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Kinetic and Mössbauer Study of the CO/H_2 Reaction over Fe/TiO_2 Reduced at Various Temperatures

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The CO/H_2 reaction over Fe/TiO_2 has been studied by Mössbauer spectroscopy and kinetic measurements after the catalyst was reduced at 558, 723, and 773 K. The particle size estimated from the uptake of H_2 by the desorption method is comparable to that from X-ray line broadening. Mössbauer parameters show that the bulk phase of fresh catalyst is essentially identical to metallic iron. Mössbauer spectroscopy indicates that carbide formation is suppressed during the CO/H_2 reaction for the catalyst reduced at 723 and 773 K. The reaction activity for the catalyst reduced at 558 K is an order of magnitude higher than that of the 773 K-reduced catalyst. The nature of the surface species formed during the CO/H_2 reaction is quite different from those found for the Fe/SiO_2 and Fe/Al_2O_3 systems. The changes in the activation energy and selectivity for the catalysts reduced at various temperatures are appreciable. The experimental results are discussed in terms of a localized charge transfer from the metal to the support during the course of high-temperature reduction. The requirement for this localized charge transfer is the presence of TiO_x species on top of the metal surface.

INTRODUCTION

Many studies have provided evidence for the existence of a high-temperature reduction effect between Group VIII metals and metal oxide supports. Most of the work has concentrated on the TiO_2-supported Group VIII metals. This high-temperature reduction effect was first observed by Tauster *et al.* (*1, 2*) and was named the "strong metal support interaction-SMSI." Recent work in this area is listed in Refs. (*3–15*). This high-temperature reduction effect not only changes the chemisorption capacity but also changes the reaction activity and selectivity. Despite the extensive studies, the nature of this high-temperature reduction effect is not yet clear. Nevertheless, the hypotheses to explain this phenomenon can be put into three categories (*65*): (1) energetic effect, (2) electronic effect, and (3) geometric effect. Some examples of these effects follow, but clearly more than one of these may be acting simultaneously in certain cases.

The energetic effect is important for small particles of only a few atoms per crystal. Borel (*16*) found that the melting point of the small particles of gold is some 500 K below the bulk phase gold. Recently, Ponec (*66*) studied the Pd system and found that the electronic and physical structures of small particles are different from those of massive metals. These points are important because in many examples of SMSI, the effect is very strong for small crystallites.

Santos *et al.* (*17*) studied ammonia synthesis over Fe/TiO_2 and presented a convincing argument for charge transfer from Fe to TiO_2 after a high-temperature reduction. Herrmann *et al.* (*18*) studied the *in situ* electrical conductivity of Pt/TiO_2 system. A migration of electrons from the anatase TiO_2 to the platinum has been inferred. Burch and Flambard (*23*) studied the CO hydrogenation and *n*-hexane and ethane hydrogenolysis over the Ni/TiO_2 system. A possibility of charge transfer has been proposed, although the geometric effect has been emphasized. Resasco and Haller (*25*)

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studied ethane and butane hydrogenolysis over the Rh/TiO_2 system and suggested that the SMSI effect is partly caused by the presence of charge transfer. Among those charge transfer arguments, Santos *et al.* (*17*) thought the transferred electrons are localized. Resasco and Haller (*25*) postulated a localized transfer of charge from the support to the rhodium after a high-temperature reduction but a delocalized transfer of charge from Rh to TiO_2 after a low-temperature reduction. Herrmann *et al.* (*18*) favor the delocalized charge transfer. Some other evidence on the charge transfer of noble metals on TiO_2 has also been presented (*19–21*). A strong argument against the charge transfer effect has been presented by Ponec (*22*). He is doubtful that the small amount of electron transfer involved for Pd/TiO_2 could change the observed activity so drastically.

Burch and Flambard (*23*) emphasized the creation of new active sites at the metal–support interface after the high-temperature reduction. These new sites are the ones responsible for the high specific activity. Santos and Dumesic (*24*) recently proposed that the so-called SMSI could be caused by the presence of a reduced form of titanium oxide on the top of the Fe metal, to explain its decreased activity for NH_3 synthesis in the SMSI state. Resasco and Haller (*25*) suggested that the migration of a reduced form of the support is partially responsible for the depression of the hydrogenolysis activity following a high-temperature reduction. An extreme case of morphology change is considered by Powell and Whittington (*26*) who studied the Pt/SiO_2 system at 1473 K. They found that after reduction at this high temperature an encapsulation phenomenon occurred, which is responsible for lowered activity.

The literature shows that the high-temperature reduction effect is different from metal to metal. The explanations are also different from reaction to reaction. The reason may be attributed to the characteristic properties of each metal, such as work function, Fermi level, electron configuration, etc. Of course, the reaction mechanism is also very important. In order to gain a better understanding of the influence of the reduction temperature for iron catalysts, we have studied the CO hydrogenation reaction over Fe/TiO_2 reduced at various temperatures. Since the magnitude and even the sign of the changes in activity brought about by high-temperature reduction of TiO_2-supported metals varies as a function of metal and of reaction, it should advance our understanding to study the nature and reactivity of the intermediates for the various cases. For this purpose we use here the transient method. We shall show some interesting differences between Fe/Al_2O_3 and Fe/TiO_2 catalysts used for the CO/H_2 reaction, and also compare these results to these for Fe/TiO_2 used for the NH_3 synthesis reaction (*17, 24*). Mössbauer effect spectroscopy was carried out for the detection of carbide formation and decarburization. X-Ray diffraction and chemisorption were used for the particle size determination.

EXPERIMENTAL

Catalyst preparation. The catalyst used in this work is 10% by weight of iron on titania (Degussa, P25) obtained by the impregnation method from a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (Bayer). After wetting the support with the solution, the catalyst was dried in an oven at 400 K for 24 hr. The gases used in this study were of high purity grade. They were used without further purification except for special cases. The catalyst pretreatment depended on the purpose of the study. It consisted of heating the sample in flowing hydrogen (30 ml/min) to 410 K for 2 hr, then heating to the desired reduction temperature and holding this temperature for a predetermined period of time before cooling the catalyst under flowing hydrogen to the chosen reaction temperature. The size range of the catalysts for the kinetic studies was 590 to 840 μm. This size range was small enough to prevent internal composition gradients and large enough to produce a reasonable pressure drop.

Chemisorption measurements. CO and hydrogen chemisorption were measured by Quantasorb (Quantachrom Corp.). The hydrogen chemisorption method has been described (*28*). We shall refer to this method as the flow desorption method. The chemisorption of CO was carried out at 195 K by both the pulse adsorption (*27, 30*) and by the flow desorption method. Both CO and hydrogen were assumed to adsorb on two Fe atoms per molecule (*30*). To calculate the sizes of the metal particles an approximate relation, $d(\text{nm}) = 0.80/D$, was used (*29*), where D is the dispersion.

Kinetic measurements. The kinetic studies were conducted in a small stainless-steel reactor. The product analysis was performed using a Nuclide 3-60-G mass spectrometer. The whole system has been described in detail previously (*30*). The catalyst charged to the reactor was 50 mg and the conversion was about 4% or less so that the reactor operated in a differential mode. The catalyst reduction time was the same as that used in the Mössbauer experiments.

