support a greater stabilization of Fe particles could be expected for the impregnated catalyst, followed by the precipitated and finally for the physical mixed catalyst. However, residual carbon resulting from an incomplete decomposition of citrate in the  $\text{Fe}(\text{c})/\text{Al}_2\text{O}_3$  could delay sinterization [15].  $\text{CO}_2$  selectivity was close to 35% for all catalysts except for  $\text{Fe}(\text{p})/\text{Al}_2\text{O}_3$  (28%), which showed the lowest conversion.  $\text{CO}_2$  was probably produced by the secondary WGS reaction.

The same possibilities mentioned above for  $\text{CO}_2$  hydrogenation could be used to explain the similarities in CO conversion. In this case conversions were high and close to thermodynamic equilibrium, thus differences between catalysts are expected to be less evident. The Fe phase composition for the catalysts at the beginning of this reaction is shown in Fig. 2b. This composition also corresponds to the catalysts after  $\text{CO}_2$  hydrogenation since the reactions were carried out consecutively. Reoxidation also took place during CO hydrogenation (Fig. 3). Considering the tendency of most catalysts to bulk reoxidation, it seems probable the existence of a high proportion of magnetite at the surface during both carbon oxides hydrogenation. Thus, a direct participation of magnetite in the transformation of reactant gases cannot be discarded.

Tendencies observed in selectivity in CO hydrogenation when the preparation method was changed and K was added are in agreement with those shown before for  $\text{CO}_2$  hydrogenation. Fig. 8 shows the percentage of alkenes in the C2–C4 fraction as a function of conversion. For each catalyst two points are



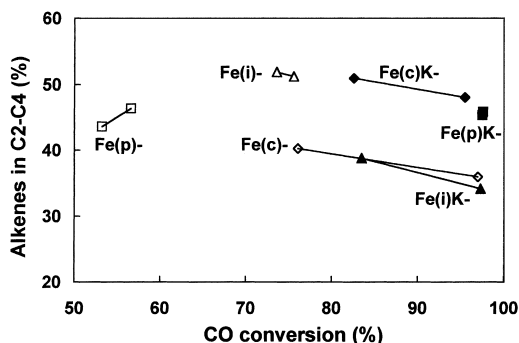


Fig. 8. Alkenes in the C2–C4 fraction vs. conversion for CO hydrogenation. (553 K, 1.2 MPa, 1.2 and 2.41/(g<sub>cat</sub> h), H<sub>2</sub>/CO = 2).

represented, which correspond to each day on stream. The observed decrease in this parameter with increasing conversion could be attributed to the participation of secondary hydrogenation. Like for CO<sub>2</sub> hydrogenation the proportion of alkenes in the C2–C4 fraction decreased in the order Fe(c)- > Fe(p)- > Fe(i)/Al<sub>2</sub>O<sub>3</sub> for the K-promoted series (Fig. 8). For the unpromoted Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst this parameter was similar to that of the K-promoted Fe(i)/Al<sub>2</sub>O<sub>3</sub>. On the other hand, the unpromoted Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalyst showed an alkenes percentage lower than its counterpart prepared by impregnation (Fig. 8), as observed for CO<sub>2</sub> hydrogenation (Fig. 6). However, a deviation is observed when these two catalysts are compared to the rest. Thus, alkenes proportion in the C2–C4 fraction for the unpromoted Fe(i)/Al<sub>2</sub>O<sub>3</sub> catalyst was higher than that of the same catalyst promoted with K and similar to that obtained with Fe(c)K/Al<sub>2</sub>O<sub>3</sub>, which showed the higher alkenes selectivity for the promoted series (Fig. 8). These trends are opposite to what normally could be expected. It is worth mentioning that the unpromoted Fe(i)- and Fe(p)/Al<sub>2</sub>O<sub>3</sub> catalysts were tested at a constant space velocity (2.41/(g<sub>cat</sub> h)) during the 2 days on stream. For the other catalysts space velocity was 1.21/(h g<sub>cat</sub>) during the first day on stream and 2.41/(g<sub>cat</sub> h) during the second one. Lower space velocities give rise to higher conversions, which lead to more oxidizing environments over the catalyst (higher partial pressures of water). The results suggest that the history of the catalyst affected its behavior and a relationship between the oxidation state of Fe and the selectivity appears again. Thus, those catalysts which were exposed to more oxidizing environments during

the first day on stream shown at the second day a lower proportion of alkenes, that is, a higher selectivity to secondary hydrogenation reaction. These results confirm the effect of reoxidation on selectivity. The buildup of wax and carbon is commonly claimed to explain the increase on secondary reactions with time on stream, as for example that observed in Table 3. This argument, however, could not explain the above results. Wax or carbon should be higher or equal for the case of higher space velocity due to the higher yield (lower conversion but higher yield). If this argument applies a higher contribution of secondary reactions should be expected for this case; which is opposite to what was observed.

