Reaction Intermediates on Fe/TiO$_2$ during CO/H$_2$ Reaction

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The nature of the surface species present on 10% Fe/TiO$_2$ in the low-temperature reduced state (558 K) has been studied after short times of reaction in 10% CO/H$_2$ at 558 K and 1 atm. After various reaction times the surface has been titrated by H$_2$, O$_2$, or D$_2$. The results show that the surface during reaction is covered with about 46 μmol/g of CH and large quantities of surface carbidic carbon. The intermediate for the reaction of 10% C$_2$H$_4$/H$_2$ appears to be only CH.

INTRODUCTION

The surface composition of iron after CO/H$_2$ reaction has been studied by Krebs *et al.* (*1*) on polycrystalline foil and by Bonzel and Krebs (*2*) on the (100) face of a single crystal. The analyses were made by Auger electron spectroscopy (AES) and by X-ray photoelectron spectroscopy (XPS). For the crystal, three types of carbon are proposed: a hydrogenated surface carbon (CH), a carbidic surface carbon (C), and a graphitic surface carbon. Bianchi *et al.* (*3, 4*) studied the CO hydrogenation over Fe/Al$_2$O$_3$ catalyst by mass spectrometry (MS) and Mössbauer effect spectroscopy (MES). After certain times of CO/H$_2$ on stream the feed was switched to H$_2$ and three peaks were observed. They proposed that three surface species exist which are very similar to those that have been observed by Bonzel and Krebs (*1, 2*). Recently, Erley *et al.* (*5*) used electron energy loss spectroscopy (EELS) to study the Fe(110) single crystal surface after the CO/H$_2$ reaction. They suggested that the reaction intermediates are CH$_2$, CH, and CCH$_2$.

In a recent paper (*6*), we studied the CO/H$_2$ reaction over the 10% Fe/TiO$_2$ system. The temperature-programmed desorption (TPD) of H$_2$ suggested that more than one active Fe site exists. The combined analysis of the MS and MES results also indi-cated that more than one active surface species exists after the CO/H$_2$ reaction. Here, we study these surface species by various transient experiments, some involving isotopes.

EXPERIMENTAL

The catalyst and the experimental methods used here are the same as those described previously (*6*). The 10% Fe/TiO$_2$ catalyst was prepared by impregnation, and after drying was reduced at 558 K for 25 h. Thus the catalyst is in the low-temperature reduced (LTR) state, in which its activity for the 10% CO/H$_2$ reaction is higher than in the high-temperature reduced (HTR) state but lower than that of 10% Fe/Al$_2$O$_3$ (*3*). All the kinetic measurements here are done at 558 K, unless otherwise noted. The MS and MES flow systems were reported elsewhere (*3, 4, 7*).

The catalyst has been characterized in its LTR state by hydrogen chamisorption, using a flow desorption method (*6*), and also by X-ray diffraction line broadening (XRD) and by MES as already reported (*6*). The chemisorption result is 25.2 μmol/g, leading to an iron area of 0.64 m^2/g, and crystallite cubes of 285 Å. The line-broadening result is about 300 Å. The MES result shows that the bulk of the iron is 56% Fe^0. The BET surface area is 37 m^2/g, which is
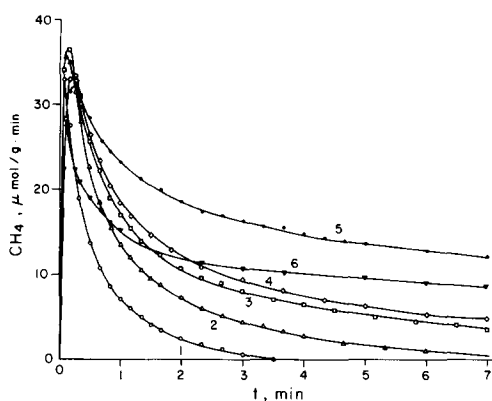
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FIG. 1. Methane produced by a switch to hydrogen at 558 K after various reaction times of 10% CO/H_2 at 558 K: (1) 10, (2) 30, (3) 60, (4) 120, (5) 300, and (6) 600 s.

close to the TiO_2 surface area (50 ± 15 m²/g).