Mössbauer spectroscopy. The Elscint constant acceleration Mössbauer spectrometer and the gas flow system used in this work have been reported elsewhere (*30, 31*). The source was 85 mCi 57 Co/Pd. The Mössbauer spectra here have a isomer shift referred to a 12.5 μm Fe foil. The Mössbauer spectra were computer fitted to Lorentzian line shapes by using a standard linear least-squares routine (*32*) in a constrained or unconstrained mode, as indicated in the following sections. The catalyst charged into the sample cell is a disk 16 mm in diameter weighing 210 mg. The effective thickness is about 4.8. The reduction times employed in the Mössbauer spectra studies were 25, 20, and 20 hr for the 558, 723, and 773 K reduced catalysts, respectively. The 25-hr reduction time assures a high degree of reduction at the low temperature—558 K. Owing to the high density of TiO_2, 36 hr of the scanning time was required for a good signal-to-noise ratio. Owing to the type of the cell used, all the Mössbauer spectra were taken at 298 K. Because the recoil-free fraction is a function of temperature (*33*), the spectra of carbide and iron oxide in this work are not as accurate as those taken at 4 K (*34*). However, the results are still meaningful if all the spectral comparisons are based on the same temperature.

X-ray diffraction (XRD). X-Ray line broadening experiments were conducted with a Philips horizontal diffractometer using Cu*Kα* radiation passed through a diffraction monochrometer. Samples were used as caving mounted. A constant scan of 1°/min was used for the 2θ range from 20 to 60°. Silicon powder (50 mesh, Alfa) was used as the standard. All X-ray diffraction measurements were performed on samples that had been previously reduced and exposed to the atmosphere. The Scherrer equation was used to calculate the particle sizes, and a K-value of 1 was used.

RESULTS

XRD Results

Figure 1 shows the X-ray powder patterns for the support and catalysts after various activation pretreatments. It is well

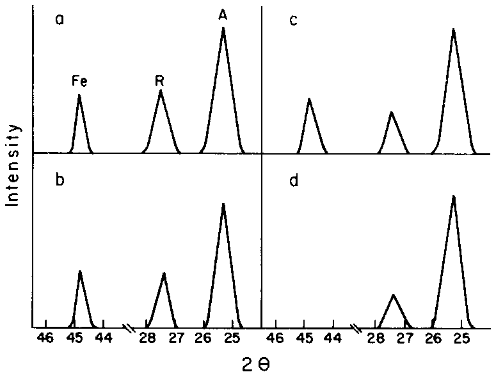

FIG. 1. Diffractometer results. A/R = anatase/rutile. Fe/TiO_2 catalysts: (a) 773 K, A/R = 2.6; (b) 723 K, A/R = 2.95; (c) 558 K, A/R = 3.6; (d) TiO_2 alone at 773 K, A/R = 4.05; original TiO_2, A/R = 4.0.

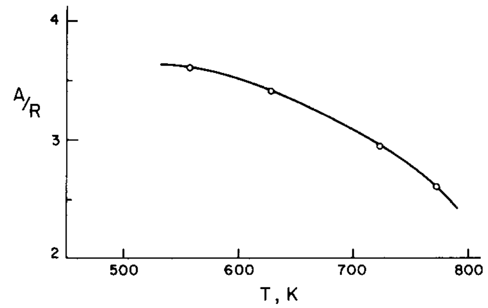

FIG. 2. A/R ratio as a function of reduction temperature for Fe/TiO_2.

known that the transformation temperature from anatase (A) to rutile (R) is about 973 K in hydrogen (*35*). Figure 1d shows the A/R ratio of pure TiO_2 reduced at 773 K, which is about the same as the original ratio (A : R = 80 : 20). This confirms the reliability of the experiment. The relation of the A/R ratio to the reduction temperature is plotted in Fig. 2. Comparing this result with a previous study (*35*), we see that iron is a catalyst for the transformation of anatase to rutile.

In addition, it is worthwhile to point out that during reductions, the white TiO_2 becomes blue. However, when the sample is exposed to the air the blue color fades away. This implies that there is no reduced phase formed during this process, since all the Ti_nO_{2n-1} ($n = 3$–10) are blue and stable. None of these species will be oxided to TiO_2 at room temperature in air. Therefore, the blue color must come from oxygen vacancies in the TiO_2 lattice and these can draw oxygen from the air at room temperature. The iron particle sizes calculated by the Scherrer equation are presented in Table 1. The particle size increases as the reduction temperature increases. This result is consistent with some of the previous studies (*12, 23*). It does not agree with most of the Group VIII/TiO_2 systems (*1, 2, 25, 36*).

We could not detect any reduced titania phase by the X-ray diffraction pattern. In order to examine this phase carefully, the Guinier method was employed. This method gives better resolution and is more sensitive than the diffractometer method. However, no reduced TiO_2 phase was observed by this method either. Therefore, we concluded that there was little reduced TiO_2 phase present after the 773 K reduction in the Fe/TiO_2 system.

Chemisorption Results

The H_2 chemisorption results are listed in Table 1. It can be seen that the high-temperature reduced catalyst chemisorbs less H_2 than the low-temperature reduced catalyst. This is consistent with other work for Group VIII/TiO_2 systems. However, the suppression of the H_2 chemisorption is not so drastic as in the other systems (*1, 2, 37*), in which the H_2 chemisorption falls nearly to zero. This difference may be caused by the experimental methods employed. Most other chemisorptions are carried out by the so-called volumetric adsorption method. In our work, a desorption method has been used (*30*).

It is appropriate to outline here the flow desorption method, as we have used it. Since the adsorption of hydrogen near room temperature is kinetically controlled ("irreversible") (*72*), the equilibrium amounts of dissociation and adsorption are probably not reached at room temperature. As the temperature is increased in flowing

TABLE 1

Particle Size Characterization and Chemisorption Results

Reduction temperature (K)	Chemisorption results (μmol/g)			Particle size (Å)		XRD result (Å)
	H_2[a]	CO[b]	CO[c]	H_2[d]	CO[e]	
558	25.2	6.4	29.5	285	245	300
723	17.4	3.65	26.1	410	275	350
773	12.4	3.85	21.8	580	330	450

[a] By desorption method, adsorption at 373 K.
[b] By pulse adsorption method, adsorption at 195 K.
[c] By desorption method, adsorption at 195 K.
[d] From H_2 chemisorption.
[e] From CO chemisorption, method *c*.

