

## Catalysis by Transition Metal Carbides

## IV. Mechanism of Ethylene Hydrogenation and the Nature of Active Sites on Tantalum Monocarbide

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The hydrogenation of ethylene on thermally activated TaC were studied. Similar to the catalysis by transition metals, the hydrogenation on TaC exhibited a maximum rate at a definite reaction temperature; the activation energy of the reaction was 33.8 kJ mole<sup>-1</sup> below 370 K, but -54.4 kJ mole<sup>-1</sup> above 420 K. The reaction of ethylene with D<sub>2</sub> at 273 K yielded ethane ranging from *d*<sub>0</sub> to *d*<sub>5</sub> and highly exchanged ethylene with increased conversions. The isotope composition of gaseous hydrogen reached nearly equilibrium when the degree of conversion exceeded 40%. The chemisorption of hydrogen on TaC obeyed the dissociative Langmuir isotherm. The application of strongly adsorbed carbon monoxide and acetylene as poison showed that about 40% of the total surface was catalytically effective, and that the reaction rate diminished with increasing fraction of poisoned surface,  $\theta_p$ , being proportional to  $(1 - \theta_p)^2$ . The accumulation of graphite-like carbon on the TaC surface occurred by heating the catalyst above 400 K in an C<sub>2</sub>H<sub>4</sub> atmosphere, and was accompanied by a drastic decrease in the catalytic activity. X-Ray photoelectron study revealed that the characteristic features of electronic states in the activated TaC were a partial electron transfer from Ta to carbon atom. The associative mechanism of hydrogenation was proposed and the possible structure of active sites on TaC was discussed.

## INTRODUCTION

In studying heterogeneous catalysis by solid surfaces, transition metal carbides have drawn considerable attention, not only because of their interesting physical properties derived from coexistence of metallic, covalent, and ionic bondings (1), but also because of a possibility of improving the catalytic properties by the modification of metals. In particular, the latter expectation is related to the recent findings that the incorporation of carbon atoms with metals leads to new catalysis which is different from that of the original metals, e.g., the carburized Ni(110) plane behaves like copper metal for the decomposition of formic acid (2), and tungsten monocarbide exhibits platinum-like behavior for the chemisorption and isomerization of 2,3-dimethyl propane (3). In spite of many studies on the physical properties of transition metal carbides, only a few investigations have been

performed so far on their catalytic behavior. Boudart *et al.* (4) reported a catalytic activity of Mo<sub>2</sub>C for the breaking of C-O, C-C, N-N, and H-H bonds. In the earlier stage of our work to examine the validity of the metal carbides as catalyst, we found that the evacuation of TaC, TiC, and WC at high temperatures was effective in producing high catalytic activity for the hydrogenation of benzene (5) and ethylene (6). X-Ray photoelectron spectroscopic (6) and poisoning (5) studies revealed that the generation of activity is associated with the exposure of a clean monocarbide surface as a consequence of removal of the surface oxygen and/or oxide layers. The synthesis of hydrocarbon from CO and hydrogen by TiC, TaC, and Mo<sub>2</sub>C has successfully been carried out with high selectivity to produce hydrocarbons of higher molecular weight than methane (7).

In the present study, we attempted to elucidate the reaction mechanism of ethyl-

ene hydrogenation on TaC and the structure of active sites. The kinetic analysis was performed in a temperature range 250–593 K and was supplemented by a tracer work using  $D_2$ . The poisoning effect of CO and  $C_2H_2$  molecules which are strongly bound on TaC surface, was employed to determine the density of the active sites. In addition, the X-Ray photoelectron spectroscopic (XPS) technique was used to reveal the electronic state of the catalytically active surface of TaC.

#### EXPERIMENTAL

TaC powder (particle size 1–2  $\mu m$ ) of high purity (>99%), purchased from Fruuchi Chemicals Co., was the same as that used in the previous study (6); it contained niobium of 0.5% and free carbon of 0.14%. The BET surface area measured by Kr was 1.1  $m^2 g^{-1}$  (6). X-Ray diffraction provided characteristic peaks due to the monocarbide structure. Hydrogen (99.999% pure), deuterium (99.5%), carbon monoxide (99.5%), ethylene (99.8%), and acetylene (99.6%) were obtained from Takachiho Shoji Co., and were used without further purification.

