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Influence of the Support on the Activity and Selectivity of High Dispersion Fe Catalysts in the Fischer–Tropsch Reaction

MARÍA V. CAGNOLI, SERGIO G. MARCHETTI, NORMA G. GALLEGOS,
ANA M. ALVAREZ, ROBERTO C. MERCADER,* AND AVEDIS A. YERAMIAN

*Centro de Investigación y Desarrollo en Procesos Catalíticos (CINDECA),[1] Calle 47 N° 257 (1900), La Plata, Argentina; and *Departamento de Física, Facultad de Ciencias Exactas, La Plata, Argentina*

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In order to study the influence of the support on high dispersion catalysts used for the CO hydrogenation reaction, two catalysts, Fe/SiO_2 and Fe/Al_2O_3, were prepared by the dry impregnation method. Selective chemisorption of CO, volumetric oxidation, and Mössbauer spectroscopy were used to determine the Fe species present as well as the metallic crystal size, the degree of dispersion, and the reduction percentage. The presence of small Fe^0 crystallites with high dispersion was determined in both catalysts. Reaction rates were measured in a differential reactor and significant differences, about one order of magnitude less for the Al_2O_3 than for the SiO_2 supported catalysts, were found in the methane turnover frequencies. They are attributed to the interaction between the metal and the supports. The selectivity difference is also discussed in connection with distinct surface properties.

INTRODUCTION

Iron has been the typical metal used for the Fischer–Tropsch synthesis; in recent years investigations have been directed toward supported metal catalysts on high specific area oxide instead of toward mass catalysts (*1–4*).

There are several reasons why high area supported catalysts are of practical importance and interest: (i) the support may interact with the metal, changing its electronic properties and concurrently its activity and selectivity; (ii) the metal dispersion becomes a parameter that may be varied for the purpose of studying the reaction sensitivity to structure; and (iii) a lower metal sintering may occur.

Since the presence of the support may alter the active phase catalytic properties (*5*) it is interesting to make a comparative study of two catalysts prepared in the same way on different supports and with very similar metallic crystal sizes.

Even though some studies have been reported regarding the effect of support, they have not dealt with iron or with the Fischer–Tropsch reaction. It has been found that, in the case of the methanation reaction, the Pt activity does not substantially vary when the support is changed. On the other hand, in the same reaction, Pd activity is much more affected by the type of support. Consequently, in this study, attention has been centered on the effect that supports may have on the activity and selectivity of highly dispersed Fe/SiO_2 and Fe/Al_2O_3 catalysts in the CO hydrogenation reaction.

The nature and extent of these effects are of interest both theoretically and practically, since not only is there a possibility of altering the product distribution by means of an adequate catalyst selection but also certain effects inherent in the small crystals may be revealed.

EXPERIMENTAL METHODS

Sample Preparation

The Fe/SiO_2 catalyst was prepared by dry impregnation of Kieselgel 100 (Merck) sili-

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[1] Attached to the Facultad de Ciencias Exactas, UNLP, associated with CONICET.

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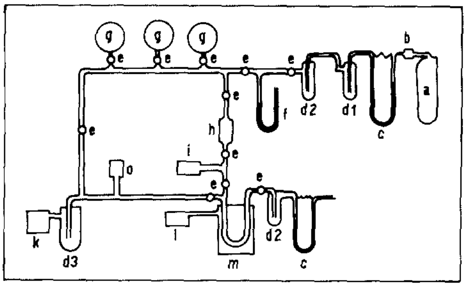

FIG. 1. Chemisorption equipment: (a) H_2 tube; (b) flow metering valve; (c) flow meter; (d1) Pd trap; (d2) molecular sieve trap; (d3) liquid air trap; (e) high vacuum valve; (f) Hg manometer; (g) gas reservoirs; (h) calibrated volume; (i) transducer; (k) pumping system; (l) temperature indicator; (m) furnace; (o) Penning gauge.

cagel with 400 m^2/g specific area, 1 cm^3/g pore volume, and 0.06–0.20 mm particle size. An impregnating solution of $Fe(NO_3)_3 \cdot 9\ H_2O$ was used with a concentration strong enough to yield a catalyst of ca. 5 wt%. The pH of this solution was 0.5. The precursor was air dried for 20 days and then vacuum dried following a heating program used by Stanfield and Delgass (*6*).