hydrogen the adsorption isobar passes through a maximum; on the high-temperature side of the maximum equilibrium is quickly attained. Now as the temperature is lowered, still in the presence of hydrogen gas, the H-coverage increases so that by the time kinetic cut-off occurs the coverage is as close to complete as possible. Further reduction of temperature to room temperature or below renders the H-adsorption irreversible again, so that a switch to flowing helium causes little desorption. Then the quantity of hydrogen desorbed can be obtained by temperature-programmed desorption (TPD) to remove all the hydrogen. With iron it is difficult to use this procedure with CO as the adsorbate, for it dissociates and forms CO_2 as the temperature is raised. However, by long exposure to CO at room temperature or below, the maximum CO adsorption is achieved. The flow desorption method thus usually indicates more adsorption than the adsorption or pulse method. In the desorption method a long time is allowed for the adsorption process (not measured), and the desorption is made to occur rapidly, and the quantities desorbed are easily measured. In the adsorption method, the quantity adsorbed must be measured as it occurs very slowly at low temperature. In the pulse method, much of the pulse can pass over the catalyst without the capture of the adsorbable gas by the slow adsorption process. It should be noted that the use of desorption isotherms to study a slow chemisorption process was suggested by Dalla Betta (*38*) about 10 years ago. The crystal sizes calculated by the H_2 chemisorption are listed in Table 1. They are comparable to the XRD results. This leads us to conclude that the desorption measurement of H_2 is an approximate method to characterize the particle size of metal/TiO_2 systems. A similar conclusion has been drawn by Jiang *et al.* (*39*). Table 1 lists the CO chemisorption results measured by two different methods. In the pulse adsorption method, little CO chemisorption is observed. In the desorption method, a considerable amount of CO chemisorbed. This difference, again, is probably caused by the slow chemisorption process. These results show that it is not surprising that the crystal size calculated by the CO chemisorption often disagrees with the XRD results. A similar observation can be found in other studies (*40, 41*).

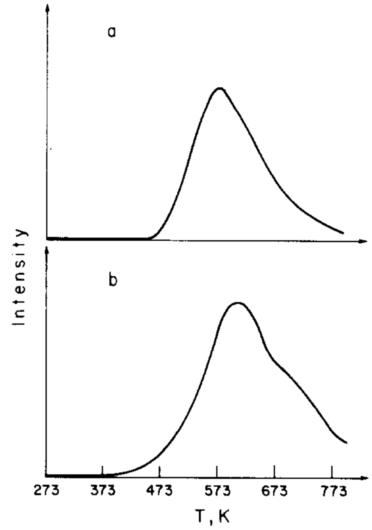

FIG. 3. Temperature-programmed desorption of hydrogen on Fe/TiO_2. (a) Reduced at 773 K; (b) reduced at 558 K.

In order to examine the effect of reduction temperature on the bonding strength of adsorbed hydrogen, the TPD of H_2 was carried out. The carrier gas was Ar with a flow rate of 16 ml/min, and the heating rate was 14 K/min. Figure 3 shows the TPD spectra. It can be seen that the main peak shifts to lower temperature when the reduction temperature increases. This implies that the Fe-H bonding decreases with increasing reduction temperature. In addition, the hump at 680 K in the spectrum (b) strongly suggests that there is more than one active surface site.

Mössbauer Results

Mössbauer spectra of the catalysts reduced at different temperatures are shown in Figs. 4a–d. The top of Fig. 4a also shows the expected peak positions of a magneti-

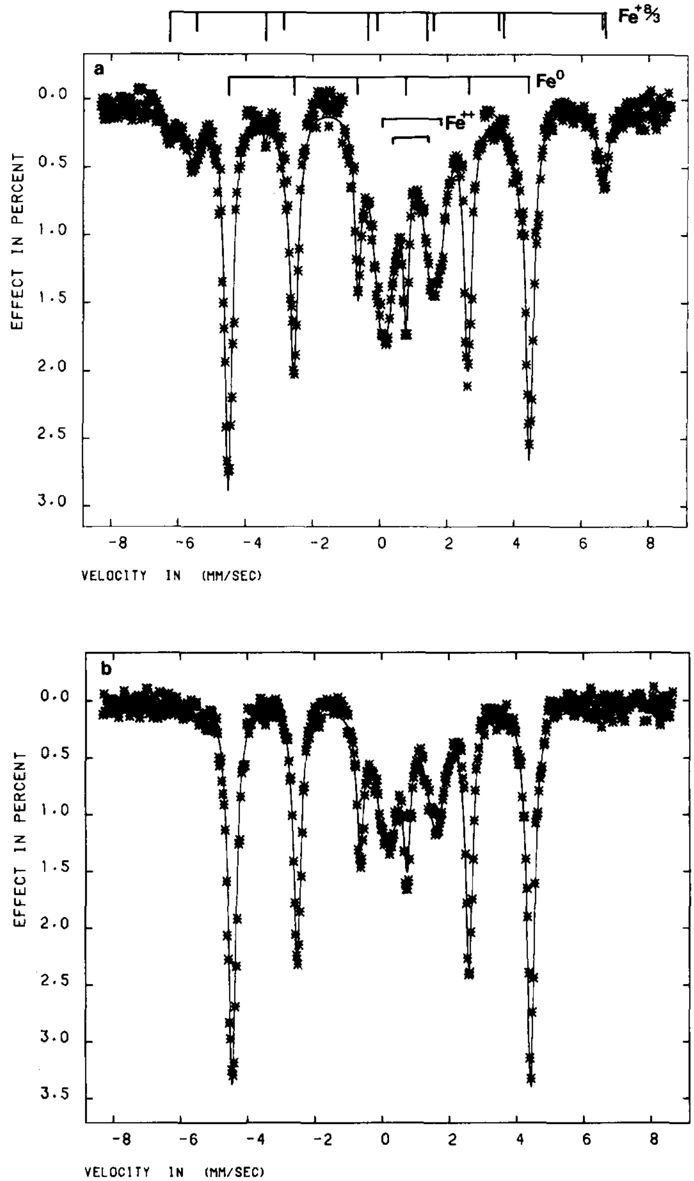

FIG. 4. Mössbauer spectra: (a) Fe/TiO_2 catalyst reduced at 558 K for 25 hr. (b) Fe/TiO_2 catalyst reduced at 623 K for 20 hr. (c) Fe/TiO_2 catalyst reduced at 723 K for 20 hr. (d) Fe/TiO_2 catalyst reduced at 773 K for 20 hr.

cally split metallic iron spectrum, two quadrupole doublets indicative of high-spin and low-spin Fe^{2+}, and a spectrum with 12 peaks for ferrimagnetic iron (Fe_3O_4). The possible contribution to the electric field gradient from, for example, surface or interface effects has not been considered in these qualitative peak positions at the top of the figure. The detailed analysis of the spectrum for the 558 K-reduced catalyst was complicated by the overlap between peaks in the central region of the spectrum. However, with the help of the 723 and 773 K-reduced catalyst spectra, the problem can be solved. During the curve fitting process all the areas in the same hyperfine