Kinetic measurements involve feeding one gas or gas mixture after another for various times. The procedures will be designated by a nomenclature such as H_2, 25 h → He, 40 s → 10% CO/H_2, 2 min → He, 40 s → H_2 (t). The result will then be expressed as a graph of production rate as a function of time t after the last switch indicated (e.g., H_2 (t)).

RESULTS AND DISCUSSION

Figure 1 shows the CH_4 formation (the main product) during the H_2 titration after various times of 10% CO/H_2 on stream. It can be seen that the height of the CH_4 peak reaches a maximum value when the CO/H_2 reaction time is somewhere around 30 s. In addition, a half-Gaussian distribution is observed when the reaction time is less than 30 s, which implies that for t < 30 s only one kind of surface species exists. However, for longer reaction times, a shoulder develops. This shoulder strongly suggests that more than one active species has reacted with hydrogen. In addition, we found, by proper deconvolution (3), that the quantity of the CH_4 arising from the first peak remains about constant (46 μmol/g)

even as the peak maximum shown in Fig. 1 diminishes.

It might be suspected that the shoulder may be formed by hydrogenation of bulk carbide. If this were true the height of the shoulder should increase to a maximum with the CO/H_2 reaction time. However, Fig. 1 shows that the height of the shoulder increases as the reaction time increases from 2 to 5 min and then decreases as the reaction time increases from 5 to 10 min. In addition, we do not observe any bulk-phase carbide by MES if the CO/H_2 reaction time is less than 10 min (6). Therefore, we propose that more than one active surface species exists on the Fe/TiO_2 surface after the CO/H_2 reaction.

The slow reaction kinetics at 558 K makes it difficult to see the separation of the peaks in Fig. 1. We have repeated the experiments of Fig. 1 except that after the CO/H_2 reaction, the temperature is increased to 723 K quickly (10 K/min) in He followed by switching to H_2 at this temperature. Figure 2 shows the CH_4 formation during the H_2 flushing. It can be seen from Fig. 2 that there is a great difference between the catalysts reacted for 10 s and 5 min. The former has only a single peak. The latter has two prominent peaks. In addition, both curves show the so-called Gaussian distributions. This result strongly indicates
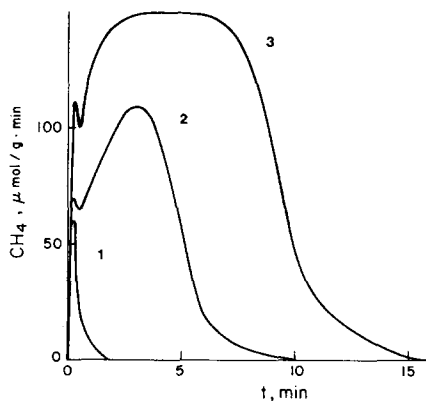

FIG. 2. Methane produced by a switch to hydrogen at 723 K after various reaction times of 10% CO/H_2 at 558 K: (1) 10, (2) 300, and (3) 1800 s.
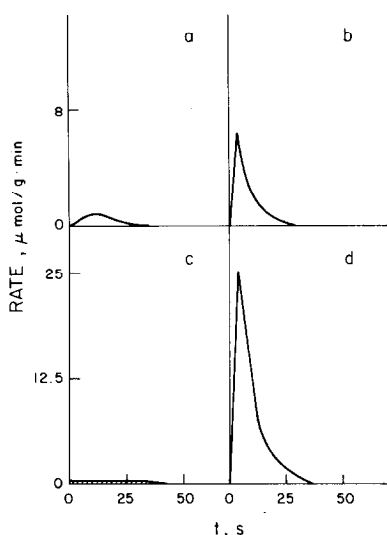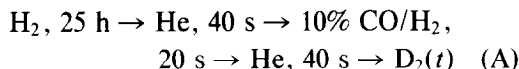
FIG. 3. Reaction rate of mass number 20 by a switch to D_2 at 558 K after 20-s reaction: (a) 10% CO/H_2 reaction, Sequence (A). (b) 10% CO/He reaction, Sequence (B). (c) 10% C_2H_4/H_2 reaction, Sequence (C). (d) The same as part (b) except purge in D_2 before 10% CO/He reaction. Sequence (D).

