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In Situ Mössbauer Spectroscopic Characterization of Fe/Al_2O_3 and Fe/ThO_2 Fischer–Tropsch Catalysts

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Mössbauer spectroscopy has been used to study *in situ* the transformation of Fe/Al_2O_3 and Fe/ThO_2 catalysts under different stages of calcination, reduction, carburization, and Fischer–Tropsch synthesis reactions. At room temperature the calcined Fe/Al_2O_3 catalyst is composed of Fe^{3+} ions strongly interacting with the alumina support, and about 10% of bulk α-Fe_2O_3. The calcined Fe/ThO_2 sample consists of a bulk phase of α-Fe_2O_3. After reduction in flowing hydrogen at 400°C, the Fe/Al_2O_3 catalyst contains about 70% of α-Fe and 30% of $FeAl_2O_4$ (a spinel phase). The calcined sample of Fe/ThO_2 is completely reduced to α-Fe in flowing H_2 at 400°C in 9 h. When the reduced Fe/Al_2O_3 catalyst is carburized at 250°C in synthesis gas ($2H_2/CO$), all the α-Fe is converted to an interstitial alloy of a composition resembling Hägg's carbide and ε'-$Fe_{2.2}C$. Carburization of the reduced Fe/ThO_2 catalyst at 250°C in $2H_2/CO$ converted about 50% of the α-Fe to χ-Fe_5C_2. However, after the Fischer–Tropsch synthesis reaction, the remaining amount of α-Fe in the catalyst is also changed to χ-Fe_5C_2. The product distribution in the case of Fe/Al_2O_3 reveals a high selectivity for unsaturated and saturated C_3 hydrocarbons. For the Fe/ThO_2 catalyst, calcined for 24 h, a high selectivity for C_5–C_{10} hydrocarbons is shown. For the sample Fe/ThO_2 calcined for 48 h, a high selectivity for C_5 hydrocarbon and oxygenated products is obtained.

INTRODUCTION

The catalytic synthesis of hydrocarbons from a mixture of carbon monoxide and hydrogen (synthesis gas) is a well-studied reaction; it was first reported by Sabatier in 1902 for the synthesis of methane over a Ni catalyst. Since then, this reaction has been extensively studied (*1–12*) by many other workers and with a variety of catalysts. Many excellent reviews have been written that describe this work (*13–16*).

However, nearly all of the early research was completed before the development of sensitive analytical instruments that can determine the surface chemistry of an *in situ* catalyst under reaction conditions. During the last 10 years many sensitive and sophisticated techniques have been developed for catalyst characterization; unfortunately most of these techniques have inherent drawbacks such as the requirements of ultrahigh vacuum or that the catalyst be in the form of a single crystal or a metal foil. The information on catalyst behavior obtained under these conditions can hardly be extended to actual reaction conditions. *In situ* Mössbauer measurements, on the other hand, are ideal in this regard as the technique can very well be used under the high-pressure and high-temperature conditions required for the reaction. Moreover, the γ-rays used in the technique have negligible interaction with the reacting gases or with the catalyst; they have high penetration power which allows the atoms inside the pores of the samples to be "seen" as easily as those of the exterior of the support particles.

Using the sensitivity of the Mössbauer technique we report various characteristics of Fe/Al_2O_3 and Fe/ThO_2 catalysts under

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reduction, carburization, and Fischer-Tropsch reaction conditions. Emphasis has been placed on the determination of any metal oxide–support interaction and the identification of various phases formed during different stages of the Fischer–Tropsch reaction. Mass spectrometry has been used to determine the distribution of reaction products for the two catalysts.

EXPERIMENTAL

Preparation of the Catalysts

The Fe/Al_2O_3 and Fe/ThO_2 catalysts were prepared from $Fe_3(CO)_{12}$ (Alfa products) and Al_2O_2/ThO_3 (Davison chemicals) by an extraction procedure following the method described in Ref. (*17*). The percentage of Fe loading in both catalysts is 14 wt% as determined by UV–visible spectroscopy. The samples just after the preparation are designated as-prepared or "AP." The AP samples were heated in air at 500°C for 24 h; they are designated as the calcined or H500 samples. The samples obtained after Fischer–Tropsch reaction will be designated as the used samples.

Mössbauer Measurements

The Mössbauer spectra were accumulated with a microprocessor-based spectrometer (Promeda) operated in a vertical geometry. The γ-ray source was a 50-mCi ^{57}Co in a Rh matrix.

The Mössbauer spectra were analyzed and fitted in terms of a set of independent Lorentzians, with the help of a nonlinear least-squares fitting procedure. The isomer shifts were calculated with respect to the centroid of α-Fe at room temperature. The points shown in all the Mössbauer figures represent the experimental data points. The full lines are the result of a computer fit of these data points. The bars with the numbers on all the Mössbauer figures represent the percentage effect.

The processes of reduction, carburization, and Fischer–Tropsch synthesis were performed in a specially designed reactor which has been described previously (*18*). The catalyst under study was in pellet form and supported by a small quartz cell inside the reactor. The sample temperature was monitored with a Chromel–Alumel thermocouple, which also provided the input signal for a proportional temperature controller. About 200 mg of each catalyst was pressed to 28 MPa pressure to form pellets (1.5 cm diameter). These pellets were used as the Mössbauer absorbers. *In situ* Mössbauer spectra were recorded during reduction, carburization, and Fischer–Tropsch synthesis reactions.

The as-prepared sample of Fe/Al_2O_3 was calcined in air at 500°C for 24 h. After cooling it was introduced in the reactor and left there until the end of the experiment. Reduction was carried out by flowing hydrogen gas in the reactor at the rate of about 100 cm^3/min at 400°C. The reduction of the Fe/Al_2O_3 catalyst was carried out for a total period of 123 h. For carburization, a mixture of $2H_2/CO$ was allowed to flow in the reactor at 250°C for 42 h. To evaluate the catalytic activity of the Fe/Al_2O_3 catalyst for synthesis gas conversion, a mixture of $2H_2/CO$ was allowed to flow over the catalyst at 300°C. The rate of flow for carburization and Fischer–Tropsch reactions was also about 100 cm^3/min. A pressure difference of about 138 kPa was maintained at the inlet (kept at 172 kPa) and the outlet for the three processes.