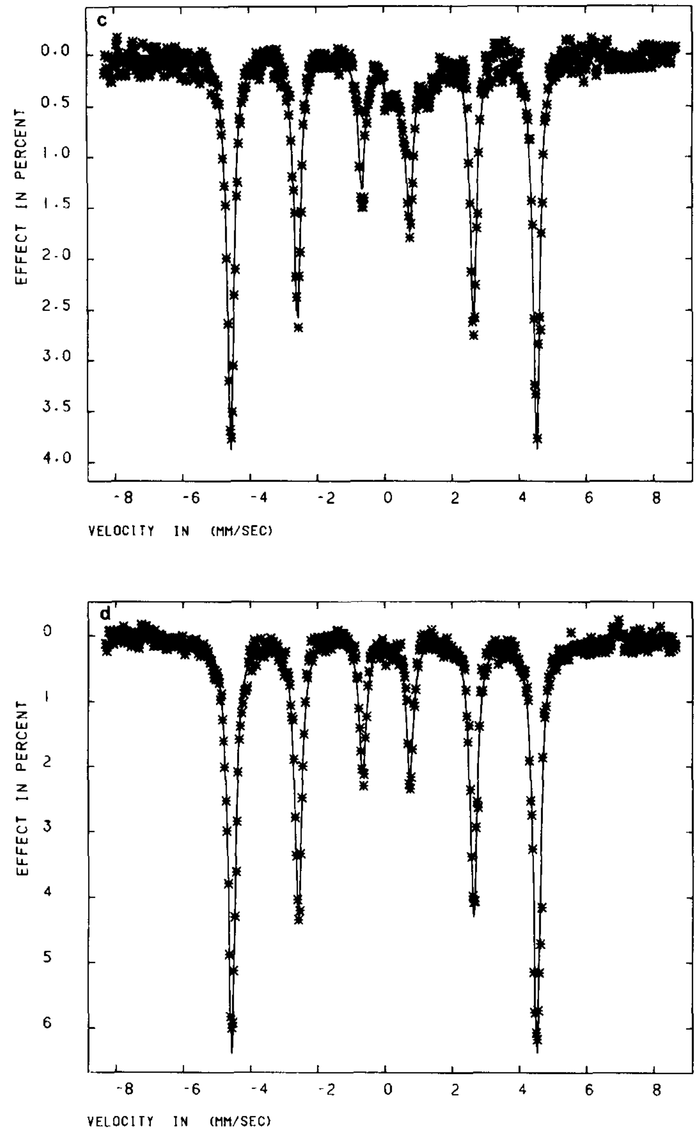

FIG. 4—*Continued.*

were constrained by the following ratios 3 : 2 : 1 : 1 : 2 : 3. The widths were unconstrained, but their ratios are assigned close to 1 in the same hyperfine set. The Mössbauer parameters are listed in Table 2. Figure 5 shows the relationship of the bulk-phase iron to the reduction temperature and the reduction time. It is understandable that the proportion of bulk phase Fe^0 increases with increasing reduction temperature and time. From Fig. 5, we see that at 558 K iron cannot be well reduced even for a very long reduction time. That is why iron catalysts are usually reduced at 723 K or higher for a long time. This is also the reason that we cannot reduce our catalyst at 473 K like the other Group VIII metals to study the low-temperature reduction effect. The percentage of Fe^0 obtained in this work is about the same as the previous work (*24*) under similar reduction conditions. The small difference may be caused by the following two

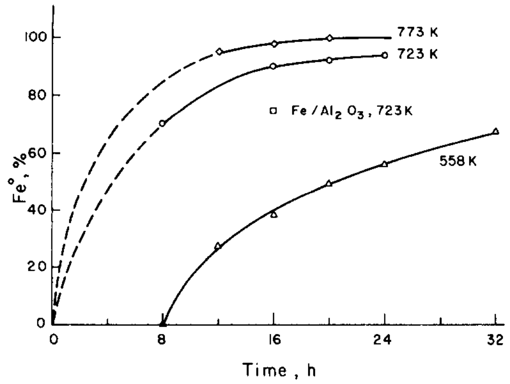

FIG. 5. Reduction of iron for various temperatures and supported catalysts.

TABLE 2

Mössbauer Parameters of Catalysts Reduced at Various Temperatures Determined at 298 K: Isomer Shift Values Reported with Respect to Iron Foil

Reduction temperature	Species	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Hyperfine field H, KOe
558[a]	Fe^0	−0.002	0.03	327.0
	$Fe^{8/3+}$	0.63	—	450
	$Fe^{8/3+}$	0.30	—	480
723	Fe^0	−0.01	0.03	334.0
	Fe^{2+}	0.84	1.38	—
	Fe^{2+}	0.75	0.44	—
773	Fe^0	−0.01	0.03	334.0

[a] Fe^{2+} in the 558 K-reduced catalyst has the same parameters as in the 723 K-reduced catalyst.

factors: (1) the H_2 concentration during the course of reduction; (2) the reduction time (*24*). However, it should be noted that after 20-hr reduction at 773 K all the bulk phase iron becomes Fe^0. This is quite different from the other metal oxide-supported Fe catalysts (*29, 30, 31, 43, 44*). In the other systems there is some residual Fe^{2+} present besides Fe^0. The details of this unusual phenomenon need further study.

Figures 6a–f shows some of the Mössbauer spectra during the 10% CO/H_2 reaction. The areas of the three chi-carbides are constrained to be 2 : 2 : 1 (*45*). The total carbide formation is plotted against the reaction time in Fig. 7. The bulk phase components are listed in Table 3 after 0, 120, and 240 min of reaction. Table 4 gives the Mössbauer parameters of the carbides. It agrees well with the previous studies. For the 773 K-reduced catalyst, Fe_5C_2 (chi-carbide) is the only carbide. For the other two catalysts both chi- and epsilon′-carbides are found. It is quite surprising that the 723- and 773 K reduced catalysts carburize very slowly during the course of the reaction when compared with the 558 K-reduced catalyst. Figure 7 also shows the carburization curve for the Fe/Al_2O_3 system. Although the shape of this curve is similar to that of the 558 K-reduced Fe/TiO_2 system,

TABLE 3

The Bulk Phase Components Analyzed by Mössbauer Spectroscopy for Various Times of Reaction, 10% CO/H_2

Reduction temperature (K)	Fe^0 (%)	Fe^{2+} (%)	$Fe^{8/3+}$ (%)	ε'-Carbide (%)	χ-Carbide (%)	Reaction time (min)
558	56.0	30.0	14.0	0.0	0.0	
723	91.2	8.8	0.0	0.0	0.0	0
773	100	0.0	0.0	0.0	0.0	
558	0.2	27.6	13.9	10.3	47.9	
723	63.7	7.2	0.0	13.9	15.2	120
773	92.1	0.0	0.0	0.0	7.9	
558	0	27.5	14.2	9.4	48.8	
723	34.0	7.3	0.0	22.3	36.4	240
773	82.8	0.0	0.0	0.0	17.2	