### 3.2.3. Selectivity in CO<sub>2</sub> and CO hydrogenation reactions

Selectivities for carbon oxides hydrogenation reactions with the unpromoted and K-promoted catalyst, prepared by citrate decomposition and physical mixing with alumina, are shown in Fig. 9. More methane and less C5+ hydrocarbons were obtained from the CO<sub>2</sub> hydrogenation reaction, which seems to indicate a lower chain growth probability for this reaction. The requirement of CO<sub>2</sub> dissociation at the surface (CO<sub>2</sub>(s) = CO(s) + O(s)) as an additional step, prior to the reaction between adjacent adsorbed carbon species for C2+ hydrocarbon formation, could be involved in this result. For both reactions K promotion decreased methane formation (Fig. 9) and increased the proportion of alkenes (Figs. 6 and 8). In the case of CO hydrogenation, selectivity to the C2–C4 alkenes fraction (C2–C4=) remained unchanged with the addition of

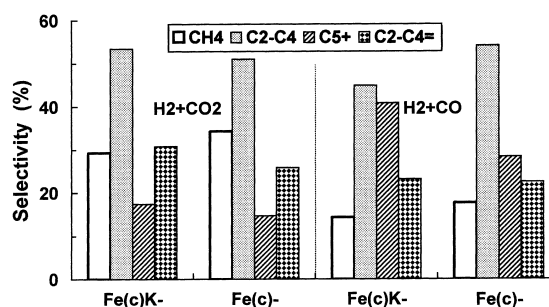


Fig. 9. CO<sub>3</sub> free selectivities for the unpromoted and K-promoted Fe(c)/Al<sub>2</sub>O<sub>3</sub> catalyst in CO<sub>2</sub> and CO hydrogenation ( $\gamma=1$  in H<sub>2</sub> + CO<sub>2</sub>,  $\gamma=2$  in H<sub>2</sub> + CO).

K. The increase in alkenes proportion was compensated by the decrease in the total C2–C4 fraction due to a higher chain growth probability. However, for the CO<sub>2</sub> hydrogenation the increase in alkene formation seemed to predominate and K addition led to a slight increase in the selectivity to the C2–C4 alkenes fraction (Fig. 9). The achievement of high C2–C4 alkenes selectivity with K-promoted Fe catalysts appears to be favored for CO<sub>2</sub> compared to CO hydrogenation.

#### 4. Conclusions

The preparation procedure of Fe/Al<sub>2</sub>O<sub>3</sub> catalysts affected the degree of reduction–carburization achieved by pretreatment. Fe transformation was more difficult for the impregnated catalyst than for the precipitated one, whereas the higher carbide proportion was achieved for a physical mixing of decomposed Fe citrate and alumina. This order of transformation can be directly related to the degree of interaction with the support. The addition of K modified in some cases the transformation of Fe, accelerating the reduction–carburization process and increasing the reoxidation during the carbon oxide hydrogenation reactions. Activity was similar for all catalysts; however, small but consistent differences in selectivity were obtained, which could be correlated to the Fe phase composition of pretreated catalysts. Higher proportions of non-carbided Fe gave rise to more methane, alkanes and internal alkenes formation, which could be associated to higher H/C surface ratios. During both hydrogenation reactions, reoxidation of carbide to magnetite took place. However, selectivity depended mainly on the Fe phases in the fresh catalyst.

Analogies between both reactions, CO<sub>2</sub> and CO hydrogenation were evidenced through the similar responses to changes in the preparation procedure of the catalysts and to the addition of K. Lighter hydrocarbons were produced from CO<sub>2</sub>, and through K promotion higher selectivities to the C2–C4 alkenes were obtained from the former reaction.

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