The solid thus obtained was characterized in a previous work (*7*), which demonstrated the existence of α-Fe_2O_3 and a low percentage of Fe^{3+} exchanged with the support. Finally, the catalyst was obtained by reduction of the precursor in flowing H_2 at 60 cm^3/min, after purification through a Pd black bed and 5-Å molecular sieve. The following program was used for thermal reduction of the sample: 0.5 h at 455 K; 0.5 h at 509 K; 0.5 h at 559 K; 0.5 h at 600 K; 0.5 h at 644 K; 26 h at 698 K.

The Fe/Al_2O_3 catalyst was prepared with Rhone Progil γ-Al_2O_3 Spheralite with 280 m^2/g specific area, 0.5 cm^3/g pore volume, and size particles less than 0.15 mm. Impregnation, drying, and reduction were carried out in exactly the same manner as those for Fe/SiO_2 and the existence of α-Fe_2O_3 was determined in the oxide precursor (*7*). An impregnating solution was used to yield a catalyst of ca. 4 wt%, in order to obtain equivalent surface concentrations on both supports.

Characterization Techniques

CO chemisorption. Measurements were made on the catalysts in conventional static volumetric equipment with grease-free vacuum valves using CO as titration reactant. An equipment diagram is shown in Fig. 1.

It has been found that CO adsorption at 195 K is an exact measure of Fe^0 surface area (*8–11*) which chemisorbs only on this species and not on Fe_3O_4, Fe_2O_3, or FeO (*12*). Therefore, the experiments were carried out under these conditions.

Five points in the 200- to 500-Torr range (1 Torr = 133.3 N/m^2) were obtained for determination of the adsorption isotherms. Twenty minutes was required to reach equilibrium pressure at the first point once the sample was exposed to adsorbate. The Emmett (*8, 9*) technique was used to measure CO chemisorption. Evacuation of the sample for 30 min at 5×10^{-5} Torr prior to the determination of the second isotherm eliminated the weakly adsorbed CO. The difference between both isotherms in the zone where they became parallel (approximately 350 Torr) was used to obtain the chemisorbed amount of CO on the superficial Fe, for which a stoichiometry of 2 : 1 was assumed for Fe : CO. Approximately 3 g of sample was loaded in the reactor, which was welded to the adsorption unit. The sample was reduced as mentioned above. After the reduction treatment the sample was evacuated for 9 h at 423 K and 1 h at 673 K to obtain a final pressure of about 10^{-6} Torr. It was then cooled under constant pumping to 195 K. This temperature was reached by means of an acetone and dry ice bath. After obtaining both isotherms, the reactor apparent volume was determined using He under the same conditions as those used for measuring adsorption. In each case a blank run was made on the corresponding supports treated in the same manner as the catalyst.

Volumetric oxidation. Volumetric oxidation experiments were performed in the adsorption equipment described above. These experiments were based on the fact that, above 620 K in O_2, all the iron species present in the catalyst in oxidation states lower than Fe^{3+} oxidize to Fe_2O_3 (*10*). Once reduced, the samples were evacuated and oxidized with an appropriate amount of pure O_2 at 620 K. The experiment was completed when oxygen pressure variation no longer occurred. The amount of O_2 uptaken was thus determined.

Mössbauer spectroscopy. The Mössbauer spectra were obtained in a 512 channel, transmission geometry, constant acceleration spectrometer. A source of ^{57}Co in Rh matrix of 10 mCi was used. Velocity calibration was performed against a 6-μm thick α-Fe foil. All isomer shifts (IS) mentioned in this paper are referred to this standard. All spectra were taken at room temperature, which was kept constant at 293 ± 1 K.

Considering the low iron content of the samples (5 wt%), the maximum possible thickness of absorber that did not produce excessive broadening of the lines was selected.

The spectra were evaluated by using a least-squares nonlinear computer fitting program with constraints. Lorentzian lines were considered with equal widths for each spectrum component. The baseline was fitted to a second-order polynomial and the velocity nonlinearity to a third order polynomial. The spectra were folded to minimize geometric effects.

The oxide precursors of the catalysts were reduced, following the above-mentioned program, in an *in situ* Mössbauer cell described in Ref. (*13*).