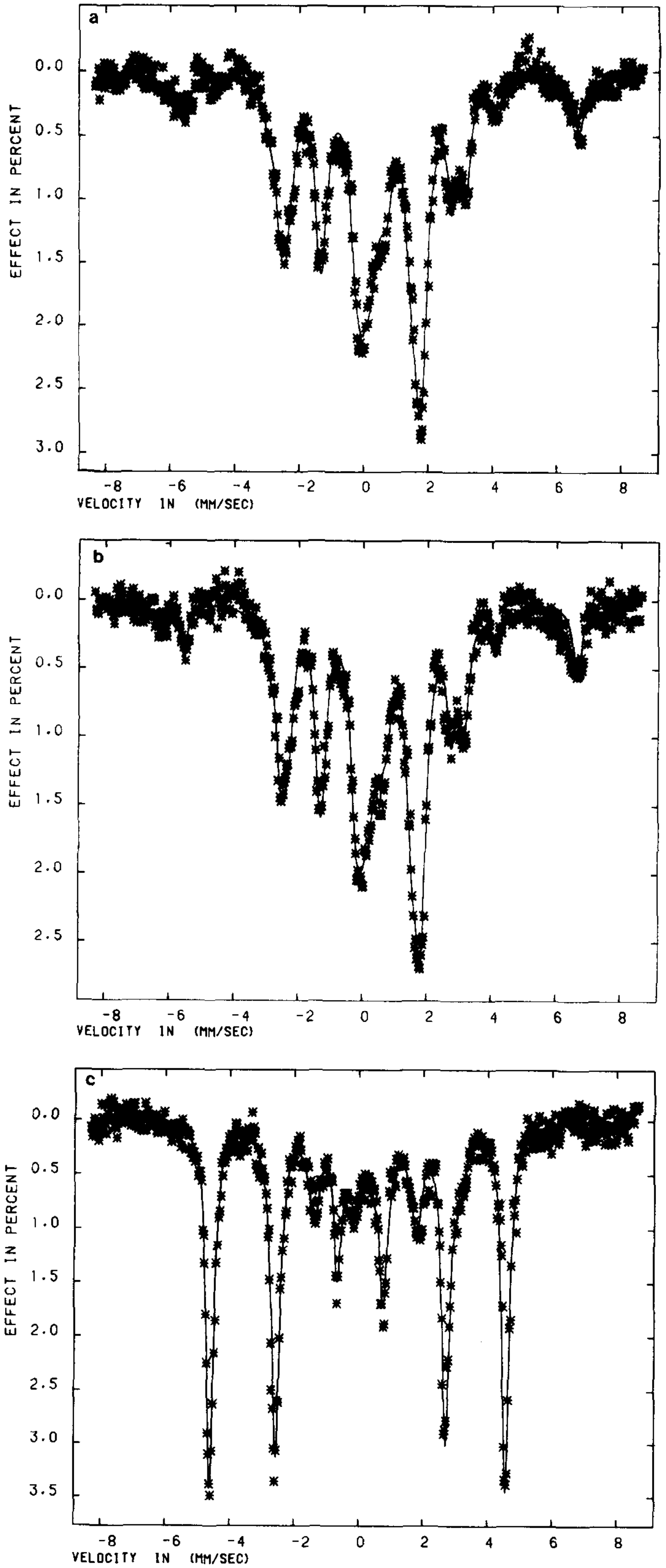

FIG. 6. Mössbauer spectra of Fe/TiO$_2$ catalysts after exposure to 10% CO/H$_2$ at 558 K. (a) Reduced at 558 K 120 min of reaction. (b) Reduced at 558 K 240 min of reaction. (c) Reduced at 723 K 120 min of reaction. (d) Reduced at 723 K 240 min of reaction. (e) Reduced at 773 K 120 min of reaction. (f) Reduced at 773 K 240 min of reaction.

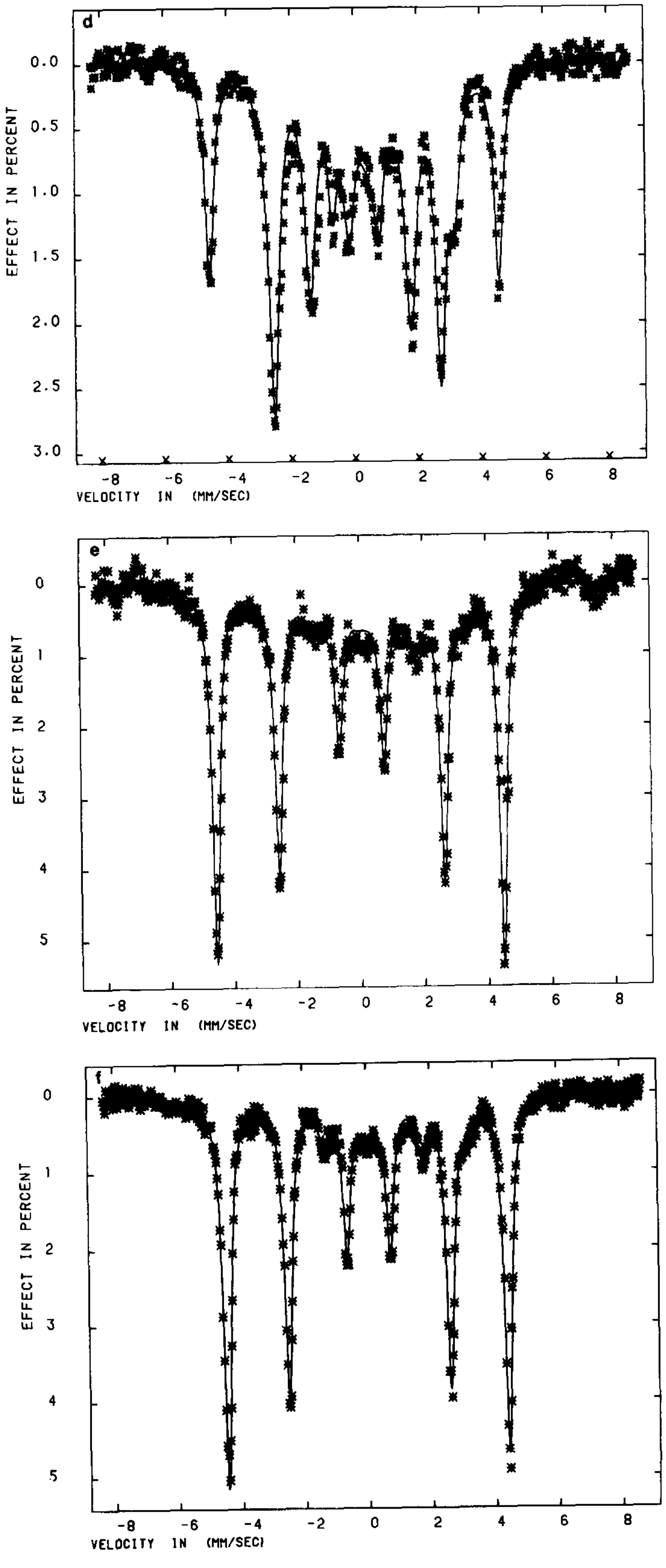

FIG. 6—*Continued.*

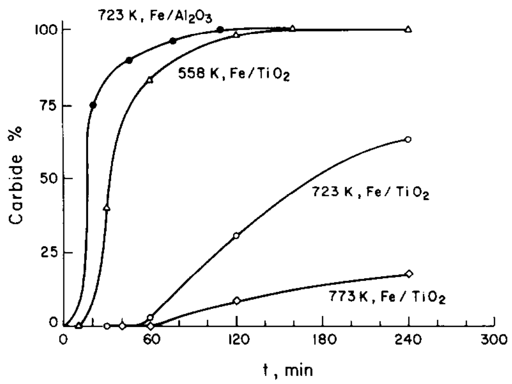

FIG. 7. Carbide formation for iron catalysts during reaction of 10% CO/H_2 at 558 K.

the latter carburizes more slowly. It is believed that the carbide formation is influenced by surface species which are related to the reaction kinetics as will be discussed later.

After a certain time on stream of 10% CO/H_2, the feed into the system was switched to H_2 to attempt to decarburize the carbide at 558 K. Mössbauer spectra show that the carbide is removed very slowly under these conditions. These Mössbauer spectra are not shown in here.