The Fe/ThO_2 catalyst was studied under two different experimental conditions. In the first set of experiments the *in situ* measurements were carried out on the sample which was calcined for 24 h at 500°C in air. After cooling to room temperature it was introduced into the reactor and was reduced in flowing H_2 (inlet at 172 kPa and outlet at atmospheric pressure) at 400°C for 9 h (rate of flow ~100 cm^3/min). Without exposing the catalyst to the atmosphere, it was carburized in a flowing mixture of synthesis gas ($2H_2/CO$) at 250°C for 4 h. The Fischer–Tropsch reactions followed at 300°C using the same composition of H_2

and CO. The rate of flow of the gases for carburization and Fischer–Tropsch synthesis reactions was about 100 cm^3/min.

A similar procedure was followed in the second set of experiments. In this case, the sample was calcined in air at 500°C for 48 h. Using the same reactor, the sample was then reduced at 400°C for about 10 h and carburized for a total period of 33 h. Finally, the Fischer–Tropsch reactions were conducted on the carburized sample for 7 h.

^{57}Fe Mössbauer spectra of the samples were recorded and computer fitted at various stages, viz., after calcination, following reduction, carburization, and Fischer–Tropsch reactions while the sample was in the reactor, and after exposure to air. A conversion electron Mössbauer spectrum (CEMS) of the Fe/ThO$_2$ used sample was also recorded by using a continuous-flow 90% He/CH$_4$ detector.

Mass Spectrometric Measurements

To determine the distribution of the hydrocarbons in the effluent gases from the reactor, a mass spectrometer (Model SM 1000 series, Spectrum Scientific) was used. Before recording the mass spectra of the products, blank runs of the line (background) were recorded. The peak heights of the background were subtracted from the heights of the respective peaks in the actual spectra when the final analyses were made. *In situ* mass spectra of the effluent gases were recorded every hour for both the catalysts.

RESULTS AND DISCUSSION

Fe/Al$_2$O$_3$ Catalyst

The ^{57}Fe Mössbauer spectrum of the as-prepared sample is shown in Fig. 1a. It consists of a symmetric broad doublet with an isomer shift (IS) value of 0.35 ± 0.03 mm s^{-1} and quadrupole splitting (QS) value of 0.85 ± 0.06 mm s^{-1}. These are the typical parameters for isolated paramagnetic Fe^{3+} ions, probably in the form of some hydroxylated iron. A similar doublet has been observed by Dézsi *et al.* (*19*) in their study on the as-prepared Fe/SiO$_2$ catalyst. The spectrum for the calcined (H500) sample (Fig. 1b) consists of a dominant central doublet and a minor component in the form of a six-line pattern. The central doublet has the Mössbauer parameters IS = 0.37 ± 0.03 mm s^{-1} and QS = 1.02 ± 0.06 mm s^{-1}. This doublet has been identified as arising from Fe^{3+} ions strongly interacting with the alumina surface forming a compound containing Fe, Al, and O. There have been several studies in the literature reporting such a behavior (*20, 21*). These studies have shown that such an interaction can make the reduction of these iron species difficult. We will notice later in the text that this is true in the present study. The minor component in the form of a six-line pattern represents the bulk phase of α-Fe$_2$O$_3$. It corresponds to a hyperfine field of 510 ± 5 kOe and IS = 0.38 ± 0.05 mm s^{-1}. It is interesting to note that the spectrum of the sample calcined at 500°C for 24 h exhibits only 10% spectral contribution from a bulk phase of α-Fe$_2$O$_3$.

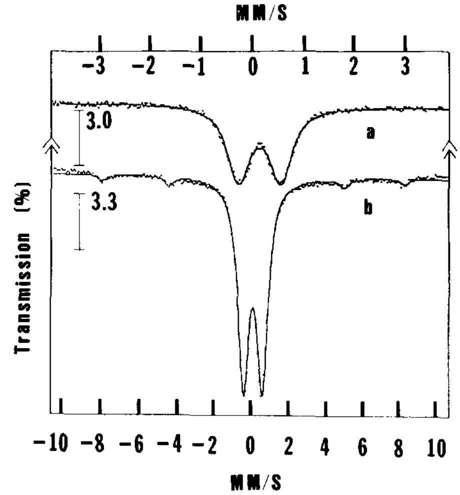

FIG. 1. ^{57}Fe Mössbauer spectra for (a) as-prepared (AP) and (b) calcined (H500) Fe/Al$_2$O$_3$ catalyst.

Figure 2 shows room temperature Mössbauer spectra of the H500 sample after reduction with hydrogen at different times. The variation of the different phases and the extent of reduction to α-Fe with time is

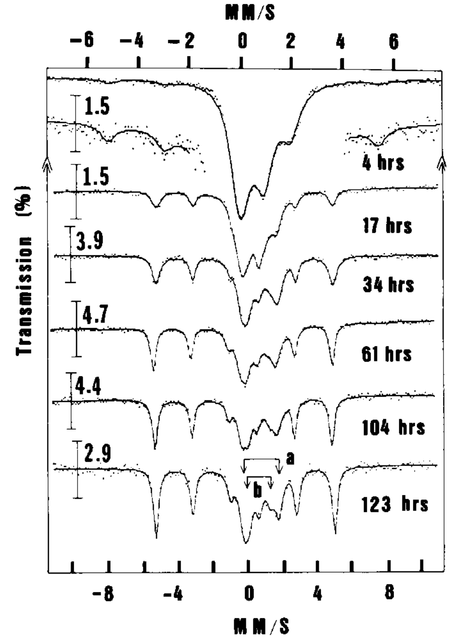

FIG. 2. Room-temperature ^{57}Fe Mössbauer spectra of the Fe/Al_2O_3 (H500) catalyst during reduction with different time of H_2 treatment. Reduction was carried out by flowing H_2 at the rate of about 100 cm^3 min^{-1} at 400°C.

