

The Chemisorption of CO on Fe/Al₂O₃

Recently, Bianchi *et al.* (1, 2) studied the Fischer-Tropsch reaction over a 10% Fe/Al₂O₃ catalyst. In one of the experiments, they passed a 10% CO/H₂ mixture (flow rate, 600 cm³/min-g catalyst) over the freshly reduced catalyst at 285°C and 1 atm. Then the feed was changed to H₂. They found that there are three methane peaks which can be detected by mass spectrometry (MS). The shapes of these methane peaks depend on the reaction time of the 10% CO/H₂ mixture over the catalyst. However, the quantity of the first methane peak is almost independent of the reaction time. They proposed that these three methane peaks represent three carbonaceous species. The first peak is CH on the surface, the second peak is a surface carbidic carbon, the third peak is associated with the bulk carbide.

Here we investigate these results further by CO chemisorption on the Fe/Al₂O₃ catalyst after various times of exposure to the CO/H₂ mixture at reaction conditions. A Quantasorb (QS) apparatus is used for the adsorption measurements on the catalyst studied (1, 2). The QS flowsheet is sketched in Fig. 1. The catalyst in the sample cell is reduced by H₂ as in the previous work (1, 2). The three-way valve T permits the reaction mixture to flow over the catalyst sample for the desired time. After reduction or reaction in 10% CO/H₂, the feed is switched to He and the system is cooled to room temperature in flowing helium. The CO chemisorption at this temperature is measured by pulses of pure CO gas over the catalyst sample.

The pulse method should give accurate results if the adsorption is strictly irrevers-

ible. However, a small part of the CO adsorbed at 25°C is reversibly adsorbed, so we have proceeded as follows. The pulse volume was adjusted so that the first four pulses were completely adsorbed, the fifth partially adsorbed, and the sixth peak was equal in area to the calibration peak. Successive peaks, separated by 2 min in helium, gave about the same area. However, 5 min in helium produced a smaller peak; larger waiting times in helium reduced the peak area until it became about constant for times above 20 min. Thus we have presumed that the decrease in the peak area represents reversibly adsorbed CO. Reported quantities chemisorbed are for irreversibly adsorbed CO obtained by accounting for the CO desorbed from the saturated surface after at least 20 min in helium.

The experimental results are shown in Fig. 2. The amount of CO adsorbed decreases from its value for freshly reduced catalyst to become zero at times of exposure to 10% CO/H₂ in the order of 20 s and above. The interesting feature of this result is that the adsorption of CO is blocked very quickly by such short times of reaction. We have been careful to use a space velocity for the reaction the same as that used in the previous study (1).

It is interesting to compare the results of this work with the previous results (1), as shown in Table 1. The amount of active Fe measured by QS at 25°C is close to the amount of active Fe measured from the first methane peak by MS; the first MS peak leads to about 50 μmol of active iron sites, whereas the CO adsorption at 25°C by QS leads to about 42 μmol, a similar quantity. Longer exposures to 10% CO/H₂ at 285°C

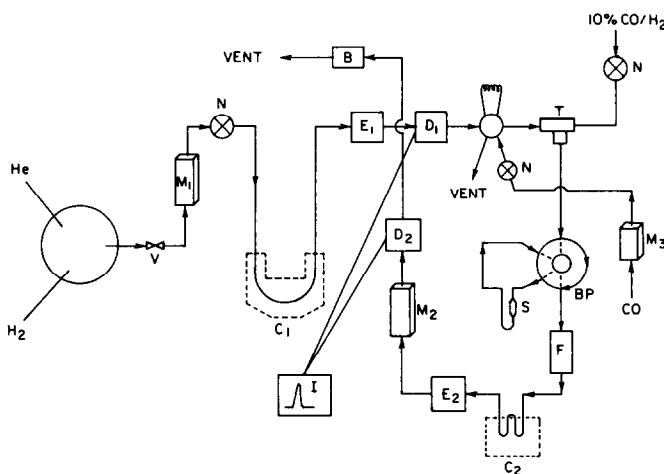


FIG. 1. Quantasorb experimental flow sheet. BP, Bypass valve; B, bubble flowmeter; C_1 , C_2 , cold traps; D_1 , D_2 , detectors; E_1 , E_2 , thermal equilibrium vessels; F, filter; I, integrator; M_1 , M_2 , M_3 , flowmeters; N, needle valve; S, sample cell; T, three-way valve; V, pressure regulator.

produce more carbonaceous material, but the sites on which it forms do not appear to adsorb CO.