Kinetic Results

Transient measurements. Figure 8 shows the CH_4 formation at 558 K after the catalyst has been reduced at different temperatures. The reactant is 10% CO/H_2, the amount of catalyst is 50 mg, and the residence time is 3×10^{-4} min. It can be seen from the figure that the activity for CH_4 decreases with increasing reduction temperature. This result is consistent with the work of Vannice and of Reymond *et al.* (*37, 67*) under similar conditions, although they observed a relatively larger change in the activity. From the Mössbauer results we know that the decrease in activity cannot be explained by the presence of less reduced iron at the higher reduction temperatures. A possible explanation could be based on the agglomeration or sintering of the catalyst during the course of reduction. The X-ray diffraction results show that the change of the particle size is relatively smaller between the 558 K and 723 K-reduced catalysts (300 Å/350 Å) than between the 723 and 773 K-reduced catalysts (350 Å/450 Å). However, on the contrary, the changes of the reaction activities show a different trend (Fig. 8). Therefore, we conclude that the sintering or agglomeration is only partially responsible for the change of the reaction activity.

TABLE 4

Mössbauer Parameters of Carbides at T = 298 K

Carbide	Fe site	IS mm/s	HF KOe
χ-Fe_5C_2	(I)	0.14	193
	(II)	0.18	216.0
	(III)	0.27	117
ε'-$Fe_{2.2}C$		0.01	176

Another possibility is a geometric effect, in which some of the titania migrate onto the top of the Fe surface during the course of the high temperature reduction (so-called decoration). Those titania species will block some of the active Fe sites, and make the reaction activity decrease. However, if this were the whole explanation, then the activation energy of the catalysts reduced at various temperatures should not change. Figure 9 shows the activation energy for the catalysts reduced at various temperatures. The activation energy for the 558 K-reduced catalyst is comparable to that of previous studies for the CO/H_2 reaction on Fe catalysts (*30, 37*). The activation energy in-

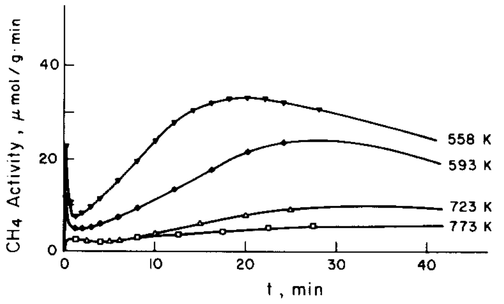

FIG. 8. Rate of CH_4 formation for the reaction of 10% CO/H_2 at 558 K over Fe/TiO_2 reduced at various temperatures.

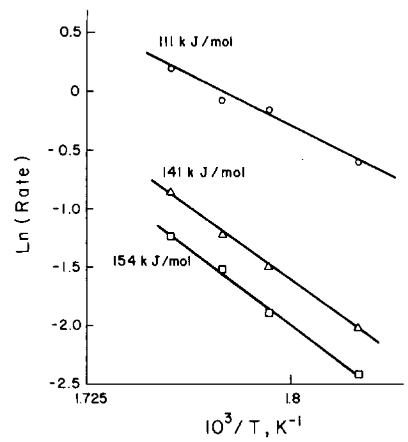

FIG. 9. Arrhenius plot from Fig. 8 for rates at 20 min.

creases with increasing reduction temperature. Table 5 shows the C1/C2+ ratio for the catalysts reduced at various temperatures under the same reaction conditions as Fig. 8. This table shows that there are some differences in the product distribution. The change in the activation energy and product distribution do not support the idea that a blocked surface is the only reason for the high-temperature reduction effect. The shifting of the main peak in the TPD spectra gives other evidence that the simple decoration is not fully responsible for the high-temperature reduction effect.

In order to study this matter further, another experiment was carried out. After reducing the catalyst at 773 K for 20 hr, the catalyst was exposed to air for 24 hr. It was found that the reaction activity of this air-exposed catalyst is about 50% higher than the same catalyst without exposure. It is hard to believe that air can remove any titanium oxide from the iron surface at room temperature. In other words, this experiment demonstrates that the simple surface blocking cannot be the only reason for the SMSI effect. Therefore, we conclude that the geometric effect cannot explain the whole phenomenon either. Now, the only apparent possibility left is the change of the electron configuration in the catalyst, which is the so-called charge transfer or electron effect. However, similar to the argument made by Ponec (*22*), a small charge transfer should not affect the activity much, especially for this system in which the Fe particle size is somewhere around 350 Å. Therefore the charge transfer necessary for a great change in the activity should be substantial. This would lead to a change in the isomer shift (Mössbauer parameter) for various reduced catalysts. However, we do not observe any significant change in the isomer shift. The details of this effect will be further discussed.

TABLE 5

The Ratio of C1/C2+ for the Catalysts Reduced at Various Temperatures[a]

Reduction temperature (K)	10% CO/H_2 reaction time (min) 15	25	35
558	2.03	2.12	2.16
723	1.4	2.13	2.19
773	1.47	1.74	1.76

[a] Reaction at 558 K.

After 30 min of 10% CO/H_2 reaction, the feed is switched to He for 30 sec (in order to desorb the chemisorbed H_2), then to H_2 to react with the surface species. Figure 10a

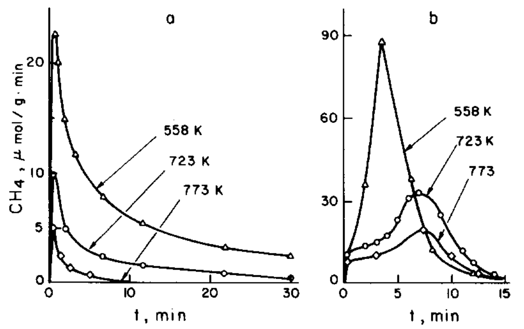

FIG. 10. (a) Methane peaks produced by a switch to hydrogen at 558 K after 35 min of reaction in 10% CO/H_2 at 558 K over Fe/TiO_2 catalysts reduced at various temperatures. Methane quantities: 558 K, 495 μmol/g; 723 K, 123 μmol/g; 773 K, 25 μmol/g. (b) Continuation of a. Methane peaks produced by a switch to hydrogen at 773 K after H_2 flushing at 558 K until no more methane was detected. Methane quantities: 558 K, 405 μmol/g; 723 K, 248 μmol/g; 773 K, 135 μmol/g.

shows the results of these experiments. As expected the low-temperature reduced catalyst gives more methane during this process. After feeding H_2 at 558 K until there is no detectable CH_4 formed we change the gas to He and quickly increase the temperature to 723 K, then switch back to H_2, and the results are shown in Fig. 10b. The huge peak of methane formed during this process implies a slow reaction kinetics at 558 K as shown in Fig. 10a. The same argument can be made from the decarburization results from Mössbauer spectroscopy. This is the reason that it takes so long to clean the reacted surface at 558 K. It is difficult to deconvolute these peaks. However, the long tails in Fig. 10a give us evidence that there are two surface intermediates during the 10% CO/H_2 reaction, since a single type of surface site should give a peak of Gaussian shape. In addition, the TPD results support this argument. The methane formed in Fig. 10b (558 K) is believed to arise from inactive carbon (graphite) and bulk carbide, since from the Mössbauer result we know that there are only 177 μmol carbide formed in 30 min of reaction for the 558 K-reduced catalyst. The total amount under the 558 K-curve is 405 μmol. In addition, we do not observe any carbide from Mössbauer spectroscopy for the 723- and 773 K-reduced catalysts after 30 min of reaction. Therefore, the methane in Fig. 10b (723 and 773 K) must come from surface graphite. The above results show that, even for the catalyst reduced at 558 K, there are important kinetic differences between the Al_2O_3-supported catalyst and the three TiO_2-supported catalysts. Although the chemisorption is not appreciably suppressed, and the activities are not drastically reduced, there are dramatic changes in the rates of carburization and in the nature of the surface species during reaction with 10% CO/H_2. It is interesting to note that carburization during reaction over iron is also suppressed when another metal, for example Ru (*47*) is alloyed with the iron. Other studies show a similar result (*28, 48*). Thus we have another argument which supports a change in the electron configuration of the iron catalyst.