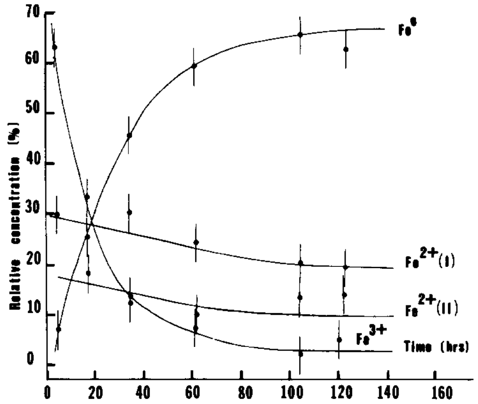

FIG. 3. Contribution of the different iron phases to the Mössbauer spectra of Fe/Al_2O_3 (H500) during reduction at 400°C.

shown in Fig. 3. In 4 h of reduction the spectral contribution of α-Fe is only 7%. On increasing the time of hydrogen gas treatment, at first the spectral contribution of α-Fe increases steadily to 45% in a period of 34 h, but after that time, the process of reduction slows down and after 104 h, only about 65–70% of the spectral contribution is attributed to α-Fe. The amount of α-Fe does not increase on further H_2 gas treatment. Therefore, about 30% of the remaining oxide apparently has strongly reacted with the support and formed a $FeAl_2O_4$ spinel phase (see below). The two doublets indicated by *a* and *b* in the Mössbauer spectrum (Fig. 2) after 123 h of reduction (they are present in all other spectra in Fig. 2 and are designated as Fe^{2+}(I) and Fe^{2+}(II) in Table 1) are due to the Fe^{2+} ions in octahedral (B site) and tetrahedral (A site) of such a spinel phase. From Fig. 3 it is evident that the spectral contribution of these two species changes very little throughout the entire process of reduction. In calculating the spectral contribution of

TABLE 1

Mössbauer Parameters for the Fe/Al_2O_3 Reduced Catalyst at Room Temperature

Time of reduction (h)	α-Fe		Fe^{3+}			Fe^{2+}(I)			Fe^{2+}(II)		
	H (kOe)	Δ*A*[a]	IS[b]	QS[c]	Δ*A*	IS	QS	Δ*A*	IS	QS	Δ*A*
4	334 ± 3	7%	0.44	0.81	63%	0.87	2.07	30%	—	—	—
17	331 ± 3	25%	0.33	1.04	33%	0.88	2.12	24%	0.76	1.05	18%
34	331 ± 3	45%	0.36	1.04	13%	0.91	2.14	30%	0.84	1.28	12%
61	335 ± 3	59%	0.44	1.03	7%	0.99	2.13	24%	0.89	1.24	10%
104	332 ± 3	65%	0.48	0.94	2%	1.07	2.11	20%	1.03	1.27	13%
123	335 ± 3	62%	0.47	0.95	5%	1.06	2.13	19%	0.98	1.28	14%

[a] Area fractions (±5%).

[b] Isomer shift values ±0.04 mm s^{-1}.

[c] Quadrupole splitting values ±0.08 mm s^{-1}.

the various species, it was assumed that the recoil-free fraction is the same for all the phases.

The various phases present in the sample during the process of reduction can be further analyzed, in particular, by a close study of the spectrum after 123 h of reduction. The major phase in the sample is that of α-Fe, the spectral contribution of which changes from about 7% in 4 h to about 70% in 123 h. The other phase is that of Fe^{3+} iron interacting with the alumina support. After 4 h of reduction the spectral contribution of this phase was about 65% in the sample; this amount is reduced to about 5% after 123 h of reduction. Apparently, this latter phase is mainly responsible for the production of metallic iron. The remaining two species as indicated in Table 1 and in Fig. 3 as Fe^{2+}(I) and Fe^{2+}(II), have the Mössbauer parameters (after 123 h of reduction) of IS $\cong$ 1.06 mm s^{-1} and QS $\cong$ 2.13 mm s^{-1}, and IS $\cong$ 0.98 mm s^{-1} and QS $\cong$ 1.28 mm s^{-1}, respectively. From the literature survey on the Mössbauer data for $FeAl_2O_4$ spinel, it was found that, in general, there is disagreement among the different reported values for the parameters of such a spinel phase. According to Rossiter (*22*) $FeAl_2O_4$ at room temperature has an isomer shift of 1.08 mm s^{-1} and total quadrupole splitting of 1.60 mm s^{-1}. These values are close to the average values of the parameters in the present study (IS = 1.02 ± 0.05 mm s^{-1} and QS = 1.70 ± 0.05 mm s^{-1}). On the other hand, from a Mössbauer and X-ray diffraction study it was found by Yagnik and Mathur (*23*) that the room-temperature Mössbauer spectrum for $FeAl_2O_4$ can be resolved into two quadrupole split doublets, one due to tetrahedral Fe^{2+} ion with IS = 1.10 mm s^{-1} and QS = 1.39 mm s^{-1}, and the other due to octahedral Fe^{2+} ions with IS = 1.52 mm s^{-1} and QS = 2.76 mm s^{-1}. However, Dickson and Smith found (*24*) that a QS value of 2.76 mm s^{-1} is not expected for octahedral Fe^{2+} in a normal $FeAl_2O_4$ spinel. They found that the QS of octahedral Fe^{2+} ions should be $\cong$ 2.00 mm s^{-1}.