Activity measurements. The experiments were carried out with a fixed-bed, Pyrex, 1-cm-diameter reactor (Fig. 2) which generally contained 800 mg of precursor. The reactor was set inside an electric furnace where the temperature was maintained by a proportional controller. The design allowed H_2 and CO to be fed into the reactor either separately or as a mixture. The O_2 was removed from the H_2 stream by means of a Pd black trap followed by a silica gel trap, whereas the $Ni(CO)_4$ that might have resulted from reaction of the CO with any equipment fittings was retained in a glass ball trap heated to 473 K.

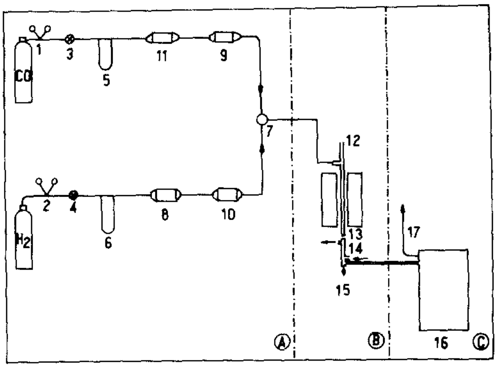

FIG. 2. Experimental equipment for measuring activity. (A) Gas flow and feed system: (1, 2) reducer gauges; (3, 4) needle valves; (5, 6) capillary flow meters; (7) mixers; (8) Pd trap; (9, 10) silica gel dehydrators; (11) carbonyl-retaining trap. (B) Reaction system: (12) reactor; (13) furnace; (14) coolant; (15) collector. (C) Analysis system: (16) chromatograph; (17) vent.

All measurements were taken at 543 K and 760 Torr of total pressure with $H_2:CO$ ratios of 3 : 1 and 2 : 1. Precursor reduction was performed *in situ* according to the above-mentioned heating program.

The products were analyzed in a Carlo Erba chromatograph equipped with a flame ionization detector, using a Chromosorb P (80/100) column impregnated with 30 wt% tricresyl phosphate. This column resolved C_1 through C_4 alkanes and alkenes, but did not separate saturated and unsaturated C_2 components.

RESULTS

The different species of iron present in the catalyst and their percentages were determined by Mössbauer spectroscopy. The percentages were calculated assuming that the Fe recoil-free fractions in the various components were equal. These results are shown in Table 1.

TABLE 1

Iron Species in Reduced Catalysts

Catalyst species	Fe/SiO_2 (%)	Fe/Al_2O_3 (%)
Fe^0_{sp} [a]	9	27
Fe_3O_4	7	—
FeO	80	—
$Fe^{3+}_{exchanged}$	4	—
$FeAlO_3$	—	27
$FeAl_2O_4$	—	46

[a] SP, superparamagnetic.

Figure 3 shows the Mössbauer spectra of both catalysts and Table 2 lists their Mössbauer parameters. From these spectra the total number of Fe^0 atoms in each catalysts was calculated.

TABLE 2

Mössbauer Parameters of Reduced Catalysts

	Parameters (mm/s)	Fe/SiO_2	Fe/Al_2O_3
a	IS	−0.03 ± 0.04	0.00 ± 0.00(*h*)
	Γ	0.60 ± 0.10	0.52 ± 0.06
b	IS	0.82 ± 0.02	—
	Γ	0.33 ± 0.12	—
c	IS	0.83 ± 0.04	—
	Δ*Q*	0.79 ± 0.07	—
	Γ	0.89 ± 0.04	—
d	IS	0.34 ± 0.00(*h*)	—
	Δ*Q*	0.79 ± 0.00(*h*)	—
	Γ	0.45 ± 0.00(*h*)	—
e	IS	—	0.32 ± 0.01
	Δ*Q*	—	1.07 ± 0.02
	Γ	—	0.52 ± 0.02
f	IS	—	1.17 ± 0.03
	Δ*Q*	—	1.29 ± 0.05
	Γ	—	0.75 ± 0.05
g	IS	—	1.22 ± 0.01
	Δ*Q*	—	1.98 ± 0.03
	Γ	—	0.49 ± 0.04

[a] Fe^0 superparamagnetic.
[b] Fe_3O_4 superparamagnetic.
[c] FeO.
[d] Fe^{3+} exchanged.
[e] Fe^{3+} ($FeAlO_3$).
[f] Fe^{2+} ($FeAl_2O_4$).
[g] Fe^{2+} ($FeAl_2O_4$).
[h] Parameter constrained in fitting.