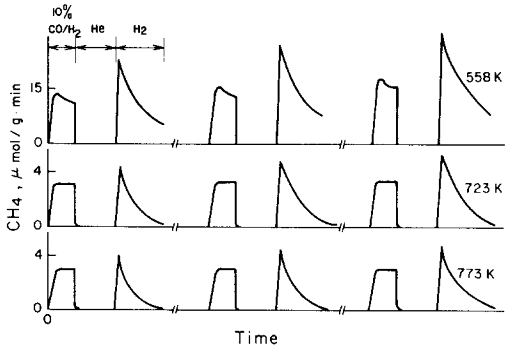

FIG. 11. Cyclic reaction at 558 K over Fe/TiO_2 reduced at various temperatures. The cycle is 10% CO/H_2,20s → He,30s → H_2 until no further CH_4 appears → He,30s → 10% CO/H_2,20s, and repeat.

Cyclic reaction. Figure 11 shows another type of experiment. The feed to the reactor is cycled as follows: 10% CO/H_2 → He → H_2 → He → 10% CO/H_2, etc. We found that during the cyclic reaction the CH_4 activity has a tendency to increase to an asymtotic value. This increase is relatively more prominent for the 558 K reduced catalyst than for the high-temperature reduced catalysts. This phenomenon is entirely different from the Fe/Al_2O_3 system, which has its highest activity for the freshly reduced catalyst. It is well known that the high-temperature reduction effect can be removed by treating the catalyst in oxygen or water (*1, 2, 17*). Therefore, it appears that during the reaction some of the oxygen and/or water formed partially removes the interaction between the metal and support increasing the activity. To study this matter further, the following two cyclic experiments have been carried out. Instead of using 10% CO/H_2 as feed, we use (1) 10% CO/He and (2) 10% C_2H_4/He. The reason for choosing these two reactions is that the first system will form some surface oxygen and the second system will not. The effect of the former is the same as the 10% CO/H_2 but with less increase in the activity (not

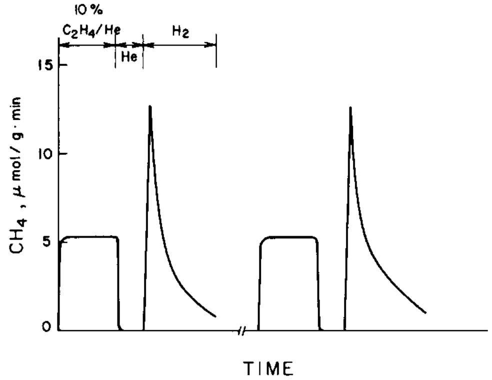

FIG. 12. Cyclical reaction at 558 K over Fe/TiO_2 for the cycle 10% C_2H_4/He,20s → He,10s → H_2 until no further CH_4 appears → He,40s → 10% C_2H_4/He,20s, and repeat. There is no effect of the reduction temperature of Fe/TiO_2.

shown). The result of the second reaction is shown in Fig. 12. Now there is no difference between the low and high-temperature-reduced catalysts and no tendency to increase the methane activity. A similar result had been observed by Burch and Flambard (*23*) for hydrogenolysis. These two experiments show that the oxygen and/or water can partially decrease the interaction between the metal and support. The electron effect is suspected since the presence of oxygen and/or water at 558 K is not likely to reverse the decoration effect. In addition, the 10% C_2H_4/He results also show that the so-called SMSI has no effect on certain reactions. The effect is not only geometric but has chemical specificity.

DISCUSSION

The results presented in the previous section clearly show that the properties of Fe supported on TiO_2 are markedly influenced by prior treatments. For the 723 K or higher temperature reduced catalysts, the crystal size of iron increases from 300 to 450 Å, i.e., some sintering or agglomeration occurs during the course of reduction. Table 1 indicates that the CO and H_2 chemisorptions are moderately suppressed. Kinetic measurements show that the reaction activity for the 773 K catalyst decreases an order of magnitude when compared with the 558 K-reduced catalyst. The Mössbauer spectroscopy results indicate that the bulk phase iron is essentially identical to metallic iron. Although the carbide formation is slow, iron carbide does form during the reaction. These results can be only partly explained by the geometric effect (decoration). It is worth while to point out that this decoration is formed by the migration of TiO_2 onto the top of the Fe surface, although the Tammann temperature of TiO_2 (925 K) is higher than that of Fe (905 K). During the course of reduction by H_2, iron oxide is reduced to Fe^0 ($\Delta H = +22.5$ kcal/mol) and TiO_2 loses interstitial oxygen to form water ($\Delta H = -58.0$ kcal/mol). According to previous studies (*50, 51, 52*), during the reduction the Tammann temperature of Fe and TiO_2 will be about 950 and 810 K, respectively. This Tammann temperature for TiO_2 (810 K) is very close to the reduction temperature used. Therefore, the small TiO_2 particles in the vicinity of the metal–support interface may have sufficient mobility to move over the top of the metal surface. Similar results have been observed (*53–55*) in the Fe/C system. Energetic effects suggest that these small, isolated particles may have different properties from the bulk phase TiO_2.

The kinetic measurements also indicate that the activation energy changes from 111 to 158 kJ/mol and the H_2 TPD spectra show that the main peak shifts from 570 to 600 K when the reduction temperature rises from 558 to 773 K. The change of the product distribution of the variously pretreated catalysts is not negligible either. Lots of the inactive surface carbon has been detected during the CO hydrogenation, which is different from the Fe/Al_2O_3 and Fe/SiO_2 systems. During the cyclic reaction the reaction activities have a tendency to increase to a certain extent instead of having an initial surge as for the Fe/SiO_2 and Fe/Al_2O_3 systems. These results cannot be explained by simple decoration and/or sintering.

These results must be associated with the change of the catalyst's chemical properties; the electron configuration of the catalyst has been changed during this high-temperature reduction.

Now let us consider the change of the electron configuration. XRD results show that the bulk TiO_2 is not reduced. The bulk phase detection technique—Mössbauer spectroscopy—indicates the bulk phase iron is the same as the metallic iron and the isomer shifts of the various pretreated catalysts are basically the same. All these results imply that there is no important electron configuration change in the bulk metal phase. In other words, the change of electron configuration is localized at the metal–support interface. A similar argument has been made by Knotek (*56*), Huizinga and Prins (*57*), Santos *et al.* (*17*), and Resasco and Haller (*25*). They claimed that the observed interaction occurred only in the vicinity of the metal–support interface.