that the 5-min reacted catalyst has two reaction intermediates and the 10-s reacted catalyst has only one reaction intermediate. Of course, the surface intermediate which forms the first peak is more active than the surface intermediate which forms the shoulder in Fig. 1. Hereafter, we refer the former as CH_x species and the latter as CH_y species, where $0 \leq x,y \leq 3$, since the reaction of the surface and bulk carbonaceous species with H_2 produces essentially no water. This means that there is no oxygen present in the surface intermediates. The 30-min reacted catalyst produces a curve of a different shape from that for the 5-min reacted catalyst. It has a flat maximum which implies that there must be some other carbon-containing species besides CH_x and CH_y. Combined with our MES results (6), we think this flat maximum must be partly associated with the bulk phase carbide and some inactive surface graphite. The detailed composition of this peak needs further study.

Knowing that there are two active reac-

tion intermediates after the CO hydrogenation, we have attempted to use deuterium and oxygen to estimate the hydrogen content of these species, i.e., to determine the x and y values. The first kind of reaction performed is

$$H_2, 25 \text{ h} \rightarrow \text{He}, 40 \text{ s} \rightarrow 10\% \text{ CO/H}_2,$$
$$20 \text{ s} \rightarrow \text{He}, 40 \text{ s} \rightarrow D_2(t) \quad (A)$$

From the previous argument, we know that for 20 s of 10% CO/H_2 reaction only the relatively active reaction intermediate, CH_x, can be formed. In other words, we analyze only the CH_x species under this reaction condition. A small quantity of product with mass number 20 is found, as shown in Fig. 3a.

We interpret this peak as arising from D_2O, because it has a broad, tailing shape, similar to that produced by H_2O when it is produced. Also, the 18-peak should have a similar broad shape, if the 20-peak were CD_4; it does not, as shown in Fig. 4b. This result implies that the x in the CH_x is not
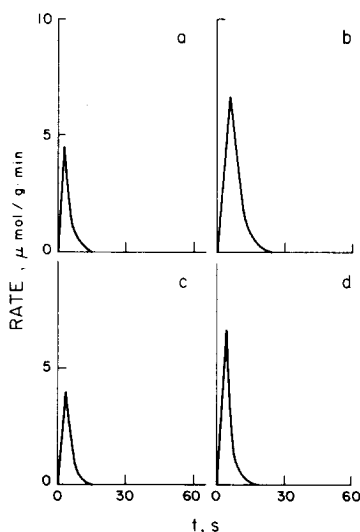

FIG. 4. Reaction rate of various mass numbers by a switch to D_2 at 558 K after 10% CO/H_2 reaction for 20 s. Sequence (A). (a) Mass number 19. (b) Mass number 18. (c) Mass number 17. (d) Mass number 17; the same reaction as part (c) except purge in D_2 before the reaction. Sequence (F).

zero. Note also the small peak area in Fig. 3a. To study this matter further, the following reaction has been carried out. Instead of using 10% CO/H_2 as feed, we followed the sequence

$$H_2, 25 \text{ h} \rightarrow \text{He}, 40 \text{ s} \rightarrow 10\% \text{ CO/He},$$
$$20 \text{ s} \rightarrow D_2(t). \quad (B)$$
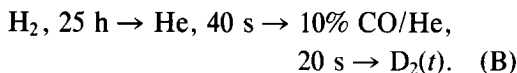
The mass number 20 obtained is shown in Fig. 3b. The peak is sharp and presents no time lag. This behavior corresponds to a methane rather than D_2O. From this experiment we conclude that CO/He does indeed produce surface carbon and that this intermediate is easily distinguished from that of Fig. 3a. A further experiment which sheds more light on the nature of the 20-peak is
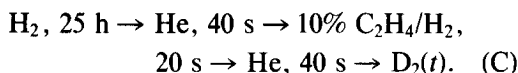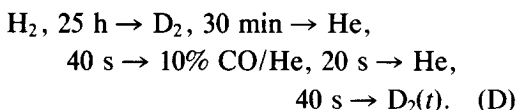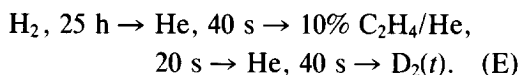
$$H_2, 25 \text{ h} \rightarrow \text{He}, 40 \text{ s} \rightarrow 10\% \text{ C}_2\text{H}_4/\text{H}_2,$$
$$20 \text{ s} \rightarrow \text{He}, 40 \text{ s} \rightarrow D_2(t). \quad (C)$$