In view of the above, Fe^{2+}(I) and Fe^{2+}(II) species observed with parameters as mentioned in Table 1 can be assigned to Fe^{2+} ions in octahedral and tetrahedral sites, respectively. The presence of these two species after 4 h of reduction indicates that these were probably formed at the early stages of reduction. It is noticed that the isomer shift values (Table 1) of Fe^{2+}(I) and Fe^{2+}(II) increases linearly from 0.87 to 1.06 and 0.76 to 0.98 mm s^{-1}, respectively, with increasing time of reduction. The quadrupole splitting values for Fe^{2+}(I) do not change much but those for Fe^{2+}(II) change from 1.05 to 1.28 mm s^{-1}. This behavior indicates that the valence state and site symmetry of the Fe atoms have been changing with the reduction. This may be interpreted to mean that the chemical state of the compound (Fe-Al-O) formed on the alumina surface during calcination has been changing. In a period of 123 h of reduction, a part of the surface compound has converted and stabilized as a bulk spinel phase of $FeAl_2O_4$ (30%) and a part has been reduced to α-Fe (60%).

Figure 4 shows the room temperature

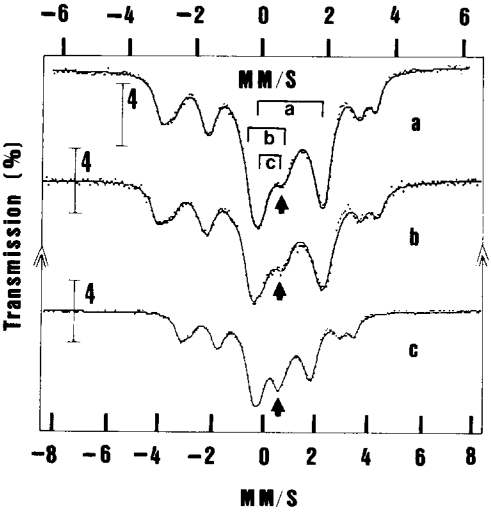

FIG. 4. Room-temperature ^{57}Fe Mössbauer spectra of Fe/Al_2O_3 (H500) catalyst: (a) after 18 h of carburization; (b) after 42 h of carburization; (c) after 7 h of Fischer–Tropsch reaction. For carburization a mixture of $2H_2/CO$ was allowed to flow in the reactor at 250°C for a total period of 42 h.

spectra of the H500 sample after 18 h (Fig. 4a) and 42 h (Fig. 4b) of carburization. Figure 4c shows the spectrum of the used catalyst after about 7 h of the Fischer–Tropsch reaction. The Mössbauer parameters of these spectra are given in Table 2. It can be seen that all the α-Fe present in the reduced sample was converted to carbides in a period of 18 h (Fig. 4a). Apparently, no changes were noticed in this spectrum after 42 h of carburization (Fig. 4b). Both spectra were fitted in terms of four hyperfine fields. The values of 212 (H_1), 190 (H_2), and 117 (H_3) kOe for these fields are close to those for bulk χ-carbide which is a monoclinic interstitial alloy of composition Fe_5C_2 (*11*). The fourth field was found to be 173 kOe (H_4) and is assigned (*6*) to ε'-$Fe_{2.2}C$. The area fractions of $H_1 : H_2 = 1 : 1$ is in agreement with the results obtained by Niemantsverdriet *et al.* (*6*). The dominant feature of the above two spectra is the presence of Fe^{2+}(I) and Fe^{2+}(II) species due to the $FeAl_2O_4$ spinel phase; the amount of this phase is not affected by the carburization. The presence of a third doublet with IS = 0.33 mm s^{-1} and QS = 0.75 mm s^{-1} (doublet c in Fig. 4a) in the carburized sample and the used H500 sample is of great interest. As indicated by arrows in Fig. 4 the intensity of this doublet has definitely increased after 7 h of the process of synthesis gas conversion. The parameters of this doublet appear to be consistent with those of the superparamagnetic particles of iron oxide. Such a species can be formed (*9, 25*) by the reaction between the oxygen (obtained by the dissociation of CO at the surface of the catalyst) and the metal (obtained by the oxidation of the iron carbide phase). It is worth mentioning again that no changes occur either in the hyperfine field of χ-carbide phase or the $FeAl_2O_4$ spinel phase after 7 h of the Fischer–Tropsch reaction.

The selectivities obtained from the carburized sample from the microreactor at different time intervals are shown in Fig. 5. It is evident that within 10 min of the experiment about 80% of the products is propylene; no methane is initially produced. The maximum amount of methane, about 10% of the products, is produced after 1 h of the experiment. With increasing time the amount of methane decreases almost to zero; the unsaturated C_3 hydrocarbon (pro-

TABLE 2

Mössbauer Parameters for the Fe/Al_2O_3 Catalyst after Carburization and Fischer–Tropsch

			After carburization					
Time (h)	Iron carbides		Fe^{3+}		Fe^{2+}(I)		Fe^{2+}(II)	
	H	IS	IS	QS	IS	QS	IS	QS
18	212 ± 5	0.28 ± 0.05	0.33 ± 0.04	0.75 ± 0.08	0.88 ± 0.04	2.28 ± 0.08	0.80 ± 0.04	1.58 ± 0.08
	190 ± 5	0.23 ± 0.05						
	117 ± 8	0.15 ± 0.07						
	173 ± 5	0.50 ± 0.05						
42	209 ± 5	0.25 ± 0.05	0.35 ± 0.04	0.77 ± 0.08	0.88 ± 0.04	2.36 ± 0.08	0.84 ± 0.04	1.72 ± 0.05
	189 ± 5	0.20 ± 0.05						
	119 ± 8	0.15 ± 0.07						
	173 ± 5	0.51 ± 0.05						
			After Fischer–Tropsch synthesis reactions					
7	211 ± 5	0.30 ± 0.05	0.36 ± 0.04	0.72 ± 0.08	0.85 ± 0.04	2.25 ± 0.08	0.73 ± 0.04	1.46 ± 0.08
	183 ± 5	0.23 ± 0.05						
	113 ± 8	0.16 ± 0.07						
	174 ± 5	0.52 ± 0.05						

Note. Units: H in kOe; IS and QS in mm s^{-1}.

