JOURNAL OF CATALYSIS 86, 433–436 (1984)

Influence of the Presence of H_2 during the CO Dissociation Reaction on Iron Catalyst

It is well known that CO dissociates at high temperature on iron surfaces according to the reaction $CO \rightarrow C_{ads} + O_{ads}$. The carbon obtained by this dissociation may stay on the surface or lead to the carburization of the catalyst. The rate of the last reaction has been found to be faster in the presence of H_2 than without it, although the catalyst is active in the Fischer–Tropsch synthesis (*1*). One can suppose that H_2 is acting very specifically during one of the steps of the production of the superficial carbon. This article attempts to describe the role of H_2 on the dissociation of CO.

The analytical system used in our study is identical to the one previously described (*2*). Mass spectroscopy is used to detect and monitor the perturbations caused by very fast changes of the gas-phase composition over the catalyst.

All gases are pure Matheson reagents. The feed is passed over a trap maintained at 300°C in order to eliminate any metal carbonyl trace. The feed is composed of two mixtures: 10% CO–1% H_2–89% He and 10% CO–90% He.

The catalyst, Fe–Al_2O_3 with a weight percentage of iron of 10%, is obtained by precipitation with sodium carbonate of iron nitrate on alumina (*2*). Before the catalytic reaction the solid is heated at 270°C in helium for 1 h, then H_2 is introduced and the temperature is raised to 450°C and maintained for 15 h. The catalyst is then cooled to 285°C and He flowed during 5 min.

The rate of carbon deposition is compared when the two feeds have reacted on the catalyst. The deposited carbon labeled here "C" means both the surface carbon and that in the carbide. Two methods were employed to measure this rate, namely determination of the amount of CO_2 formed during the contact of the mixture with the surface or measurement of the quantity of CH_4 produced by etching the spent catalysts with pure H_2. This reaction is conducted at the normal reaction temperature (285°C) and also after an increase to 440°C at the end of the first etching test (*2*). Before the introduction of H_2 the catalyst is flushed for 40 s in He.

It has been observed that with the mixture containing 1% of H_2 neither H_2O nor CH_4 (or other hydrocarbons) are detected.

Table 1, column 2 shows the amount of CO_2 formed with time on stream (given by column 1) when the 10% CO–He mixture is flowed. Column 3 gives the quantity of CH_4 produced during etching by H_2 after the reaction has been followed for identical contact times (column 1). Finally, column 4 gives the ratio CH_4/CO_2. This ratio is practically 1 during the reaction and it decreases slightly with time on stream. The value of unity for this ratio seems to show that the Boudouard equation is representative of the chemical process even though other steps must be taken into account:

$$CO_{(g)} \rightarrow CO_{ads} \qquad (1)$$

$$CO_{ads} \rightarrow C_{ads} + O_{ads} \qquad (2)$$

$$O_{ads} + CO_{(g)} \text{ or } CO_{ads} \rightarrow CO_{2(g)} \qquad (3)$$

It is obvious that for each CO_2 formed, one "C" is deposited which by hydrogenation at 285°C can also give one molecule of CH_4. This means also that the dissociation of CO in our experimental conditions does not leave an oxygen atom in an adsorbed state on the iron surface. Indeed the same results were reported with Ni instead of Fe (*3, 4*). The value of 0.948 for the CH_4/CO_2

0021-9517/84 $3.00

TABLE 1

Characterization of the Deposition of Carbon "C" with 10% CO/He Mixture at 285°C

Time of reaction (s)	CO_2 production during the contact (μmol/g^{-1})	CH_4 production by hydrogenation at 285°C (μmol/g^{-1})	Ratio CH_4/CO_2
40	22.2	22.45	1.06
100	59.2	64.3	1.08
182	115.6	121.4	1.05
285	185.1	185.6	1.00
360	225.8	230.4	1.02
895	622.7	590.4	0.948

ratio which is observed at 285°C when the contact time is 895 s can be explained by the fact that not all of the "C" can be hydrogenated when the contact time is too long. In fact, if the temperature of the system is now raised to 440°C in He and the catalyst submitted again to H_2, a supplementary amount of CH_4 (26.4 μmol/g) is formed. The ratio [CH_4 (at 285°C) + CH_4 (at 440°C)]/CO_2 is then again found to be close to 1 (0.99). It is likely that the fraction of the carbon "C" which does not react at low temperature (285°C) after a long contact time is the surface graphitic carbon which was observed formerly (*2*).