The iron sites for freshly reduced catalyst have been estimated by using the ratio $[Fe/CO] = 2$. This choice is extensively discussed in our previous study (1), and the results are compared to those for crystallite

size obtained by X-ray diffraction line-broadening work.

Item 2 of Table 1 is included as a reminder that the CH species does not desorb in helium. As argued previously (2), any C_nH_x with n or x greater than 1 is expected to desorb or revert to CH when exposed to helium at 285°C after reaction at that temperature. Item 3 shows that lots of carbon can be formed on the surface after the iron which will adsorb CO is covered up by CH. Items 4 and 5 in the table show that at lower

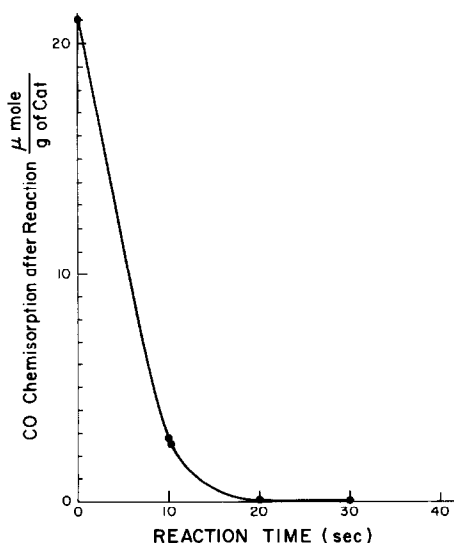


FIG. 2. Effect of reaction time on amount of CO adsorbed.

TABLE I

Some Comparisons between the QS and MS Results

1. CH_4 associated with the CH peak of Ref. (2) after the final switch to H_2 after the sequence: 10% CO/H_2 , 10 s \rightarrow He, 20 s \rightarrow H_2 , at 285°C (MS): 50 $\mu\text{mol/g}$
2. CH_4 as above but after 600 s of helium purge (2): 50 $\mu\text{mol/g}$
3. CH_4 associated with the two surface peaks CH and surface carbide after 600 s of reaction (MS) (1): 359 $\mu\text{mol/g}$
4. CO adsorbed on freshly reduced catalyst at 25°C (QS): 21 $\mu\text{mol/g}$
Iron sites at 2Fe/CO: 42 $\mu\text{mol/g}$
5. CO adsorbed on freshly reduced catalyst at -82°C (QS): 59 $\mu\text{mol/g}$
Iron sites at 2Fe/CO: 118 $\mu\text{mol/g}$

temperatures CO will adsorb on some iron sites which do not adsorb at 25°C.

Other work has shown that a switch to H₂ after exposure to 10% CO/H₂ at 285°C produces three peaks of methane but practically no water (1, 2). This has led us to conclude that the working surface contains no adsorbed CO nor oxygen (1).

Since the catalyst after 20 s of CO/H₂ reaction and subsequent exposure to helium at 285°C seems to have only CH on its surface, this must be what is blocking the CO adsorption at 25°C.

The results of this note furnish more evidence of the difficulty of using CO as a measure of iron surface area. In particular, the CO adsorbed at 25°C corresponds only to a small, active part of the iron surface, approximately that which is covered with CH species during reaction.

ACKNOWLEDGMENT

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REFERENCES

1. Bianchi, D., Borcar, S., Teule-Gay, F., and Bennett, C. O., *J. Catal.* **82**, 442 (1983).
2. Bianchi, D., Tau, L. M., Borcar, S., and Bennett, C. O., *J. Catal.* **84**, 358 (1983).

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