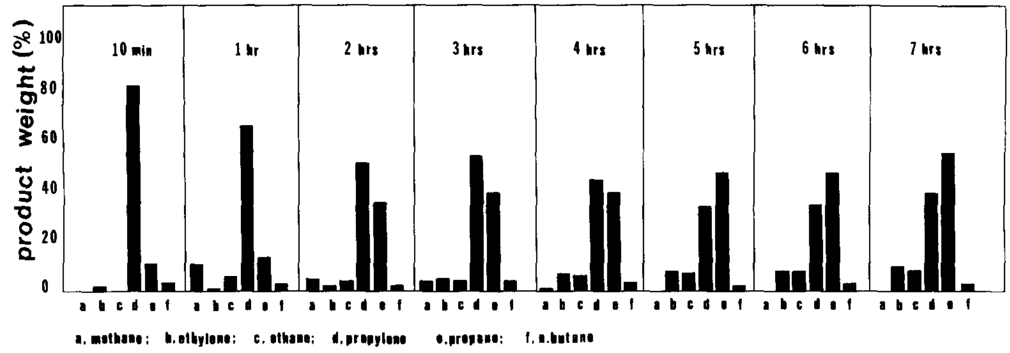

FIG. 5. *In situ* study of the product distribution for Fischer–Tropsch reaction of carburized Fe/Al_2O_3 catalyst with different time.

pylene) decreases while the saturated C_3 hydrocarbon (propane) increases.

Fe/ThO_2 Catalyst

The Mössbauer spectrum of the AP sample (Fig. 6a) is characteristic (*19*) of Fe^{3+} ions (IS = 0.33 ± 0.04 mm s^{-1} and QS = 0.77 ± 0.08 mm s^{-1}) in the form of some hydroxylated iron. The Mössbauer spectrum of the H500 (24 h) catalyst (Fig. 6b) shows the presence of a six-line magnetically split hyperfine pattern with an internal field H = 519 ± 5 kOe and isomer shift (IS) = 0.41 ± 0.04 mm s^{-1} (Table 3). These parameters are characteristic of a bulk phase of α-Fe_2O_3. It is noticed that the calcination for 24 h at 500°C totally converted the ferric hydroxyl-complex phase to a bulk α-Fe_2O_3 phase. A single line near 0 mm s^{-1} in Fig. 6b is due to the Fe impurity in aluminum foil used to prepare the Mössbauer absorber. Reduction for 9 h in flowing hydrogen at 400°C changed almost all the iron oxide to α-Fe, as evidenced by the characteristic six-line pattern in Fig. 7a. It is important to mention that, unlike the Fe/Al_2O_3 catalyst, no spectral evidence of metal oxide–support interaction was noticed. When the reduced sample is exposed to the synthesis gas ($2H_2$ + CO) at 250°C, a complex spectrum is observed (Fig. 7b) that is produced

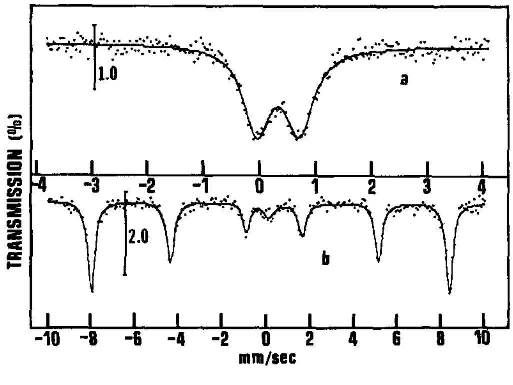

FIG. 6. ^{57}Fe Mössbauer spectra for the Fe/ThO_2 catalyst: (a) AP; (b) H500 (24 h).

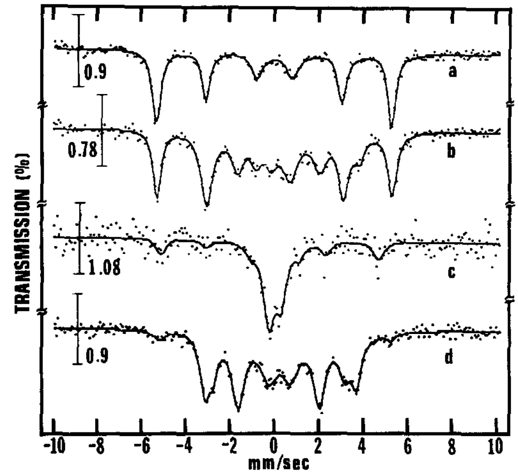

FIG. 7. ^{57}Fe Mössbauer spectra for the Fe/ThO_2 catalyst: (a) at room temperature after reduction in flowing H_2 at 400°C for 9 h; (b) at room temperature after carburization at 250°C for 4 h; (c) at 300°C during the Fischer–Tropsch reactions; (d) at room temperature after 6 h of the Fischer–Tropsch reactions. Note: All the spectra of this figure were recorded while the sample was inside the reactor.

TABLE 3

Mössbauer Parameters for the Fe/ThO_2 Catalyst

Sample status	Temp.	Hyperfine field (kOe)	Quadruple splitting (mm s^{-1})	Isomer shift (mm s^{-1})	Remarks
As prepared	Room		0.77 ± 0.08	0.33 ± 0.04	Fe^{3+} ions in hydroxylated iron
		I Set of experiments (sample calcined for 24 h)			
After calcination for 24 h at 500°C	Room	519 ± 5		0.41 ± 0.04	α-Fe_2O_3 (bulk)
After reduction in H_2 flow for 9 h at 400°C	Room	334 ± 3		0.02 ± 0.02	α-Fe (bulk)
After carburization in H_2/CO flow for 4 h at 250°C	Room	212 ± 5 183 ± 6 113 ± 8		0.33 ± 0.03 0.21 ± 0.04 0.27 ± 0.06	Fe_5C_2 (χ-carbide)
		333 ± 3		0.01 ± 0.02	α-Fe
During F.T. synthesis	300°C	311 ± 3	—	—	α-Fe
			0.54 ± 0.08	0.09 ± 0.04	Fe_5C_2 (χ-carbide)
After F.T. reactions (after 6 h)	Room	216 ± 5 187 ± 6 116 ± 8		0.30 ± 0.05 0.22 ± 0.06 0.20 ± 0.06	Fe_5C_2 (χ-carbide)
		II Set of experiments (sample calcined for 48 h)			
After calcination for 48 h at 500°C	Room	508 ± 5		0.40 ± 0.05	α-Fe_2O_3 (bulk)
After reduction in H_2 flow at 400°C for 10 h	Room	331 ± 3		0.02 ± 0.02	α-Fe (bulk)
After carburization in H_2/CO flow at 250°C for 33 h	Room	218 ± 5 186 ± 6 114 ± 8		0.33 ± 0.05 0.22 ± 0.06 0.26 ± 0.06	Fe_5C_2[a] (χ-carbides)
During F.T. synthesis	300°C	—	0.52 ± 0.08	0.01 ± 0.04	Fe_5C_2
		312 ± 3	—	—	α-Fe
After F.T. reactions	Room	219 ± 5 190 ± 5 117 ± 8		0.31 ± 0.05 0.22 ± 0.05 0.28 ± 0.06	Fe_5C_2