Table 2 gives the same data as Table 1 but for the 10% CO–1% H_2–89% He mixture. Now during the first period of the reaction the ratio CH_4/CO_2 is much greater than 1. This means that some fraction of the adsorbed oxygen remains on the surface and is not removed either by CO (as CO_2) or H_2 (as H_2O). Because of this new behavior it is obvious that neither the Boudouard equation or Eqs. (1) to (3) are consistent with the mechanism of the reaction. As this behavior is not registered with the mixture which does not contain H_2, it must be deduced that the stabilization of O species on the surface is obtained by interaction with H_2 by some steps additional to the series proposed.

TABLE 2

Characterization of the Deposition of Carbon "C" with 10% CO/1% H_2/89% He Mixture at 285°C

Time of reaction (s)	CO_2 production during the contact (μmol/g^{-1})	CH_4 production by hydrogenation at 285°C (μmol/g^{-1})	Ratio CH_4/CO_2
75	22.07	49.8	2.25
140	71	143	1.998
244	194.9	299.2	1.54
380	477.3	483.5	1.01
512	708.8	640.7	0.904

Hydrogen influences also the rate of "C" deposition. As hydrogen stabilizes an oxygenated species on the surface of metallic iron, the production of CO_2 does not reflect the formation of "C." Only the value of CH_4 obtained by H_2 etching gives the true rate of "C" deposition. Figure 1 compares the mean rate of "C" deposition using the values of column 3 of Tables 1 (curve A) and 2 (curve B) for the two mixtures. This rate is higher in the presence of 1% H_2 than for pure CO. Curve C is obtained from previous results (*2*) and shows that this rate is still higher for a high concentration of H_2 (90%). These results are in agreement with a former observation concerning the rate of carburization which is higher with H_2 than without (*1*).

These two phenomena, namely stabilization of an oxygenated compound on iron surface in the presence of H_2 and a simultaneous increase of the rate of "C" deposi-

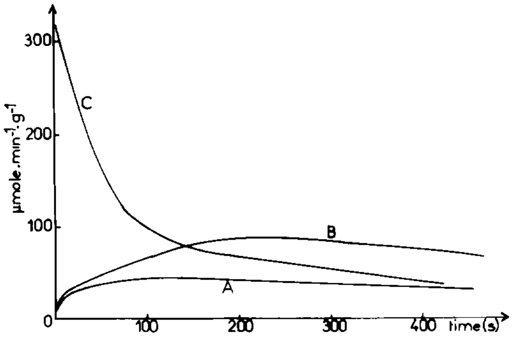

FIG. 1. Rate of "C" deposition as a function of the concentration of H_2 in the reactants calculated from the rate of formation of CH_4 by H_2 etching. (A) 10% CO/90% He. (B) 10% CO/1% H_2/89% He. (C) 10% CO/90% H_2.

tion may be explained by the interaction of hydrogen in the step involving the dissociation of CO. This hydrogen-assisted CO dissociation process has been already proposed by various authors. Ho and Harriot (*3*) in their study of the CO/H_2 reaction on a Ni catalyst propose the following steps:

$$CO_{ads} + H_{ads} \rightleftarrows COH_{ads}$$

$$COH_{ads} + H_{ads} \rightarrow C + H_2O_{(g)}$$

In the present studies $H_2O_{(g)}$ is not detected in the effluents during the reaction. The COH_{ads} is said to be obtained by a fast reversible reaction (*3*). Considering that before etching by H_2 we desorb the catalyst with He, COH_{ads} would not be stable and the two preceding steps can be discarded.

In a comparable study of the CO/H_2 reaction on Pd the authors (*5*) propose a hydrogen-assisted CO dissociation according to the following step:

$$CO_{ads} + yH_{ads} \rightarrow C_{ads} + OH_{y\,ads}$$

If $y = 2$, H_2O is formed directly (*5*). This step explains the increase of "C" deposition by the interaction of H_2 during the CO dissociation and it explains also the formation of an oxygenated compound different from that formed (CO_2) without H_2. If $y = 1$ the adsorbed oxygenated compound would be a OH_{ads} group as H_2O is not detected. Therefore in the presence of hydrogen steps (4) and (5) can be added to steps (1)–(3).

$$H_2 \rightleftarrows 2\ H_{ads} \qquad (4)$$

$$CO_{ads} + H_{ads} \rightarrow C_{ads} + OH_{ads} \qquad (5)$$

If the concentration of H_2 is higher than 1% as in a 10% CO/H_2 mixture (*2*) step (5) is probably followed by the step:

$$OH_{ads} + H_{ads} \rightleftarrows H_2O_{(g)}$$

In fact, H_2O is the main oxygenated compound (*2*) on the iron catalyst working in the Fischer–Tropsch conditions (high concentration of H_2).