The total number of superficial Fe^0 atoms was calculated from the chemisorption measurements. The ratio of superficial Fe^0 atoms/total Fe^0 atoms is a measure of the metal dispersion (*D*) on the support. The average volumetric-superficial diameters were calculated from the following expression (*11, 14*): $d_{VA}(\text{Å}) = 7.53/D$. When these calculations were carried out, it was taken into account that the alumina support showed an important CO chemisorption (28 μmol of CO/g of catalyst) which was subtracted from the total value. The silica did not adsorb CO under test conditions. Figure 4 shows two typical isotherms.

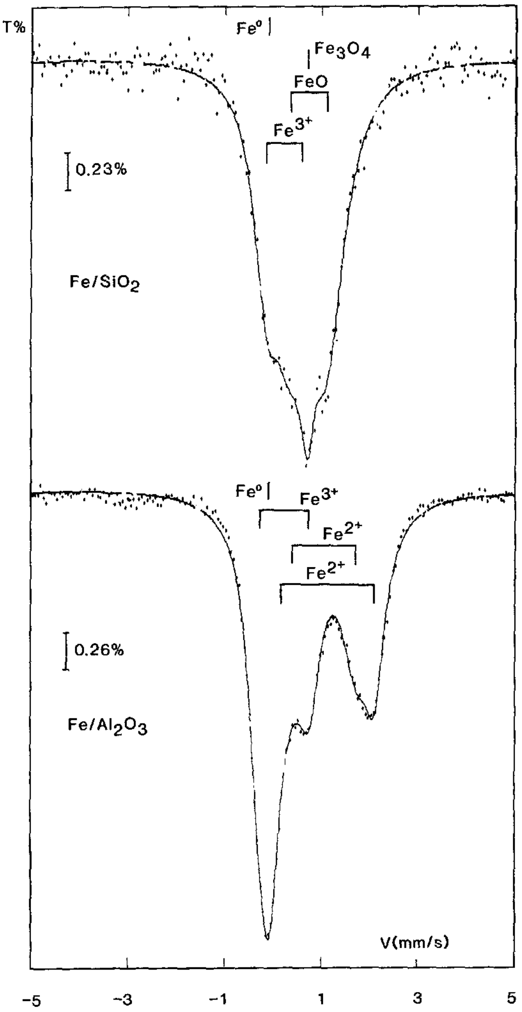

FIG. 3. Mössbauer spectra of reduced catalysts.

TABLE 3

General Characterization of Reduced Catalysts

Catalyst	wt% Fe[a]	n_{co}[a] (μmol/g)[b]	MA (m²/g)[c]	% R[d]	% D[e]	d_{VA}(Å)[f]	O$_2$ consumption (μmol/g)		ε%[g]
							Mössbauer	Exp.	
Fe/SiO$_2$	5.78	29 ± 2	3.3	9	63	12	283	276 ± 14	3
Fe/Al$_2$O$_3$	4.17	52 ± 3	5.9	27	52	14	236	238 ± 12	1

[a] wt% Fe, all weights reported on a dry, reduced basis (determined in Ref. (*7*)).

[b] n_{co}[a], number of micromoles chemisorbed per gram of catalyst (determined by triplicate).

[c] MA, metallic area.

[d] % *R*, percentage of reduction to Fe^0.

[e] % *D*, percentage of dispersion.

[f] d_{VA}, average volumetric-superficial diameter.

[g] ε%, relative error.

From the results shown in Table 1 the amount of O$_2$ necessary to oxidize all Fe species to Fe$_2$O$_3$ was calculated. This value was experimentally tested through the volumetric oxidation measurements. The results obtained are shown in Table 3.

Activity and selectivity measurements for both catalysts were made using a fresh sample in each experimental run. The time on stream for each run was 168 h in all cases. CH$_4$ turnover frequencies vs time are plotted in Figs. 5 and 6 for H$_2$: CO ratios of 3 : 1 and 2 : 1. In order to calculate these values, one active site per atom of surface Fe^0 was considered for comparative purposes. The number of atoms of surface Fe^0 was evaluated from the chemisorption experiments mentioned above.

Figures 7 and 8 show hydrocarbon selectivity of the catalysts. The histograms represent the product distribution after the steady state was achieved.