[a] With traces of α-Fe.

by the superposition of spectra from α-Fe and the iron carbide phases. This spectrum is fitted in terms of a six-line pattern due to α-Fe, and three six-line patterns corresponding to the three different iron sites in the iron carbide. Values of these fields, as given in Table 3, match well with literature values (*11*) for the Hägg carbide, Fe_5C_2. The possibility of the presence of a small amount of Fe_3C (cementite) cannot be ruled out, but the amount of this phase is certainly not enough to cause any distortion in the spectrum.

Two studies reported in the literature are worth mentioning in relation to the values of the hyperfine field and the isomer shift values for the Hägg carbide (Fe_5C_2). The values of the hyperfine fields according to

Bernes *et al.* (*26*) were found to be 222 ± 3 kOe for site I, 184 ± 3 kOe for site II, and 110 ± 7 kOe for site III. The corresponding IS values were 0.30 ± 0.04, 0.35 ± 0.04, and 0.30 ± 0.08 mm s^{-1}, respectively. On the other hand. La Caër *et al.* (*27*) found the values of these parameters to be 216 ± 2, 185 ± 2, and 124 ± 4 kOe for the hyperfine fields and 0.27 ± 0.02, 0.20 ± 0.02 (or 0.17 ± 0.02) mm s^{-1} for the isomer shifts. The IS value for site III was not reported by the latter authors.

Several studies report the various kinds of iron carbides during carburization or pretreatment and Fischer–Tropsch reactions. Amelse *et al.* (*1, 2*) observed that in the case of the Fe/SiO_2 catalyst, carburization in CO and H_2 at 250°C resulted in the Hägg carbide, Fe_5C_2, and ε'-$Fe_{2.2}C$. Similar results have been reported by Maksimov *et al.* (*28*) on the study of Fe/TiO_2/CaO. Niemantsverdriet *et al.* (*6*) found that even at 350°C, 12% of the carbides present in the sample were ε'-$Fe_{2.2}C$, 47% was the Hägg carbide, and the remaining 41% was cementite (Fe_3C). In the present study on the Fe/Al_2O_3 catalyst we also observed the formation of the Hägg carbide, Fe_5C_2 and ε'-$Fe_{2.2}C$.

The Mössbauer spectrum of the carburized sample during Fischer–Tropsch synthesis at 300°C is shown in Fig. 7c. The Curie temperatures for iron carbides are about 450°C for ε'-$Fe_{2.2}C$, 380°C for ε-Fe_2C, 247–250°C for χ-Fe_5C_2, and 205–220°C for Fe_3C (*11, 12*). Therefore, the magnetically split six-line pattern due to χ-Fe_5C_2 collapses at 300°C into a quadrupole split doublet, whose parameters are given in Table 3. Figure 7d shows the room-temperature Mössbauer spectrum of the sample after 6 h of Fischer–Tropsch reaction. This spectrum clearly shows the presence of χ-Fe_5C_2. A small amount of residual iron can also be seen outside the carbide spectrum. When the sample was exposed to the atmosphere and the transmission Mössbauer spectrum recorded, no change in the nature of the spectrum was observed. This indicates that the surface-to-volume ratio of the iron particles is very small and that the iron particles are large.

In order to know more about the near-surface region of the used catalyst, a conversion electron Mössbauer spectrum of the sample was recorded (Fig. 8). The ^{57}Fe CEMS technique involves the detection of back-scattered iron conversion electrons (mainly 7.5-keV *K* shell) which are emitted with a 90% probability during the decay of ^{57}Fe subsequent to absorption or resonant γ-photons. Because these electrons are attenuated within the solid material the probing depth of CEMS is limited to the outermost 300 nm or so of the surface. The spectrum, shown in Fig. 8, once again, is characteristic of the Hägg carbide. This further shows that after 6 h of Fischer–Tropsch reaction, the bulk as well as the near-surface region of the partially carburized samples becomes totally carburized.

Very interesting results were obtained when the mass spectra of the products, recorded after 15 min, 1, 3, and 5 h of Fischer–Tropsch reactions on the H500 (24 h) catalyst were analyzed (Fig. 9). Within 15 min of the reaction about 50% of the products were found to be hydrocarbons in the range of C_5–C_{10}. This observation is in good agreement with the gas chromatographic result on the sample. By this technique the selectivity for the formation of C_{5+} products was found to be 56% (Table 4). As the time of Fischer–Tropsch reaction increases, the amount of the heavier products decreases and more of the lighter products

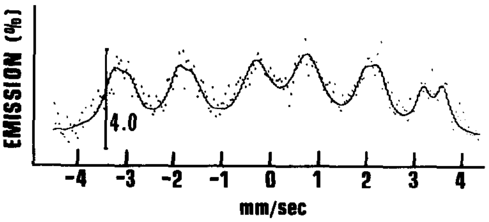

FIG. 8. ^{57}Fe conversion electron Mössbauer spectrum of the Fe/ThO_2 used catalyst.