The reason and the direction of the electron transfer are discussed as follows. In 1967, Hilsch and Naugle (*58*) postulated that when a semiconductor and a metal are in contact, their Fermi levels should be aligned and electrons will diffuse from the high Fermi level phase (low work function) to the low Fermi level phase (high work function). For a monocrystal placed in vacuum, the work function of TiO_2 (6.2 eV) (*59*), and even that of reduced titania, Ti^{3+}, (4.6 eV) (*60*), exceeds that of iron (4.5 eV) (*61*). Consequently, in iron–titania systems, the alignment of the Fermi levels will correspond to a transfer of electrons from the iron to the titania. In addition, from the activation energy point of view, the same conclusion can be drawn. This interpretation was first given by Schwb (*62*), who correlated changes in activation energy with collective properties of the semiconductor. This theory has been applied by Santos *et al.* (*17*) and Resasco and Haller (*25*). Accordingly, the activation energy for an acceptor reaction would increase when charge is transferred from the metal to the support. This is the case in this study, since from previous work (*63*), we know that the CO hydrogenation over an iron catalyst is an acceptor reaction. The rate determining step is the hydrogenation of the CH_x, $x \leq 1$. The above arguments lead us to propose that electrons transfer from the metal to the support during the course of the high temperature reduction. A similar proposal was made by Santos *et al.* (*17*) and Jiang *et al.* (*39*) for Fe/TiO_2. Different arguments have been made by Resasco and Haller (*25*), Herrmann *et al.* (*18*), and Greiner and Menzee (*64*). They claimed that the charges transferred from the support to the metal for the supported noble metals studied. The difference in direction of electron transfer may be caused by the work function. Most of the Group VIII metals have a higher work function than the reduced titania (Table 6), but iron does not. This implies the Fermi level alignment will cause electron transfer in the opposite direction from that of the Fe/TiO_2 system. In addition, they observed a great enhancement in the reaction activities for the CO hydrogenation, which implies a decrease of the activation energy. Moreover, CO hydrogenations over the other Group VIII metals tend to be donor reactions. In general, the rate determining

TABLE 6

Work Function of Group VIII Metals (*61*)

	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt	TiO_2	Ti^{3+}
Work function (eV)	4.5	5.0	5.2	4.7	4.98	5.12	4.83	5.3	5.65	6.2	4.6

step is at least partly the dissociation of CO. Therefore, the electron transfer from the support to the metal is logical.

In addition, it is well known that a certain amount of potassium compound present on an iron catalyst can increase the CO/H_2 reaction activity and shift the selectivity (*68, 69*). However, in contrast to the iron-based catalysts, the activity of Ni/SiO_2 is decreased by potassium addition (*70, 71*). It has been postulated for a long time that potassium promotion is electronic in nature (*42*). This is consistent with the results for the Fe/TiO_2 and Ni/TiO_2 systems.

It is appropriate at this point to suggest a possible model for the SMSI effect. During the high-temperature reduction, the Tammann temperature of TiO_2 is reached. Small TiO_2 particles move over onto the top of the iron surface. These small, migrated TiO_2 particles have different chemical properties from the bulk phase TiO_2. For example, they easily lose interstitial oxygen. In addition, they have a relatively larger contact area with iron than the bulk phase TiO_2, which will give them a better chance to get the spilled over hydrogen atom. This hydrogen atom will react with oxygen to form water and TiO_x ($1 < x < 2$), and these oxygen deficient TiO_x species will draw electrons from the metal to align the Fermi levels. It should be pointed out that this electron transfer affects only the metal underneath and at perimeter the TiO_x species. This is the so-called localized charge transfer effect. The necessary requirement for this localized effect is the occurrence of the decoration and the presence of the TiO_x species on top of the iron surface.

We have referred several times to the work of Santos *et al.* (*17*). They also studied Fe/TiO_2 catalysts, and our results are in agreement with theirs on the characterization of the catalysts. A principal conclusion is that the high-temperature-reduced catalysts show well reduced iron, no reduction of TiO_2, and moderate change in particle size from the low-temperature-reduced solids. Their test reaction was ammonia synthesis, and like the CO/H_2 reaction, the rate-determining steps is inhibited by the electronic transfer from iron to titania. We have shown that ethylene hydrogenation over iron is not affected by the SMSI and indeed the effect of SMSI on the CO/H_2 reaction over nickel system is the opposite of what it is for iron (*6*). We have also shown that the surface carbonaceous materials present during the CO/H_2 reaction on Fe/TiO_2 system are quite different in reactivity from those present on Fe/Al_2O_3, for both the low- and high-temperature-reduced Fe/TiO_2 catalysts. These differences are reflected in changes in the behavior of the bulk carburization of the iron during reaction. In the work of Santos *et al.* (*17*) the SMSI effect is also explained by an electronic effect associated with migration of TiO_x onto the surface of the iron. We show that the simple geometric effect is not the only reason for SMSI, since it can be removed by exposure of the high-temperature reduced catalyst to air at room temperature.

SUMMARY

The experimental results furnish many arguments in favor of the existence of electron transfer as an explanation of the effect of the TiO_2 support and its reduction temperature. Changing this temperature leads to a change in activation energy consistent with electron transfer from the metal to the support. The selectivity, the nature of the surface carbon-containing species, and the rate of carburization during CO/H_2 reaction are all considerably changed by the reduction effect. However, direct measurement of the bulk properties of iron via Mössbauer spectroscopy leads us to conclude that there is little change in the bulk electron density. There is little isomer shift. In contrast to TiO_2 used as a support for noble metals, there is no apparent bulk reduction of TiO_2, as measured by X-ray diffraction. If we turn to the migration of TiO_2 onto the iron (decoration) as the explanation of our results, it cannot explain many of the phenomena mentioned above. It has been successful in explaining some other experiments (*17, 23*). We propose that decoration does occur in our system but that its effect is not principally geometric, as for the Rh/TiO_2 system studied by Resasco and Haller (*25*). For the Fe/TiO_2 system we think that the migration of TiO_2 onto the iron surface during reduction leads to dispersed particles of TiO_x ($1 < x < 2$). In particular, there is now a large interface or perimeter available between the iron and the TiO_x, so that appreciable electron transfer can occur per atom of iron. The reservations of Ponec (*22*) on this matter are thereby circumvented. Thus because of the decoration charge transfer can occur even though it is not detectable through change in bulk phase properties. The transfer from metal to support is consistent with our kinetic data, involving a lowered activity for the CO/H_2 reaction over Fe/TiO_2. For Ni/TiO_2, for which the activity for the CO/H_2 reaction is enhanced (*23, 37*), a similar explanation is probably valid, but with charge transfer in the opposite direction. A final argument against the geometric effect alone is furnished by the lack of SMSI effect for self-hydrogenation of C_2H_4 on Fe/TiO_2. The difference between the behavior of CO/H_2 and C_2H_4/He can be understood better in terms of electronic effects than in terms of geometric effects.

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