JOURNAL OF CATALYSIS 89, 168–171 (1984)

Catalysis by Transition Metal Carbides

V. Kinetic Measurements of Hydrogenation of CO over TaC, TiC, and Mo_2C Catalysts

The transition metal carbides have been extensively studied because of their unique physical properties such as extremely high melting points, metal-like thermal and electronic conductivities, and superconductivity. Furthermore, they have recently been shown to form an interesting new group of catalysts (*1–7*); the ordered incorporation of carbon atoms into a metal lattice creates materials with chemisorptive and catalytic properties different from those of the original pure metal catalysts. As a result of the extremely high melting points of the transition metal carbides these catalysts have the advantage that they resist sintering. As part of a program for characterizing these catalysts, we have investigated the catalytic activities of the carbides TaC, TiC, WC, and Mo_2C and found that they exhibit high activities for the hydrogenation of benzene (*1, 2*), ethylene (*4, 6*), and carbon monoxide (*5*).

The catalytic synthesis of hydrocarbons from a mixture of CO and H_2 gases has been one of the most important problems in heterogeneous catalysis, and various mechanisms have been proposed for supported- and unsupported-metal catalysts (*8–10*). However, very few have been reported for other kind of catalysts. In a previous paper (*5*), it was found that powdered TaC, TiC, and Mo_2C catalyze the hydrogenation of CO to produce methane and higher molecular weight hydrocarbons. The distribution of the hydrocarbons products was rather different from that for the metallic catalysts such as Ni and Ru. In the present note we report the kinetic results of the hydrogenation on these metal carbide catalysts and discuss a possible reaction mechanism on the basis of the previous and present results.

The kinetic measurements of the reactions were carried out using a recirculation reactor, 520 ml in volume, with a liquid-nitrogen cold trap for removing the condensable products from the reaction system during the course of the reaction. The reaction products were analyzed using gas chromatography and mass spectrometry. All the runs of the reactor were carried out at 300°C. The powdered materials, TaC, TiC, and Mo_2C (200–300 mesh) were purchased from Materials Research Company. Before the measurement, TaC and TiC were catalytically activated by heating *in vacuo* at 1000°C. The Mo_2C was reduced at 600°C in an atmosphere of hydrogen at 100 Torr (1 Torr = 133.3 Pa) until there was no further formation of H_2O, and subsequently evacuated at the same temperature. The cleanliness of the treated surfaces was confirmed by XPS measurements (*4*). BET surface areas of TaC, TiC, and Mo_2C, measured by Kr adsorption at 78 K, were found to be 1.0, 0.46, and 0.62 m^2g^{-1}, respectively. The main products over these carbide catalysts were found to be CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, H_2O, and CO_2.

Figures 1a–c show typical reaction curves indicating the variations of reaction products with the reaction time on Mo_2C, TaC, and TiC, respectively. The order of the amounts produced is $CH_4 > H_2O > CO_2 > C_2H_x$, and it is of note that there is considerable CO_2 and H_2O formation even in

0021-9517/84 $3.00

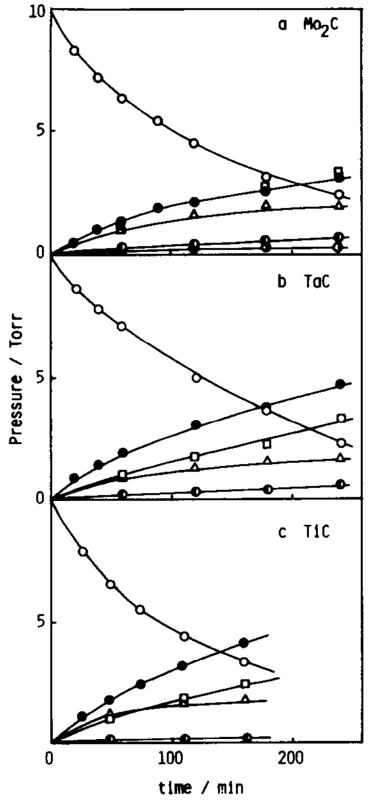

FIG. 1. Variations of products with reaction time on Mo_2C, TaC, and TiC. Initial pressures of H_2 and CO are 100 and 10 Torr, respectively. ○; CO, ●; CH_4, ◐; C_2H_6, ◑; C_2H_4, □; H_2O, and △; CO_2. The amounts of the condensable products are converted into corresponding pressures.