The kinetics of the reaction was studied in a temperature range between 250 and 593 K and total pressures up to 50 Torr were studied (1 Torr = 133.3 N  $m^{-2}$ ) using a conventional closed circulation system. The course of reaction was followed by measuring the change in pressure with a glass Bourdon gauge equipped with a signal transducer (8) and by the gas chromatographic analysis of products. Under the present experimental conditions, the product was found to be ethane only, and thus we took the initial rate of pressure change as a measure of the catalytic activity. In the experiments using  $D_2$  as tracer, the reactant and product were separated gas-chromatographically and the deuterium distributions were obtained from the analysis by means of a Hitachi RMU-7 mass spectrometer. The isotopic composition of hydrogen in the gas phase was determined by using a

gas chromatograph (9). The poisoning of TaC catalyst was undertaken by exposing the fresh surface to a CO or  $C_2H_2$  atmosphere prior to the reaction study and the amounts of adsorbed poisons were evaluated from those of their irreversible adsorption.

X-Ray photoelectron spectra were recorded at room temperature on a Hewlett-Packard 5950A ESCA spectrometer using monochromatic  $AlK\alpha$  exciting radiation. The TaC sample, after being pressed into disks was transferred into the preparation chamber of the spectrometer, and subjected to the *in situ* heat treatments; the background pressure during the heat treatment at 1370 K was kept below  $5 \times 10^{-7}$  Torr. The C 1s peak of graphite at 284.8 eV was taken as reference.

#### RESULTS

In the previous study, the heat treatment *in vacuo* above 1270 K was found to be effective in activating TaC (6). The effect of heating in a hydrogen atmosphere was examined in comparison to the previous result, it was found that though heating at temperatures higher than 1270 K was also necessary for the activation, the latter treatment led to less-reproducible results and about one-half of the activity of that obtained by the former one. The decreased activity in hydrogen atmosphere is probably due to the fact that the catalyst surface would be partly covered again by gases discharged from the catalyst, since the heat treatment was carried out in the closed system in this case. Thus, we heated TaC *in vacuo* at 1370 K for 1 h as the treatment prior to the kinetic study, which yielded almost the same activity as in the previous study (6).

Figure 1 shows representative pressure changes during the reaction. It is found that the deactivation of the catalyst became appreciable at high reaction temperatures; at 273 K, for example, we observed little deactivation, whereas, at 593 K, the activity dropped to one-tenth of the initial rate in a

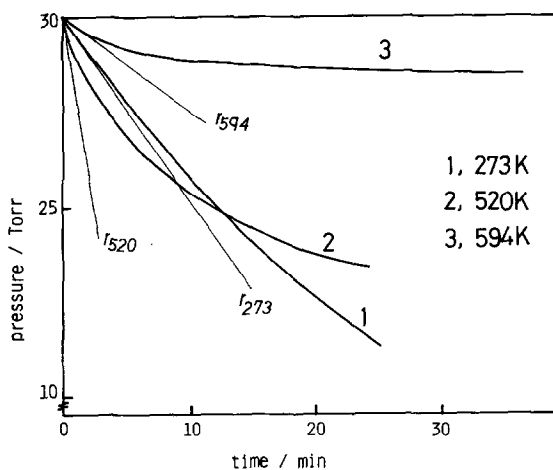


FIG. 1. Total pressure changes with reaction time at various temperatures. The slopes by which the initial rates of the reactions were determined are also shown. One-tenth gram of TaC powder was used for reaction 1, and 0.05 g for reactions 2 and 3.

small conversion range 10%. Therefore, we obtained the slope of the initial pressure decrease as a measure of the catalytic activity.

Figure 2 illustrates the Arrhenius plots of the reaction in the temperature range 250–593 K. The rates were evaluated per unit

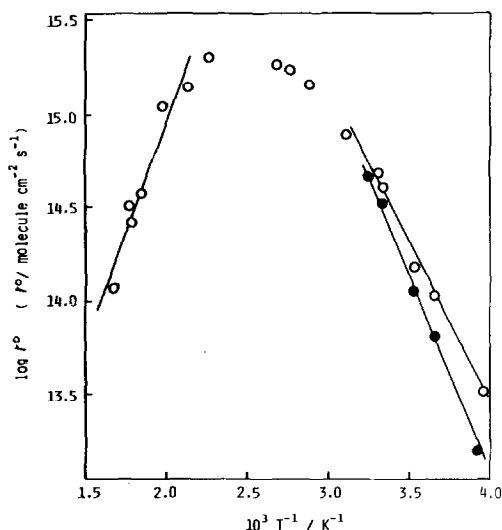


FIG. 2. The dependence of reaction rates ( $r^0$ ) on reaction temperatures. The initial hydrogen (○) or deuterium (●) pressure = 20 Torr; ethylene pressure = 10 Torr.