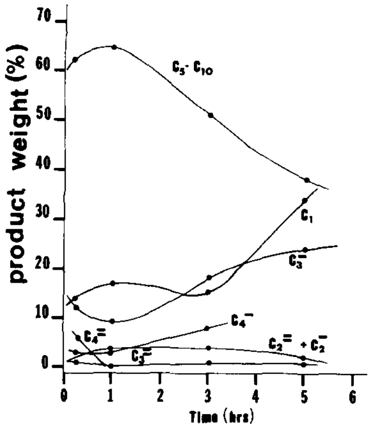

FIG. 9. Selectivities on an Fe/ThO$_2$ catalyst calcined for 24 h and carburized for 4 h. C_1, methane; $C_2^=$, ethylene; C_2^-, ethane; $C_3^=$, propylene; C_3^-, propane; $C_4^=$, unsaturated C_4 products; C_4^-, saturated C_4 products.

(viz. methane and propane) are produced (Fig. 9).

In the second set of experiments, the as-prepared sample was calcined for 48 h at 500°C in air; as a result, a bulk phase of α-Fe_2O_3 was obtained. The Mössbauer spectrum of this sample is identical to that of the sample calcined for 24 h (Fig. 6b). The above sample was exposed to flowing H_2 at 400°C and was reduced to α-Fe in 9 h. To determine the effect of the longer period of carburization on the activity, the sample was carburized for 2, 6, 10, 14, and 33 h until no further carburization was obtained. The *in situ* Mössbauer spectra at room temperature after the above periods of carburization are shown in Fig. 10. All these spectra are the superpositions of the spectra due to α-Fe and χ-Fe_5C_2. However, the presence of small amounts of ε′-$Fe_{2.2}C$ and Fe_xC carbides cannot be ruled out. One can easily monitor the height of the first peak due to α-Fe to determine the extent of carburization; the height of this peak decreases as the amount of carburized species increases. The height of the first peak becomes smallest after 14 h of carburization and remains almost constant after 33 h of carburization. It is worth noting that even after 33 h of carburization, some iron remains unreacted. Figure 11 shows the variation of the ratio of the spectral area $A(t)/A(0)$ vs time of carburization ($A(t)$ = spectral area of the first peak of α-Fe after t

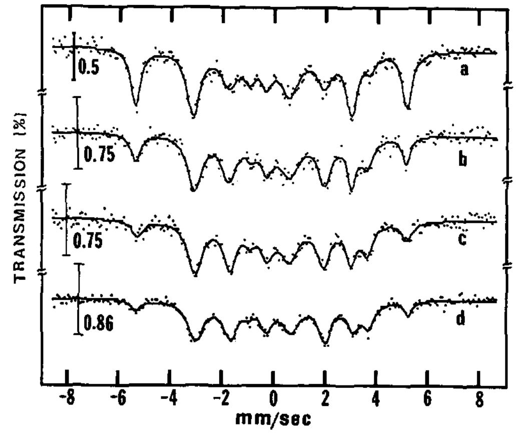

FIG. 10. Room-temperature ^{57}Fe Mössbauer spectra of the Fe/ThO$_2$ catalyst after calcination at 500°C for 48 h and reduction in flowing hydrogen at 400°C for 10 h and after (a) 2 h; (b) 6 h; (c) 10 h; and (d) 14 h of carburization at 250°C in a flowing mixture of synthesis gas (2H$_2$/CO).

TABLE 4

Catalytic Conversion Data for the Fe/ThO$_2$ Catalysts

Catalysts	CO conversion	Selectivity for C_{5+}
AP (as prepared)	15	15
Calcined at 300°C	12	30
Calcined at 500°C	19	56

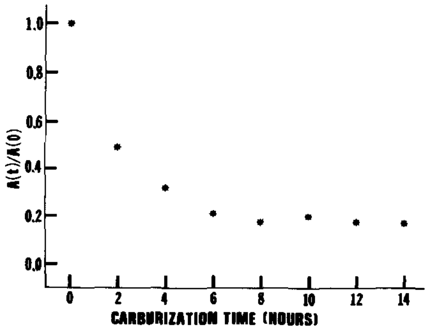

FIG. 11. Diagram showing the amount of iron changed to iron carbides with time for the Fe/ThO$_2$ catalyst under carburization conditions.

hours of carburization and $A(0)$ = spectral area of the first peak of α-Fe initially at $t = 0$). It is clear from this figure that the amount of carburized species in the catalyst increases rapidly for the first 5 or 6 h, after which the process slows down; after 12–14 h, the spectral area of the carbide phase does not change indicating that no further carburization of the sample occurs.

All the Mössbauer spectra recorded after different periods of carburization were fitted in terms of a six-line pattern due to α-Fe and three six-line patterns due to three different iron sites in the χ-carbide phase. The values of these parameters are given in Table 3.

A Fischer–Tropsch synthesis reaction was carried out on the above-described carburized sample. Figures 12a and 12b depict the Mössbauer spectra recorded at 300°C during the reaction, and at room temperature (sample inside the reactor) after the reaction, respectively. A broad unresolved doublet with parameters given in Table 2 is obtained at 300°C. When the sample is cooled to room temperature the characteristic spectrum of χ-Fe_5C_2 is obtained (Fig. 12b). The latter spectrum is once again fitted with the superposition of three magnetic hyperfine fields due to the three sites of iron in the carbide phase. The spectrum (Fig. 12b) does not show the presence of any traces of α-Fe in the used sample. Also, even at 300°C, χ-Fe_5C_2 has not converted into cementite (Fe_3C). Finally, when this sample is removed from the reactor, exposed to air, and its Mössbauer spectrum recorded, no changes were noticed; this suggests the presence of iron carbide particles of large size in the catalyst.