DISCUSSION

Characterization of Reduced Catalysts

As shown in Table 1, the iron species found in the catalysts depend on the type of

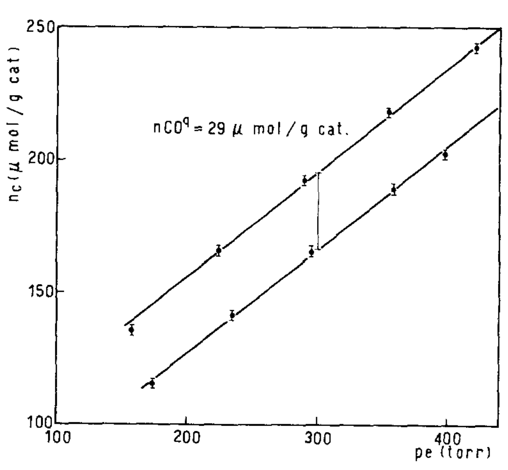

FIG. 4. Adsorption isotherms for catalyst Fe/SiO$_2$.

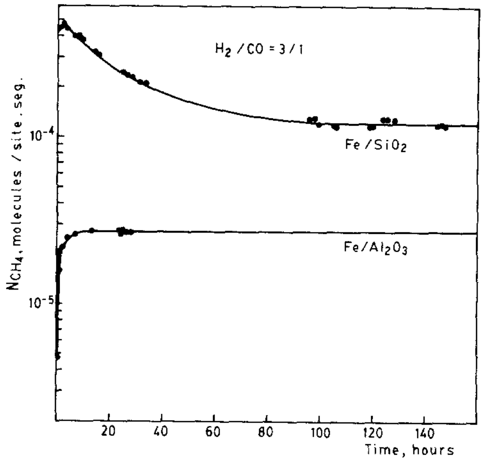

FIG. 5. Turnover frequencies of CH$_4$ vs time of reaction.

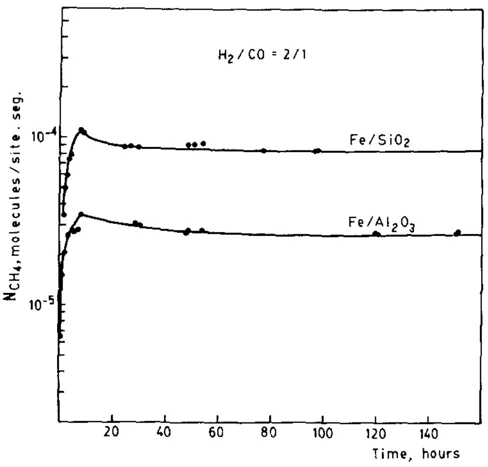

FIG. 6. Turnover frequencies of CH_4 vs time of reaction.

support used; e.g., neither Fe_3O_4 nor FeO was observed on Al_2O_3, but considerable amounts of both were present on SiO_2.

The existence of superparamagnetic Fe_3O_4 has been reported by several authors as bulk microcrystals. McNab *et al.* (*15*) reported the Mössbauer parameters of spectra produced by magnetite particles of 99 Å in diameter. They observed, at room temperature, an unsplit broad signal (Γ = 2.8 mm/s) and an isomer shift of about 0.6 mm/s. Mørup and Topsøe (*16*) found, for particles of 60 Å diameter at 260 K, an isomer shift of 0.6 mm/s and a Γ of 1.2 mm/s. The isomer shift of the Fe species reported here, 0.82 ± 0.02 mm/s, is rather high compared to the values found in the literature. However, despite the much narrower linewidth in comparison to the wider lines observed in the previous papers (*15*, *16*), the present data point to the presence of superparamagnetic Fe_3O_4.

The Mössbauer parameters for FeO are similar to the values reported by Hobson and Gager (*17*) (IS = 0.76 mm/s; ΔQ = 0.98 mm/s) for small crystallites of ferrous oxide on silica, assuming that the Fe^{2+} ion occupies an octahedral position of a cubic lattice of oxide ions in a (100) face. These cations would have four oxide ions in the same plane and one below as nearest neighbors. This indicates the presence of FeO as clusters where most of the Fe^{2+} is at the surface.

Table 1 also shows a certain amount of Fe^{3+} which corresponds to a small fraction exchanged with the silica support during the preparation stage (*7*). The Mössbauer parameters of this species are similar to those reported by Huang and Anderson (*18*) (IS = 0.41 mm/s; ΔQ = 0.69 mm/s) for Fe^{3+} exchanged with silica.