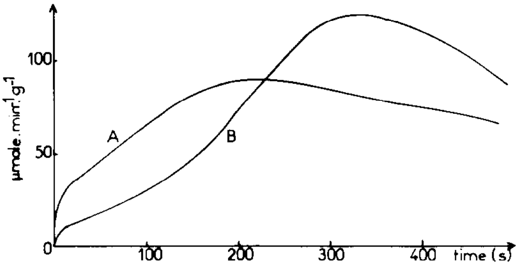

FIG. 2. Rate of "C" deposition for the 10% CO/1% H_2/89% He using the formation of CH_4 by H_2 etching or the production of CO_2. (A) Formation of CH_4 by H_2 etching at 285°C. (B) Production of CO_2 during the reaction at 285°C.

Table 2 shows that the ratio CH_4/CO_2 first decreases, goes through the value of unity and becomes smaller than one when the contact time increases. It can therefore be assumed that OH species formed on the iron surface at the beginning of the reaction finally react with CO to give CO_2 for higher contact time. Figure 2 gives another picture of this phenomenon. We report here the mean rate of "C" deposition using the values of CO_2 or CH_4 (Table 2) as a function of the mean time on stream $(t_i + t_{i+1})/2$. It can be seen that for short contact time the rate based on CH_4 values (curve A true rate of deposition) is higher than the rate based on CO_2 values (curve B). It means that some oxygenated species (OH) are stabilized on the iron surface as they are not eliminated as CO_2 or H_2O. An inversion of rates is finally observed. The oxygenated compound reacts with CO to give CO_2 and hence more CO_2 is formed than that corresponding to the actual quantity of CO really dissociated. In fact, it is necessary to correct slightly the curve B by the quantity of CH_4 formed by H_2 etching at higher temperature (440°C) (the whole quantity of the carbon hard to remove is 61.3 μmol/g at 512 s).

It should be mentioned that a simple explanation of the experimental results could be that first water is indeed formed with the 1% H_2–10% CO–89% He mixture but not detected because it is totally irreversibly adsorbed on the alumina surface (as OH groups) at the beginning of the reaction. Second, after the saturation point of alumina, water reacts totally with the excess of CO to give the shift reaction on the metallic part of the catalyst. However, this does not explain the results of Fig. 2. The higher rate of CO_2 formation after the initial CO_2 deficiency compared to the rate of deposition means that the oxygenated species adsorbed at the beginning react now with CO to give CO_2. This is also shown in Table 2 where the ratio CH_4/CO_2 goes down from 2.25 to 1. It is well known that the OH groups of alumina can react with CO to give CO_2 but above the range of temperature used in this study. The study of the water–gas shift reaction on alumina (*6*) in static conditions has shown that the rate of the reaction CO + H_2O is not measurable for a reaction temperature lower than 500°C. Also the OH groups should be on the iron part of the catalyst to have the possibility to react at lower temperatures.

The following step is proposed to explain these results:

$$OH_{ads} + CO_{ads} \text{ or } CO_{(g)} \rightarrow CO_{2(g)} + H_{ads} \qquad (6)$$

Step (6) has been already proposed as the possible rate-determining step for the CO/H_2O conversion on Pt (*7*) and Ru (*8*). The final elimination of the OH_{ads} species when the time on stream increases can be correlated with the change in the surface composition of the catalyst or with the carbide formation. Initially the surface contains metallic iron only, then carbon is deposited on the surface but migrates partially in the bulk giving the carbide (ε' and χ carbide) (*2*) whereas the OH species are accumulated on the surface. This change may weaken the M–OH bond and allow the elimination of OH_{ads} through step (6).

In conclusion, the present study shows that on an iron surface, the dissociation of CO in the presence of H_2 proceeds by a concerted mechanism which assists the Boudouard reaction. This dissociation is assisted by hydrogen and explains the increase of the rate of "C" deposition from CO and the delay in the elimination of an oxygenated compound like CO_2 (because H_2O is not detected). The most likely species formed in this hydrogen-assisted dissociation of CO is $OH_{(ads)}$.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation for support. We also thank Professor S. J. Teichner for helpful discussions.

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Received February 10, 1983