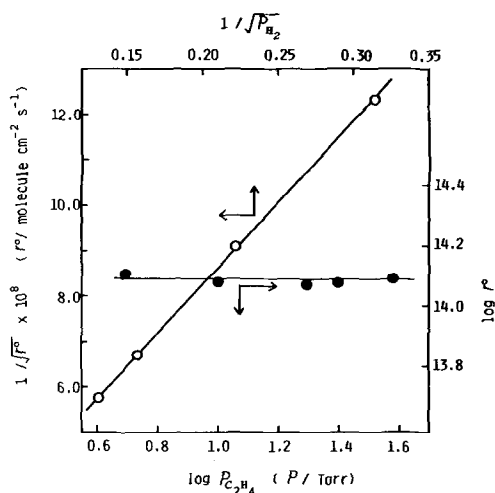


FIG. 3. The dependence of reaction rates on the initial pressures of hydrogen (○) and ethylene (●).

BET surface area. The initial rate of hydrogenation exhibited a maximum at around 400 K. Apparent activation energy,  $E_a$ , was determined to be 33.8 kJ mole<sup>-1</sup> below 370 K and -54.4 kJ mole<sup>-1</sup> above 420 K. Pressure dependence of the rates was examined at 273 K in a pressure range 5–40 Torr for hydrogen and 5–20 Torr for ethylene; the

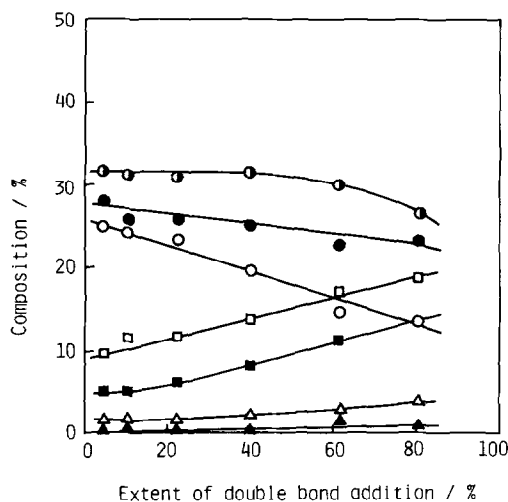


FIG. 4. Deuterium distribution in ethane as a function of extent of double-bond addition during the deuteration of ethylene at 273 K (○, C<sub>2</sub>H<sub>6</sub>; ●, C<sub>2</sub>H<sub>5</sub>D; ●, C<sub>2</sub>H<sub>4</sub>D<sub>2</sub>; □, C<sub>2</sub>H<sub>3</sub>D<sub>3</sub>; ■, C<sub>2</sub>H<sub>2</sub>D<sub>4</sub>; △, C<sub>2</sub>HD<sub>5</sub>, and ▲, C<sub>2</sub>D<sub>6</sub>). Initial pressures of deuterium and ethylene are 20 and 10 Torr, respectively.

reaction orders with respect to the hydrogen and ethylene pressures were found to be 0.9 and nearly zero, respectively (Fig. 3).

The reaction of ethylene with hydrogen at 273 K was 1.5 times faster than that of ethylene with deuterium, indicating that the kinetic isotope effect is straightforward. The latter reaction gave an  $E_a$  value of 41.9 kJ mole<sup>-1</sup> in the temperature range 240–340 K (Fig. 2). The deuterium distributions in ethane and ethylene are shown in Figs. 4 and 5. Even at a low conversion of 5%, the wide distributions of deuterium atoms were observed in ethane; the fractions of ethane- $d_0$ ,  $d_1$ , and  $d_2$  amounted respectively to 25–35%, and those of ethane- $d_3$  and  $d_4$  to 5–10%. The deuterium distribution in ethylene exhibited considerable fractions of  $d_1$  and  $d_2$  species from the initial stage of reaction. Figure 6 shows the isotopic distributions in the gaseous hydrogen during the deuteration of ethylene at 273 K. HD and  $D_2$  were found to produce from the beginning of reaction, and the rate of the isotopic mixing for hydrogen was almost comparable to that for ethylene. The value of