Figure 3c shows that this sequence produces essentially no CD_4. As expected, the hydrogenation of C_2H_4 does not lead to the accumulation of surface carbide. Sequences (B) and (C) thus show that if surface carbide were present, we would detect it, and when it is not present, there is no 20-peak. It should be pointed out that the CD_4 activity in Fig. 3b is quite low when compared with the similar reaction of CH_4 in Fig. 1. This is caused by the exchange of deuterium with hydrogen which exists in the OH groups on the support. To show this we have performed the same reaction as Fig. 3b except that after 25 h reduction in H_2, we switch to D_2 for 30 min:

$$H_2, 25 \text{ h} \rightarrow D_2, 30 \text{ min} \rightarrow \text{He},$$
$$40 \text{ s} \rightarrow 10\% \text{ CO/He}, 20 \text{ s} \rightarrow \text{He},$$
$$40 \text{ s} \rightarrow D_2(t). \quad (D)$$

The purpose of the D_2 purging is to exchange the OH groups to OD. Figure 3d shows that the activity of CD_4 is comparable to that of CH_4 in Fig. 1, and much higher than that of Fig. 3b.
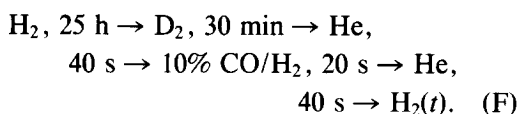
The mass numbers 19, 18, and 17 are also detected for the sequence (A) and are plotted in Figs. 4a–c. The shape of mass numbers 19 and 18 shows that there are some CHD_3 and CH_2D_2 formed during this reaction. The mass number 17 is a bit complicated since the possible contributions are CH_3D, CH_2D_2, and CHD_3. When the cracking patterns are taken into account mathematically, there remains very little mass number 17 which is contributed by CH_3D. In other words, the active reaction intermediates CH_x does not have $x = 3$. To study this further, two more experiments have been carried out. The first one is similar to sequence (A) except that we use C_2H_4/He instead of CO/H_2:

$$H_2, 25 \text{ h} \rightarrow \text{He}, 40 \text{ s} \rightarrow 10\% \text{ C}_2\text{H}_4/\text{He},$$
$$20 \text{ s} \rightarrow \text{He}, 40 \text{ s} \rightarrow D_2(t). \quad (E)$$

The analysis of this experiment leads to the conclusion that there is no contribution to the observed 17-peak by CH_3D; the peak arises from the cracking patterns from $CH_x D_{4-x}$ for $x < 3$. As expected, in the absence of hydrogen, ethylene does not lead to the accumulation of CH_3 species on the surface. Since sequence (A) leads to a similar result, this evidence favors a value of x less than 3.

To test the preceding assertion, we use a sequence which should produce some CH_3D, to see if we could detect it after CO/H_2 if it existed:

$$H_2, 25 \text{ h} \rightarrow D_2, 30 \text{ min} \rightarrow \text{He},$$
$$40 \text{ s} \rightarrow 10\% \text{ CO/H}_2, 20 \text{ s} \rightarrow \text{He},$$
$$40 \text{ s} \rightarrow H_2(t). \quad (F)$$

The D_2 purging converts most of the OH on the support into OD. Therefore, during the CO/H_2 reaction and H_2 titration the deuterium atoms can exchange with H atoms and react with surface carbon species to form CH_3D. The result for mass number 17 is shown in Fig. 4d; this peak is larger than that of Fig. 4c. After the mathematical manipulation based on the cracking patterns of the 19 and 18 peaks there remains considerable mass number 17 which comes from CH_3D. By sequence (F) we show that if CH_3 were present on the surface we

would observe a CH_3D contribution. When there is no CH_3 present, as for sequence (E), we observe no CH_3D contribution. Therefore, since for sequence (A) we see no CH_3D contribution, we conclude that x is not 3 in CH_x.