the initial stages of the reaction. The distribution of higher mass hydrocarbons produced is given as a function of the H_2/CO ratio in Fig. 2. As is usually observed on metallic catalysts, the fraction of CH_4 formation increases with increasing H_2/CO ratio. One of the characteristic features of the carbide catalysts is that the fraction of higher molecular weight hydrocarbons is appreciable even for a high H_2/CO ratio and high reaction temperature. Further, with the Mo_2C catalyst the fraction of ethylene in C_2-compounds reaches 91% for a H_2/CO ratio of unity. Tables 1 and 2 show the results obtained at a reaction temperature of 300°C. The pressure dependence of the products widely varies for the different catalysts in this study. However, it is seen that the pressure dependence of the pair of CH_4 and H_2O, and the group of CO_2 and C_2-hydrocarbons is similar for each catalyst. It is also notable that CO_2 formation is enhanced by an increase in hydrogen pressure for all the catalysts used here and, that the reaction order of H_2O formation with respect to the H_2 pressure exceeds unity of TaC and TiC, suggesting that some attractive interaction occurs between the adsorbed CO molecule and adsorbed H atoms.

TABLE 1

Kinetic Parameters for the Rates of CO Consumption and CH_4 Formation

	N_{CO}			N_{CH_4}		
	k	*n*	*m*	*k*	*n*	*m*
TaC	1.1×10^{11}	0.27	0.51	3.3×10^{10}	0.57	0.18
TiC	2.7×10^{11}	0.43	0.31	9.8×10^{10}	0.80	−0.29
Mo_2C	2.1×10^{10}	0.50	0.52	1.6×10^{9}	1.0	0.20

Note. $N = kP_H^n P_{CO}^m$, where N is the initial rate of the consumption of CO or of the formation of CH_4, and k has units molecule cm^{-2} s^{-1} $Torr^{-(n+m)}$.

There is presently no general agreement on the nature of the reaction intermediates or on the reaction mechanism for CO hydrogenation on metallic catalyst surfaces (*8–10*): Some authors have proposed that

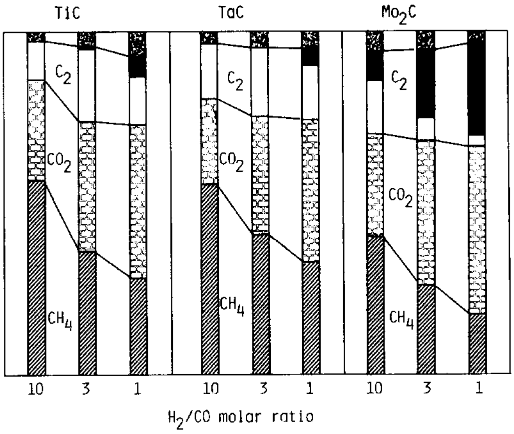

FIG. 2. Distribution of carbon in products as a function of H_2/CO ratio. The shaded fractions in C_2-hydrocarbon is the contribution of C_2H_4.

TABLE 2

Pressure Dependence for the Formation of H_2O, CO_2, and C_2-Hydrocarbon

	A_{H_2O}		A_{CO_2}		A_{C_2}	
	n	m	n	m	n	m
TaC	1.3	0.29	0.16	1.3	0.22	0.60
TiC	1.4	−0.70	0.40	0.80	0.30	0.92
Mo_2C	0.90	0.10	0.39	1.0	0.51	0.75
$x = 0$	−0.5 ~ 1	−2 ~ 1	−1 ~ 0	0 ~ 2		
1	0 ~ 1.5	−2 ~ 1	−0.5 ~ 0.5	0 ~ 2		
2	0.5 ~ 2	−2 ~ 1	0 ~ 1	0 ~ 2		
3	1 ~ 2.5	−2 ~ 1	0.5 ~ 1.5	0 ~ 2		

Note. Ranges of the reaction order estimated from the equations (I) and (II) are given in the lower column. $A_X \propto P_H^n P_{CO}^m$, where A_X is the amount of the product, X after 10 min. Here, x is the number of H atoms in CH_xO intermediate.

CO molecules first dissociate into the carbon and oxygen atoms on the surface. This is followed by the hydrogenation of the former adsorbate to produce methane or other higher hydrocarbons, and by hydrogenation of the adsorbed oxygen atoms to produce water or by their reaction with CO to produce CO_2 molecules (*11–13*). However, other investigators advocate that the adsorbed CO and H_2 form an oxygen-containing surface species, CH_xO (x = 1–3), prior to the C–O bond breaking (*14–16*). As previously described in detail (*1, 2, 4*), the adsorbed oxygen atoms on these carbide catalysts are very tightly bound on the surfaces and can not be eliminated at 300°C, regardless of the presence or absence of hydrogen in the gas phase. Therefore, the latter reaction mechanism which does not require the dissociation of CO would be a more reasonable mechanism for the formation of H_2O and CO_2. Thus, as a whole, the following reaction scheme is possible for the present catalysts:

$$CO \overset{K_1}{\rightleftharpoons} CO(a) \quad (1)$$

$$H_2 \overset{K_2}{\rightleftharpoons} 2H(a) \quad (2)$$

$$CO(a) + xH(a) \overset{K_3}{\rightleftharpoons} CH_xO(a) \quad (3)$$

$$CH_xO(a) + 2H(a) \xrightarrow{k_4} CH_x(a) + H_2O \quad (4)$$

$$CH_xO(a) + CO(a) \xrightarrow{k_5} CH_x(a) + CO_2 \quad (5)$$

$$CH_x(a) + (4 - x)H(a) \xrightarrow{k_6} CH_4 \quad (6)$$

where (a) denotes an adsorbed state, and K_i or k_i is the equilibrium or rate constant, respectively, of step i. The $CH_x(a)$ species may further combine to form carbon chains that result in the production of higher hydrocarbons.

Assuming that the rate-determining step is the elimination of the oxygen atom from the CH_xO species to cause the C–O bond rapture and that all preceding steps are in quasi-equilibrium, the rates of the formation of H_2O (R_{H_2O}) and of CO_2 (R_{CO_2}) are given as

$$R_{H_2O} = \frac{k_4 K_1 (K_2)^{1+x/2} K_3 P_H^{1+x/2} P_{CO}}{(1 + \sqrt{K_2 P_H} + K_1 P_{CO})^3} \quad (I)$$

$$R_{CO_2} = \frac{k_5 K_1^2 (K_2)^{x/2} K_3 P_H^{x/2} P_{CO}^2}{(1 + \sqrt{K_2 P_H} + K_1 P_{CO})^2}. \quad (II)$$

These rate equations imply that the reaction order of H_2O formation stands between ($x/2$ − 0.5) and ($x/2$ + 1) with respect to hydrogen pressure and between $(x/2 - 1)$ and $x/2$ for CO_2 formation. Substituting the possible values, 0, 1, 2, and 3 for the x, one can obtain ranges for the reaction order, these ranges are given in Table 2. Comparing these ranges with the experimental results, one can estimate that the values of x is 1 or 2. This estimate for x is consistent with that proposed previously in line with the scheme of direct CO hydrogenation.

On the other hand, the mechanism involving CO dissociation can also result in the reaction law rate expressions of a similar power to those given in Tables 1 and 2. However, connecting the present data with the fact as described above that the oxygen atoms adsorbed on the metal carbide catalysts are not removed by hydrogen at the same reaction temperature due to strong bonding with the surfaces, the mechanism involving dissociative process of CO is not applicable to the process of CO hydrogenation over the transition metal carbides.

ACKNOWLEDGMENT

The authors thank Professor D. E. Beck for reading the manuscript and for valuable suggestions.

REFERENCES

1. Miyazaki, E., and Fuse, K., *J. Chem. Soc. Jpn. (Nippon Kagaku Kaishi)* 815 (1972).
2. Miyazaki, E., *J. Chem. Soc. Jpn. (Nippon Kagaku Kaishi)* 1388 (1973).
3. Levy, R. B., and Boudart, M., *Science* **181,** 547 (1973).
4. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **59,** 472 (1979).
5. Kojima, I., Miyazaki, E., and Yasumori, I., *J. Chem. Soc. Chem. Commun.* 573 (1980).
6. Boudart, M., Oyama, S. T., and Leclercq, L., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 578. Kodansha, Tokyo, 1981.
7. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **73,** 128 (1982).
8. Vannice, M. A., *Catal. Rev.—Sci. Eng.* **14,** 153 (1976).
9. Ponec, V., *Catal. Rev.—Sci. Eng.* **18,** 151 (1978).
10. Bell, A. T., *Catal. Rev.—Sci. Eng.* **23,** 203 (1981).
11. Araki, M., and Ponec, V., *J. Catal.* **44,** 462 (1976).
12. Kellner, S. C., and Bell, A. T., *J. Catal.* **67,** 175 (1981).
13. Kobori, Y., Yamasaki, H., Naito, S., Onishi, T., and Tamaru, K., *J. Chem. Soc. Faraday I* **78,** 1473 (1982).
14. McKee, D. W., *J. Catal.* **8,** 240 (1967).
15. Vannice, M. A., *J. Catal.* **37,** 462 (1975).
16. Mori, T., Masuda, H., Imai, H., Miyamoto, A., Baba, S., and Murakami, Y., *J. Phys. Chem.* **86,** 2753 (1982).

ISAO KOJIMA
EIZO MIYAZAKI

Department of Chemistry
Tokyo Institute of Technology
Ookayama, Mequroku
Tokyo 152, Japan

Received August 18, 1983