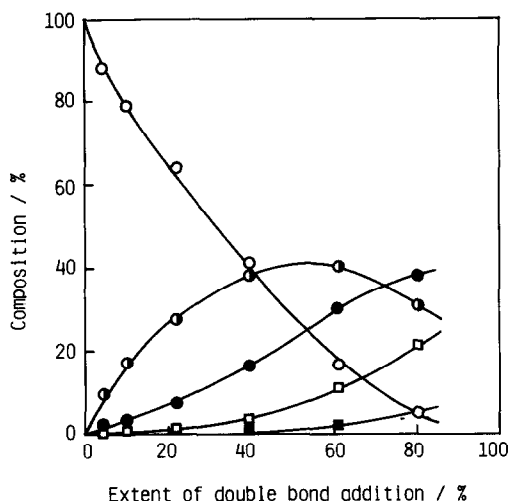


FIG. 5. Deuterium distribution in ethylene as a function of extent of double-bond addition during the deuteration of ethylene (○, C<sub>2</sub>H<sub>4</sub>; ◐, C<sub>2</sub>H<sub>3</sub>D; ●, C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>; □, C<sub>2</sub>HD<sub>3</sub>; and ■, D<sub>2</sub>D<sub>4</sub>). The experimental conditions are the same as those in Fig. 4.

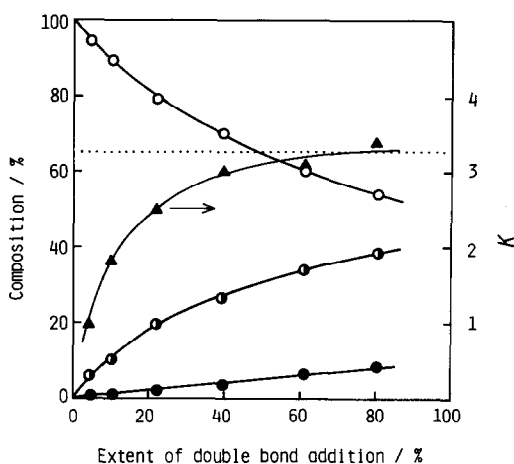


FIG. 6. Deuterium distribution in gaseous hydrogen during the deuteration of ethylene as a function of extent of double-bond addition (○, D<sub>2</sub>; ◐, HD; ●, H<sub>2</sub>). The experimental conditions are the same as those in Fig. 4. The variation of the  $K$ -value is given by ▲, and the dotted line corresponds to the value at equilibrium of the isotope composition at 273 K.

$P_{HD}^2/P_H P_D$  ratio,  $K$ , reached the value at equilibrium when the conversion became higher than 40%. However, in the reaction of ethylene with equimolar mixture of H<sub>2</sub> and D<sub>2</sub> at 273 K, the rate of HD formation was rather low; the values of  $K$  were 0.23 and 1.05 at the conversions of 10.9 and 39.3%, respectively. In the absence of ethylene, however, the H<sub>2</sub>-D<sub>2</sub> isotopic exchange reaction at 273 K proceeded at the rate approximately 50 times higher than in the above one.

The adsorption of CO or H<sub>2</sub> on an activated TaC was investigated at 273 K in a pressure range  $1 \times 10^{-2}$ –40 Torr. A linear relationship was observed in the plot of the amount of CO adsorbed,  $V_{CO}$ , vs the logarithm of its pressure, indicating that the adsorption follows the Frumkin-Temkin isotherm. At the highest pressure employed,  $V_{CO}$  amounted to  $4 \times 10^{14}$  molecule cm<sup>-2</sup>. With hydrogen, the isotherm was well represented by a linear relation between  $V_{H_2}^{-1}$  and  $P_{H_2}^{-1/2}$ , suggesting that the adsorption of H<sub>2</sub> obeys the Langmuir isotherm of dissociative adsorption. The satu-

ration amount of adsorbed hydrogen is evaluated to be  $8 \times 10^{13}$  atom  $\text{cm}^{-2}$  from the intercept of the plot.

CO and  $\text{C}_2\text{H}_2$  were found to chemisorb strongly on the TaC surface and to inhibit the hydrogenation. Figure 7 shows the monotonous decrease in the catalytic activity with increasing fraction of covered surface with CO or  $\text{C}_2\text{H}_2$ . It is of note that the shapes of the two poisoning curves by CO and  $\text{C}_2\text{H}_2$  molecules are quite similar and these poisonings caused the almost complete disappearance of the activity at the same surface concentration,  $4 \times 10^{14}$  molecule  $\text{cm}^{-2}$ .