In Fe/Al_2O_3 catalyst, the Fe^{3+} can be assigned to a $FeAlO_3$-type compound (*19*). Other authors (*20*, *21*) also have proposed the existence of a reduction-resistant Fe^{3+} species. This compound might have gone unnoticed in the precursor characterization (*7*) because its Mössbauer parameters are

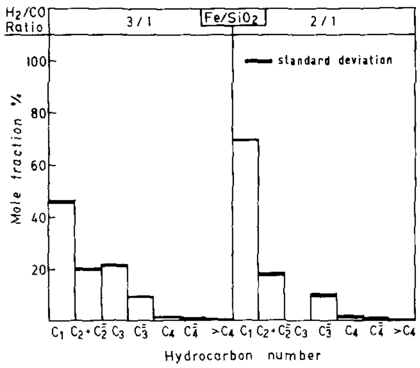

FIG. 7. Product distribution for Fe/SiO_2 catalyst.

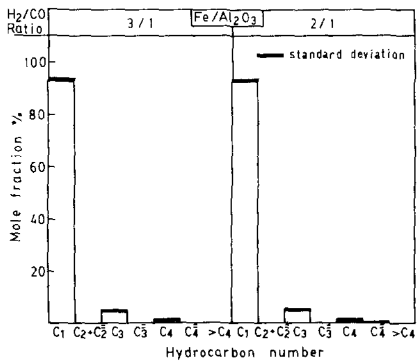

FIG. 8. Product distribution for Fe/Al_2O_3 catalyst.

the same as those for α-Fe_2O_3, the Fe^{3+} environment being identical in both compounds. Also, diffuse reflectance spectroscopy (DRS) shows a very low continuous absorption which is completely masked by the precursor spectrum. Moreover, in the temperature range studied by temperature programmed reduction in Ref. (*7*) (293–1373 K) the compound shows a small hydrogen uptake which is almost continuous between 673 and 1273 K and appears in the precursor study by TPR as a long tail. DRS and TPR studies carried out on the $FeAlO_3$ prepared in the laboratory according to the technique described in Ref. (*22*) confirmed these results. As can be seen in Table 2, there is agreement between the Mössbauer parameters obtained for this species and those reported by Sueiras *et al.* (*20*) (IS between 0.17 ± 0.02 and 0.28 ± 0.03 mm/s; ΔQ between 0.73 ± 0.01 and 1.92 ± 0.01 mm/s).

Table 2 also shows the presence of a large amount of $FeAl_2O_4$. Its Mössbauer spectrum consists of two doublets assigned to Fe^{2+} occupying the octahedral holes (larger ΔQ) and Fe^{2+} situated in tetrahedral positions. This identification with a spinel having a partial inversion agrees with the results of Yagnik *et al.* (*23*) (IS = 1.43 ± 0.10 mm/s, ΔQ = 2.76 ± 0.10 mm/s, and IS = 1.01 ± 0.10 mm/s; ΔQ = 1.39 ± 0.10 mm/s). The difference observed could be attributed to the distinct structure of α-Al_2O_3 used by these authors and the γ-Al_2O_3 used in this work.

Superparamagnetic Fe^0 appears on both supports. Its signal displays one broadened singlet instead of the sextuplet that is characteristic of larger crystals, denoting the presence of particles having diameter smaller than 25 Å (*20, 21, 24, 25*).

It was easy to assign the signals originated in each of the Fe species present in the catalysts after a review of the previous work on this same type of system. Indeed, for Fe/Al_2O_3 catalyst, the Mössbauer lines were assigned to different species, in consideration of very similar spectra reported in the literature (*20*). It is worth mentioning that, unlike the procedure of Sueiras *et al.* (*20*), in this work the Fe^{2+} species were fitted with two doublets according to the two previously mentioned sites of Fe^{2+} in a partially inverted spinel in agreement with Refs. (*23, 26, 27*). These assumptions, based on physical facts, produced fits with more reasonable linewidths. The characterization of Fe/SiO_2 is not so straightforward since the iron species present in this catalyst contribute to the Mössbauer spectrum with unresolved signals. Nevertheless, performing the fits as previously described according to the reports in the literature gave consistent results. Thus, taking into account that for supported materials lower loadings mean lower crystalline size and reducibility (*21*), the values observed in this work are consistent with those reported by Raupp and Delgass (*28*). These authors, for a catalyst of Fe/SiO_2 prepared in a very similar way, with a 10 wt% loading, observed, according to the analysis of their Mössbauer spectra, a supported particle size of less than 40 Å and attained a degree of reduction of only 15%. Niemantsverdriet *et al.* (*25*) for a 5 wt% iron on carbon catalyst obtained a Mössbauer spectrum very similar to the one reported in this paper. The different species involved in the spectra reported by these authors were discriminated when the Mössbauer studies were extended to temperatures of 77 and 4.2 K. In this work the identification is achieved by the combined use of Mössbauer spectroscopy and volumetric oxidation.

