

## Hydrogen Chemisorption in the Mechanism of Gas-Carbon Reactions

R. T. Yang and K. L. Yang  
Department of Chemical Engineering  
State University of New York at Buffalo, N.Y. 14260

The etch decoration-transmission electron microscopy technique (EDTEM), first developed by Henning [1], has been used to obtain important results in advancing our understanding on the kinetics and mechanisms of the gas-carbon reactions, by Hennig, Thomas, et al. [2], Feates, et al. [3] and more recently in this laboratory [3,4].

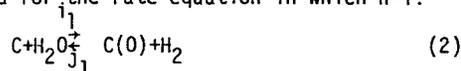
Both  $O_2$  and  $CO_2$  create round pits on the basal plane of graphite. Interpretation of the rates on these reactions have been made [3,4].

The  $C-H_2O$  reaction produced hexagonal pits, bounded by zig-zag faces. The turnover frequencies for the reaction  $C + H_2O \rightarrow CO + H_2$  at  $700^\circ C$ ,  $800^\circ C$  and  $900^\circ C$  are shown in Figure 1. These were rates with no hydrogen added. With added hydrogen in the gas phase, the reaction rates were substantially lowered. The rate equation fitted by the turnover rate data was:

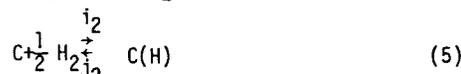
$$\text{Rate} = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2}^n + k_3 P_{H_2O}} \quad (1)$$

where  $n=0.50$  at  $700^\circ C$ ;  $n=0.85$  at  $800^\circ C$ ; and  $n=1.0$  at  $900^\circ C$ .

The following mechanism, Mechanism B, was proposed for the rate equation in which  $n=1$ :



whereas another mechanism, Mechanism C, was proposed for the case when  $n=0.5$ :



It should be pointed out that the values of  $i_3$ , calculated from data for the separate reactions with  $CO_2$  and  $H_2O$ , were surprisingly close [3].

Using the EDTEM technique, strong evidence has been provided by several independent experiments to

show that the dissociative chemisorption of  $H_2$ , taking place preferentially on zig-zag faces (as opposed to armchair faces), plays a key role in the  $C-H_2O$  reaction mechanism. Before a detailed discussion of these experiments, the results are summarized below:

1. The  $C+CO_2$  reaction with added  $H_2$ : With trace amounts of  $H_2$  added in  $CO_2$ , the etch pits all became hexagonal bounded by zig-zag faces. The  $C+CO_2$  reaction was strongly inhibited by  $H_2$ .
2. Mixed reactions with  $CO_2$  and  $H_2O$ : The etch pits were all hexagonal, bounded by zig-zag faces, in both of the following reaction sequences: first, etching by  $CO_2$  followed by  $H_2O$ ; and in the reverse order.

It has long been known that, qualitatively, the inhibition of the  $C+H_2O$  reaction by  $H_2$  is much stronger than that of the  $C+CO_2$  reaction by  $CO$ .

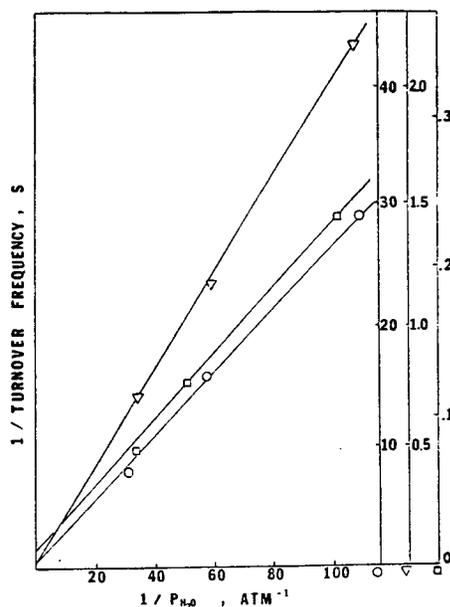


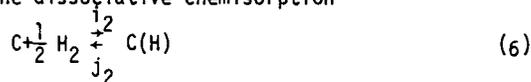
Fig. 1. Turnover frequencies of the  $C-H_2O$  reaction at  $700^\circ C$  (○);  $800^\circ C$  (▽) and  $900^\circ C$  (□), with no hydrogen added.