The previous XPS measurements of TaC showed that an evacuation at high temperature of 1370 K produced an almost oxygen-free surface. In this paper, this technique was extended to the study of the electronic structure of carbon and the valence band. The results were demonstrated in Fig. 8. By evacuating TaC at 1370 K for 1 h, an intensive peak appeared at 283.1 eV, although there still remained a small peak due to free carbon atoms at around 284.6 eV (spectrum A). The exposure of this surface to 5 Torr

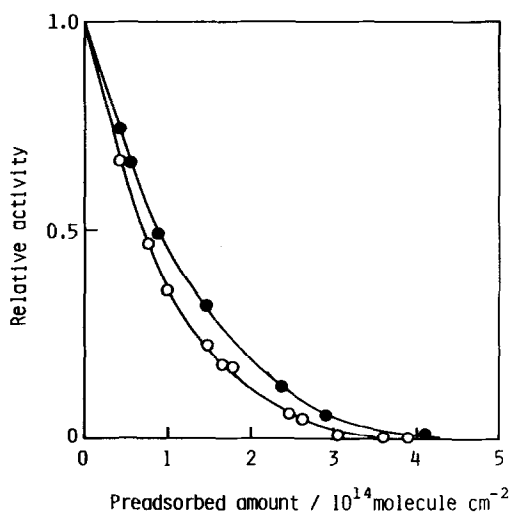


FIG. 7. The decrease of relative activities of the hydrogenation as a function of the preadsorbed amounts of CO (○) and  $\text{C}_2\text{H}_2$  (●). The initial pressures of hydrogen and ethylene are 20 and 10 Torr, respectively, and the reaction temperature is 273 K.

of ethylene at 570 K lowered its catalytic activity to one-hundredth, and it also caused the broadening of the latter peak toward higher binding energy side (spectrum B). The subtraction of spectrum A

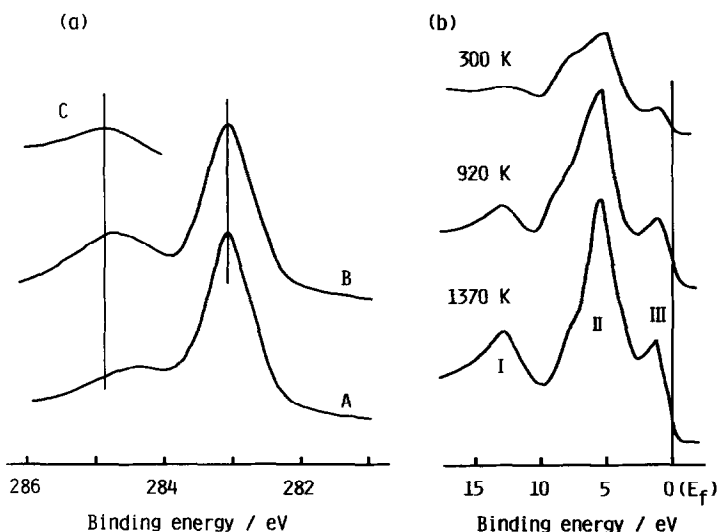
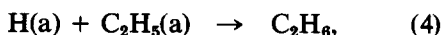
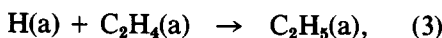
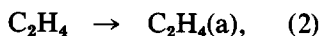
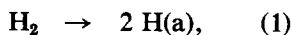


FIG. 8. X-Ray photoelectron spectra of TaC: (a) C 1s region; spectrum A—after evacuating TaC at 1370 K; spectrum B—subsequent heating of the sample at 570 K in ethylene atmosphere, and spectrum C—difference spectrum between spectra B and A. (b) Valence region after evacuating TaC at various temperatures.

from spectrum B indicated the existence of a new peak at 284.9 eV, a binding energy value close to that of graphite carbon. The valence band spectrum, as shown in (b), had a broad peak at around 5 eV below the Fermi level,  $E_f$ . With increasing temperature of evacuation, peaks I and II, which arose mainly from C 2s and C 2p electrons, respectively, were intensified. By further evacuation of the catalyst at 1370 K, there appeared a characteristic peak III having a sharp edge near Fermi level.