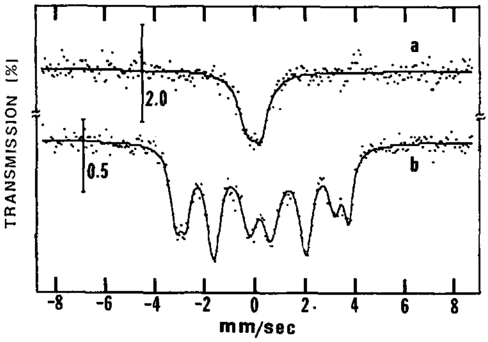

FIG. 12. ^{57}Fe Mössbauer spectra of the Fe/ThO_2 catalyst: (a) at 300°C during the Fischer–Tropsch synthesis reaction; (b) at room temperature after 7 h of the Fischer–Tropsch synthesis reactions. (Sample was kept inside the reactor.)

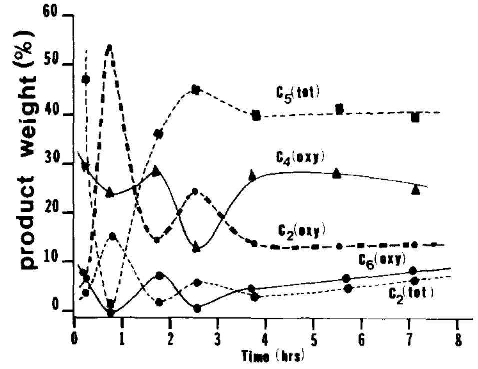

FIG. 13. Selectivities on an Fe/ThO_2 catalyst calcined for 48 h and carburized for 32 h. C_2(tot), total of C_2 (in the hydrocarbons); C_2(oxy), oxygenated C_2; C_4(oxy), oxygenated C_4; C_5(tot), total of C_5 (in the hydrocarbons); C_6(oxy), oxygenated C_6. The maximum selectivity for C_1 is 4%; for C_3(hydrocarbons), 4%; and for C_6(hydrocarbons), 2%. (These are not shown in the diagram.)

Analysis of the mass spectra of the products recorded during the Fischer–Tropsch reaction are shown in Fig. 13. After approximately 15 min of the reaction, about 50% of the total products were found to be C_5 hydrocarbons and about 30% C_4 oxygenated products. However, after 45 min of the Fischer–Tropsch synthesis reaction, the amount of C_5 products was reduced almost to zero and a maximum of C_2 oxygenated products was formed. The remaining major products at this time were also in the form of C_3 and C_4 oxygenated products. When the reaction time was increased to 2 h, about 35% of the products were C_5 hydrocarbons. At this time C_4 oxygenated products were also formed. After 2.5 h the selectivity for the formation of C_5 hydrocarbons increased to 45% and for C_2 oxygenated products, to 25%. For C_4 oxygenated products, selectivity decreased to

TABLE 5

Summary of the Characteristics of Fe/Al_2O_3 and Fe/ThO_2 Catalysts

Catalyst	As prepared	Calcined	Reduced	Carburized	Used	Selectivity
Fe/Al_2O_3	Fe^{3+} ions in hydroxylated iron	90% Fe–Al–O phase + 10% α-Fe_2O_3 (bulk phase)	70% Fe + 30% $FeAl_2O_4$ (spinel phase) (123 h)	All the iron was carburized to χ-Fe_5C_2 + ε'-$Fe_{2.2}C$ (spinel phase was not affected)	χ-Fe_5C_2 + ε'-$Fe_{2.2}C$ SP particles of α-Fe_2O_3 + $FeAl_2O_4$ (7 h)	Higher selectivities for propylene and propane
Fe/ThO_2	Same	(a) α-Fe_2O_3 bulk (100%) (24 h)	(a) α-Fe (100%) (9 h)	(a) α-Fe + χ-Fe_5C_2 (4 h)	(a) 100% χ-Fe_5C_2 (after 6 h of F.T.)	(a) Higher selectivities for C_5–C_{10} hydrocarbons
		(b) α-Fe_2O_3 bulk (100%) (48 h)	(b) α-Fe (100%) (10 h)	(b) 90% χ-Fe_5C_2 + 10% α-Fe (33 h)	(b) 100% χ-Fe_5C_2 (after 7 h of F.T.)	(b) Higher selectivities for C_3–C_4–oxygenated product + C_5 hydrocarbons

about 10%. Practically no variation in the amounts of the products was observed after 3 h of the Fischer–Tropsch synthesis reactions.

Finally, it will be useful and interesting to compare the results for the Fe/ThO_2 catalyst with the Fe/Al_2O_3 catalyst. Such a comparison has been given in Table 5. The important conclusions from this table can be stated as follows.

The as-prepared samples of the two catalysts show the presence of Fe^{3+} ions of some hydroxylated iron. However, in the calcined (H500) state, they are composed of different phases. The Fe/Al_2O_3 calcined sample contains 90% of an iron species containing Fe–Al–O which is being formed at the alumina surface as a result of the strong metal oxide–support interaction, and 10% of bulk α-Fe_2O_3. The calcined sample of the Fe/ThO_2 catalyst contains mostly bulk α-Fe_2O_3.

After reduction in flowing hydrogen, the two catalysts show different phases. About 70% of α-Fe and a spinel phase of $FeAl_2O_4$ are produced when the Fe/Al_2O_3 catalyst is reduced, thus demonstrating a metal oxide–support interaction. In the case of the Fe/ThO_2 catalyst, no evidence of the presence of any kind of metal support interaction is observed as all the α-Fe_2O_3 is reduced to α-Fe.

Under carburization conditions, almost all the reduced α-Fe produced in the reduction of the catalysts in H_2 for Fe/Al_2O_3 and Fe/ThO_2 catalysts is converted to χ-Fe_5C_2. The spinel phase formed in the Fe/Al_2O_3 catalyst apparently remains unaffected by the process of carburization. No major changes are observed in the nature of the catalysts under Fischer–Tropsch reaction conditions.

The small yield of methane in the reaction products in the two catalysts in the present study is surprising. This clearly deviates from the Anderson–Schulz–Flory (ASF) distribution of the products in the Fischer–Tropsch reaction. Detailed discussion of such a behavior of the catalysts will be presented elsewhere (*29*).

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