The work by Biederman, et al. [5] further showed that H<sub>2</sub> has a very strong inhibition effect on the C+CO<sub>2</sub> reaction. The proposed mechanism for the reaction C+CO<sub>2</sub>+H<sub>2</sub> is: Reactions (2),(5),(3),(Mechanism D).

It is seen that the inhibition by CO and that by H<sub>2</sub> are entirely different in nature; but the inhibitions by H<sub>2</sub> in the reactions C+CO<sub>2</sub> and C+H<sub>2</sub>O seem to be the same (compared Mechanisms C and D).

As mentioned, the reaction C+CO<sub>2</sub> produces round pits [3,4]. However, with the addition of H<sub>2</sub> in the gas phase, the pits became hexagonal, and their growth rate was substantially lowered.

The turnover frequency at 700°C, is lowered by H<sub>2</sub> from the H<sub>2</sub>-free value of 0.51 s<sup>-1</sup> to 0.048 s<sup>-1</sup>. This strong inhibition was apparently caused by the dissociative chemisorption



From the rate data, the adsorption constant is, at 700°C,

$$K = \frac{i_2}{j_2} = 96 \text{ atm}^{-1/2} \quad (7)$$

The above results further indicated that the dissociative chemisorption was preferred on the zig-zag {1010} face, which caused the change of the pit conformation. In other words, the K value shown in Eq. 7 was for zig-zag face, which was higher than that on the armchair face. The stronger chemisorption on the zig-zag face would result in the observed anisotropy in reactivities between the two edge planes.

The rate of the reaction C+CO<sub>2</sub>+H<sub>2</sub> is

$$\text{Rate} = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2} + K P_{H_2}^{1/2}} \quad (8)$$

as can be derived from Mechanism D.

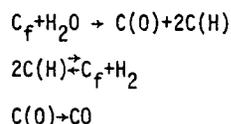
Our data on the effects of H<sub>2</sub> inhibition on

the C+H<sub>2</sub>O reaction yielded the following value for the inhibition constant [3]:

$$k_2 = i_2/j_2 = 71 \text{ atm}^{-1/2} \quad (9)$$

This value, according to Mechanism C, would be the dissociative chemisorption constant of H<sub>2</sub> on the zig-zag face. Comparison of the values in Eqs. 7 and 9, obtained from two independent experiments, was indeed satisfactory.

Another conclusion may be drawn from the above results regarding the mechanism of the C+H<sub>2</sub>O reaction with no added H<sub>2</sub> in the gas phase (i.e., P<sub>H<sub>2</sub>O</sub> = 0). The pits etched by H<sub>2</sub>O (with P<sub>H<sub>2</sub>O</sub> = 0) are also hexagonal with zig-zag faces. Since this hexagonal conformation appears to be caused by chemisorbed hydrogen on the zig-zag faces, the mechanism for the C+H<sub>2</sub>O reaction should be more reasonably written as:



#### Acknowledgements

This research was supported by the National Science Foundation under Grant CPE-8120569.

#### References

1. G. R. Hennig, in Chemistry and Physics of Carbon (Edited by P. L. Walker, Jr.), Vol. 2, p.1, Marcel Dekker, New York (1966).
2. J. M. Thomas, Carbon, **8**, 413 (1970).
3. R. T. Yang, in Chemistry and Physics of Carbon (Edited by P. A. Thrower), Vol. 19, Marcel Dekker, New York (1984). pp. 163-210.
4. C. Wong, Ph.D. Dissertation, State University of New York at Buffalo, Buffalo, NY (1983).
5. D. L. Biederman, A. J. Miles, F. J. Vastola and P. L. Walker, Jr., Carbon **14**, 351 (1976).