As can be observed in Table 3, there is a good agreement between the experimental oxygen uptake for the complete reoxidation of the reduced catalyst and the consumption of oxygen that should occur if the percent amounts of each species obtained from the Mössbauer spectra are considered correct. Any other tentative assignment leads to unacceptable differences between both techniques, as can be seen in Table 4. This correspondence is evidence of the reliability of the method used.

TABLE 4

Comparison of the Oxygen Consumption with the Amounts Turning Out from the Proposed Mössbauer Fits

	Calc. O_2 consumption (μmol/g)	$\varepsilon\%$[a]
Fe/SiO_2		
Correct fit adopted	283	3
Fit without Fe^0	208	25
Fit without Fe_3O_4	339	23
Fit without Fe^0 and Fe_3O_4	225	18
Fe/Al_2O_3		
Correct fit adopted	236	1
Fit without $FeAlO_3$	315	32

[a] $\varepsilon\%$, relative error with respect to experimental oxygen consumption per gram of catalyst (see Table 3).

The dispersion and d_{VA} values obtained from chemisorption of CO and Mössbauer spectra are presented in Table 3. It can be observed that there are not differences for the Fe^0 crystallite diameters for both catalysts (within the experimental error). The values of d_{VA} obtained from the chemisorption of CO fall below 25 Å, the upper limit indicated by the Mössbauer spectra.

Activity and Selectivity Measurements

For each CO/H_2 relationship (Figs. 5 and 6) the activity of Fe/Al_2O_3 catalyst is one order of magnitude lower than that of Fe/SiO_2. Since in both catalysts the crystallite size is equal, the difference in activity can be attributed to the different degrees of metal–support interaction.

As has already been mentioned, electronic properties of the metallic crystallites may be affected by the support. A decrease in the electronic charge of the orbitals of the metallic atoms might be expected (*4, 14*). This would cause a reduction in the degree of back-donation from these orbitals toward the antibonding orbitals of the chemisorbed CO, i.e., the C–O bond is weakened in a lower degree. Since dissociation of the adsorbed CO is considered to be a critical stage in the synthesis mechanism, this effect would cause a reduction in the catalyst activity which is more significant when the degree of metal/support interaction is higher. Thus, on this basis, the relationship of activities between both catalysts can be justified, being independent from the CO/H_2 ratio used. Assumption of a greater metal–support interaction in the Fe/Al_2O_3 is justified by the formation of an important amount of two compounds like $FeAlO_3$ and $FeAl_2O_4$. On the other hand, in the Fe/SiO_2 catalyst only a small amount of Fe^{3+} is exchanged with the support.

There are also considerable differences in the selectivities. Thus, for $H_2:CO = 3:1$, the Fe/Al_2O_3 catalyst yields almost exclusively methane and absolutely no olefins, whereas for Fe/SiO_2 the methane fraction is very low (compared to what is normally reported (*3*) for this catalyst) and there is considerable production of olefins. These differences cannot be attributed to different conversion values. If it is assumed that, just as for Ru on different supports, a lower CO conversion favors olefin production (*29, 30*), in this case the lower conversion corresponds to the Fe/Al_2O_3 catalyst (0.1 vs 0.8% for Fe/SiO_2). There are only two possible explanations: (i) that again the effect of metal–support interaction is responsible for this behavior, and (ii) that Al_2O_3 has sites capable of chemisorbing olefins (*31*) and these may easily hydrogenate (ethylene may hydrogenate between 393 and 773 K on Al_2O_3 (*31*)), so it is reasonable to expect that no olefins will be found when using the Fe/Al_2O_3 catalyst, in contrast to what occurs with Fe/SiO_2.