Now the only possibility for the reaction intermediate CH_x would be CH or CH_2. Owing to the exchange effect between H_2 and D_2 and the strong stability of the symmetric product (CH_2D_2), it is impossible to distinguish the difference between CH and CH_2 by the isotope experiments. We need to use the reaction of oxygen with the surface species to determine CH_x and CH_y.

The basic principle of the oxygen experiment is shown by the reaction

$$CH_x + H_2 \rightarrow CH_4 \qquad (1)$$

$$CH_x + O_2 \rightarrow \frac{x}{2} H_2O + CO_2 \qquad (2)$$
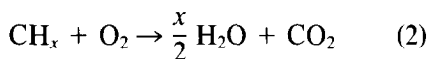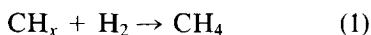
Thus we have

(Measured CH_4/Measured H_2O)

$$= 2/x \qquad (3)$$

By measuring the CH_4 and water formation for a reaction time less than 30 s, we can calculate the x value. After knowing the x value, we simply repeat the experiment but with longer CO/H_2 reaction time and calculate the y value. It should be pointed out that the quantity of H_2O in Eq. (2) should be corrected so as not to include water which comes from the support. The details of the water measurement and the method of calculating x and y values have been described elsewhere (4). The reactions carried out are

H_2, 25 h $\rightarrow$ He, 40 s $\rightarrow$ 10% CO/H_2,

$\qquad (t_1) \rightarrow$ He, 5 min $\rightarrow O_2(t_2)$. (G)
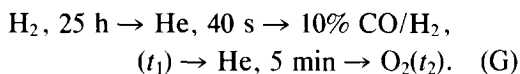
The t_1 are fixed as 10 s, 30 s, 60 s, 2 min, and 5 min. The water curves for this sequence are presented in Fig. 5. To our surprise, the water curve is not a function of 10% CO/H_2 reaction time except at very short time of reaction. In other words, the shoulder which exists in the CH_4 curves
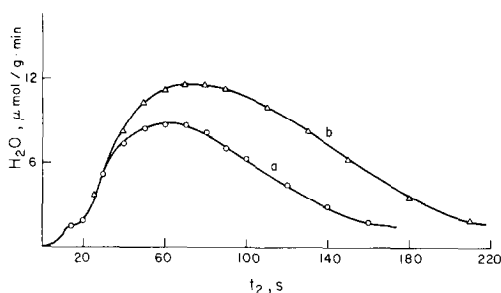

FIG. 5. Water produced by a switch to O_2 after various reaction times of 10% CO/H_2 at 558 K. Sequence (G). (a) 10, (b) 30, 60, 120, and 300 s.

does not show in the water curve. In addition, the quantity of water is almost constant and is listed in Table 1. This implies that either the two reaction intermediates, CH_x and CH_y, have the same reactivity with oxygen, or only one of them contains hydrogen. However, the previous argument indicates that for the reaction time less than 30 s, only the first reaction intermediate, CH_x, can be formed. Therefore, we easily draw the conclusion that y is zero in the CH_y species. Table 1 shows that the amount of CH_4 produced for $t > 30$ s continue to increase. The second species contains no hydrogen, so there is no further increase in the amount of water evolved in the oxygen titration.

The oxygen titration has also been performed after exposure of the catalyst to

TABLE 1

The Results of the H_2 and O_2 Reactions after the Catalyst is Exposed to 10% CO/H_2 for Various Times. Temperature 558 K

10% CO/H_2 reaction time t (s)	10	30	60	120	300
Water[a] formation by O_2 (μmol/g)	10.1	20.6	23.9	21.1	22.7
CH_4 formation by H_2 (μmol/g)	21.5	46.2	83.3	119.5	383.6
x	0.94	0.90			
y	—	—	0	0	0

[a] The water that comes from the support has been subtracted.

TABLE 2

Stability of Surface Exposed to Helium at 558 K
10% CO/H$_2$, 20 s → He^a (t) → H$_2$

Purge time t (s)	0	5	20	40	60	180	720
CH$_4$ height^b	55	35	35	35	34	35	34

^{a} With liquid-nitrogen trap.
^{b} The widths of the peaks are the same. Arbitrary units.

10% CO/He. The amount of water evolved is the same as that of obtained after zero time of reaction in 10% CO/H$_2$, the reference condition for this experiment (4).

We conclude that the surface reaction intermediates after the CO/H$_2$ reaction over the Fe/TiO$_2$ catalyst are CH and carbidic carbon. This results agrees with some of the previous observations (2, 3). It should be pointed out that in Erley's work (6), they found CCH$_2$ as one of the reaction intermediates, which has the same C/H ratio as CH. In this work, we cannot distinguish the difference between the CH and CCH$_2$ species.

It is interesting to study some other properties of these reaction intermediates. We consider the experiment 10% CO/H$_2$, 20 s → He, (t) → H$_2$. Table 2 shows that this peak is remarkably stable in He, since the maximum rate is the same and the width is the same. This stability implies that the bulk phase carbide formation has nothing to do with this surface species, for otherwise, during the He purging this species would diffuse into the bulk and react with iron to

form bulk phase carbide. This result also indicates that the O$_2$ and H$_2$O levels in the He are low. Otherwise, this extremely reactive peak would be changed by the extended exposure to He. The only variation of peak area of Table 2 is observed at the zero helium purge time. The large excess of hydrogen on the surface accounts for this high initial methane peak.

A similar experiment is carried out with 10% CO/He. The results are listed in Table 3. In contrast to the 10% CO/H$_2$ reaction, the maximum rate decreases with increasing He purging time. The width of the peak increases and the tail gets longer so that the area remains about constant. This behavior may be caused by the tendency of these carbidic carbons in the CH$_x$ sites migrate to the less-active surface sites to form CH$_y$, with $y = 0$. To support our point, a similar reaction with 10% C$_2$H$_4$/H$_2$, which does not give any carbidic carbon, is performed. The maximum rate of CH$_4$ formation, just like the CO/H$_2$ result, does not change with the He purging time at all. These experiments indicate that the stability of the first reaction intermediate depends, more or less, on the hydrogen which is bonded by the carbidic carbon. Another interesting experiment is 10% C$_2$H$_4$/H$_2$, (t) → He, 40 s → H$_2$. The results are presented in Table 4. It can be seen that the height and width of the peak are almost independent of C$_2$H$_4$/H$_2$ reaction time except for the shortest reaction time. This seems to indicate that the reaction intermediate of C$_2$H$_4$ hydrogenation is the same as the first reaction intermediate of CO/H$_2$ reaction. If this is true then accord-

TABLE 3

Stability of Surface Exposed to Helium at 558 K
10% CO/H$_2$, 20 s → He^a (t) → H$_2$

Purge time t (s)	0	5	60	150	360	720	1800
CH$_4$ height^b	55	39.5	34	33	30.5	24.5	20

^{a} With liquid-nitrogen trap.
^{b} The areas of the peaks are the same. Arbitrary units.

TABLE 4

Species Accumulated during Exposure to 10%
C$_2$H$_4$/H$_2$ at 558 K 10% C$_2$H$_4$/H$_2$ (t) → He,^{a}
30 s → H$_2$

Reaction time t (s)	5	10	30	60	120	360	1500
CH$_4$ height^b	27.3	33.8	40.4	49.2	51.3	50.0	52.2

^{a} With liquid-nitrogen trap.
^{b} The widths of the peaks are about the same. Arbitrary units.

ing to our previous argument, the first reaction intermediate of CO/H_2 reaction has nothing to do with the bulk phase carbide formation; the C_2H_4 hydrogenation should not form any bulk phase carbide. When we perform the C_2H_4/H_2 reaction in our Mössbauer instrument, there is no carbide detected after 2 h of C_2H_4/H_2 reaction. This result supports our last argument.

SUMMARY

Surface intermediates of CO/H_2 reaction over the TiO_2 supported iron catalyst have been determined by H_2, O_2, and D_2. After CO/H_2 reaction over Fe/TiO_2 catalyst at 558 K, there are two active surface species. The relatively active one is CH and the less-active one is C. The quantity of CH species is about 46 μmol/g. This reaction intermediate is very stable under He flushing and has nothing to do with the bulk phase carbide formation. There is also some surface graphite, but surface graphite is inactive at this temperature. In addition, the reaction intermediate for C_2H_4 hydrogenation behaves similarly to the CH surface species observed during the CO/H_2 reaction. No second species (surface C) is observed.

ACKNOWLEDGMENTS

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