The absence of ethane on Fe/Al_2O_3 is attributed to its hydrogenolysis on the metal, which increases the CH_4 percentage (*4, 32*). This hydrogenolysis can only occur, to a considerable extent, in low-molecular-weight hydrocarbons, since the heaviest require the presence of several contiguous vacant sites (*32*). In the Fe/SiO_2 catalyst this effect was not noticed and should not be present since there is a larger and stronger adsorption of CO. Therefore, there are no contiguous vacant metallic sites which should allow the aforementioned effect. For both catalysts the selectivities show a similar trend for the reactants ratio $H_2:CO = 2:1$.

If the selectivities for the same catalyst are compared for two $H_2:CO$ ratios, it is observed that the Fe/Al_2O_3 is insensitive to feed composition changes (Fig. 8). Strikingly, for Fe/SiO_2, the methane percentage increases when the CO amount in the gas phase is increased. It should be mentioned that for the ratio $H_2:CO = 3:1$ the overall carbon monoxide conversion increases markedly. The change in selectivity is attributed to an enhancing effect of the higher partial pressure of H_2 on the adsorption of CO. This effect was detected on Ru/SiO_2 catalyst (*33*) up to 473 K. Since the heat of adsorption of carbon monoxide on iron is 30–35 kcal/mol (*2*) and 32 kcal/mol for H_2 (*34*) a similar effect should be expected for the Fe/SiO_2 catalyst. Subramanyam *et al.* (*35*) have measured the coadsorption isotherms for H_2 and CO at different ratios of these gases at 370 K on iron catalyst. If the isotherms presented in Fig. 8 of Ref. (*35*) are extrapolated to higher pressures, one can assume that for the partial pressures used in this work, an increase in the hydrogen partial pressure in the gas phase will lead to an increase in the amount of CO chemisorbed. This effect, namely a higher adsorption of CO, should lead to a different ratio of adsorbed carbonaceous species and hydrogen. This should produce a lower percentage of methane and a higher percentage of hydrocarbons. However, the possibility of a kinetic effect should not be discarded. The crystallite size used in this work should be associated with this effect. As the crystallite size decreases the dissociation time for CO is increased since the active phase is less basic; small metal particles have a higher ionization potential and electron affinity (*36, 37*). When the iron crystal size is big enough the carbon monoxide dissociation proceeds rapidly even at room temperature (*38*). For very small crystallites, molecular CO would stay adsorbed for a period long enough to observe the coadsorption effect.

The values obtained here for turnover frequencies differ greatly from those obtained by Amelse *et al.* (*3*) when referred to the conditions of the present experiments (1.4×10^{-4} molecules site^{-1} s^{-1} vs 6.5×10^{-3} molecules site^{-1} s^{-1} for Amelse). If one keeps in mind that the catalyst of Amelse *et al.* has crystals of about 130 Å diameter, whereas those used in this work are about 12 Å, the differences would confirm the sensitivity to structure of the methanation reaction, as mentioned by different authors for Fe and other metals (*4, 39*).

Finally, although iron is carburized during the reaction, to correlate the activity with the Fe^0 crystal size of the fresh catalyst seems to be adequate. This correlation has already been used by other authors (*11, 39, 40*). One of the models that explains this reaction, namely the competition model, provides a possible justification for the correlation (*41*).

CONCLUSIONS

(1) Two catalysts have been obtained: Fe/SiO_2 and Fe/Al_2O_3. The iron species present in the former are: Fe^0, FeO, Fe^{3+} exchanged with the support, and probably Fe_3O_4. In the latter, there are Fe^0, $FeAlO_3$, and $FeAl_2O_4$.

(2) Using CO chemisorption and Mössbauer spectroscopy, it was determined that the Fe^0 crystal size is about 12 Å for Fe/SiO_2 and 14 Å for Fe/Al_2O_3. Therefore, both sizes are similar enough to prevent attributing the differences in the catalytic properties of the solids to dispersion effects.

(3) Differences in activity between both catalysts are the results of different degrees of metal–support interaction, the turnover frequency decreasing as the interaction is greater (from SiO_2 to Al_2O_3).

(4) The results reported in this paper do not allow the observed differences in selectivity to be attributed definitely to a metal–

support interaction or to the disparity of surface properties between Al_2O_3 and SiO_2. However, we believe that the latter interpretation is more likely.

(5) For the same catalyst, namely Fe/SiO_2, the differences in selectivity observed for distinct ratios of H_2 to CO were attributed to coadsorption properties of the reactants.

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