#### DISCUSSION

Ethylene hydrogenation on a thermally activated TaC was characteristic in showing a maximum in the rate with the variation of reaction temperature. This is similar to the feature of the same reaction on metallic catalysts. In the reaction of ethylene with  $D_2$ , the deuterium distribution in ethane was  $d_1$  (31.6%),  $d_2$  (27.4),  $d_0$  (24.9),  $d_3$  (9.6),  $d_4$  (4.8),  $d_5$  (1.5), and  $d_6$  (0.2) at 5% conversion. This result seems to contrast to the findings on the metallic catalysts; ethane- $d_0$  was the predominant species at small conversions on catalyst such as Ni (10) and Pd (11), whereas ethane- $d_2$  was main product on Ru, Os, and Ir (12, 13). Further, it was found on TaC that the considerable amounts of deuterium-exchanged ethylene, HD and  $H_2$  were produced in the gas phase with increasing conversion. These distinctive results together with the dissociative adsorption of hydrogen lead to the following Horiuti-Polanyi mechanism (14) for the hydrogenation, viz.,



where (a) denotes adsorbed species.

The linear relationship for  $1/r^{0.1/2}$  vs  $1/P_h^{1/2}$  plot shown in Fig. 3 yields the expression of the hydrogenation rate,  $r^0$ , at 273 K;

$$r^0 = \frac{kK_h P_h}{[1 + (K_h P_h)^{1/2}]^2}, \quad (5)$$

where  $k$  is an apparent rate constant,  $K_h$  is the adsorption constant of hydrogen, and  $P_h$  is the pressure of hydrogen. The superscript,  $^0$ , refers to the fresh catalyst. The invariance of the rate with ethylene pressure indicates that the surface is covered mainly with  $C_2H_4(a)$  whose concentration is nearly constant. On the other hand, it is likely that desorption of ethylene would become significant at temperatures above 400 K, which is probably responsible for the existence of the maximum catalytic activity at about 400 K.

As is seen from Fig. 7, the two poisoning curves are analogous in nature, hence both CO and  $C_2H_2$  molecules occupy the same active sites in a similar way. The adsorption of reactants,  $H_2$  and  $C_2H_4$ , was inhibited by the presence of these strongly adsorbed molecules. Figure 9 shows the variation of  $\log(r/r^0)$  against  $\log(1 - \theta_p)$ , where  $\theta_p$  was evaluated as the ratio of the concentration of adsorbed poison to its saturation value, 4

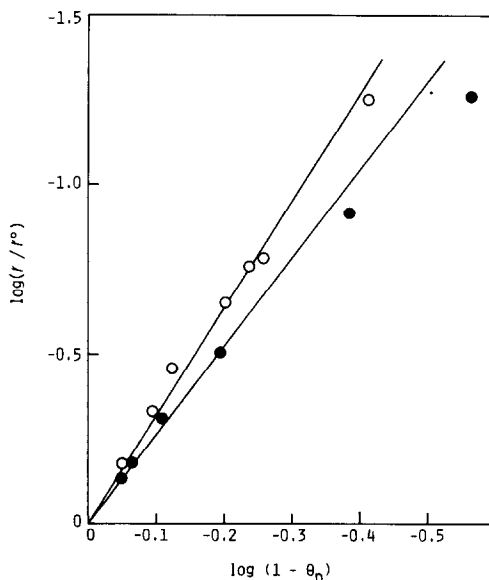


FIG. 9. Logarithmic plots of  $r/r^0$  against  $(1 - \theta_p)$ .  $r/r^0$  = relative activity of the hydrogenation, and  $\theta_p$  = fractional coverage of poison, CO (○) or  $C_2H_2$  (●).

$\times 10^{14}$  molecule  $\text{cm}^{-2}$ . When the coverage of poison was below a half of the saturation, the observed relative rates are on a good straight line with a slope of 3. Then, the reaction rate in this case,  $r$ , is given by

$$r = r^0(1 - \theta_p)^3. \quad (6)$$

This equation suggests the structure of the catalytic active site to be composed of an assembly of the three adsorption sites; i.e., a dual sites for the dissociative adsorption of hydrogen and a single site adjacent to the dual site for ethylene adsorption. This consideration is also based upon the experimental results that ethylene adsorbs more strongly than hydrogen to reduce surface diffusion of the reaction intermediates.

The almost complete poisoning of ethylene hydrogenation occurs at the concentration of  $4 \times 10^{14}$  molecule  $\text{cm}^{-2}$  of the preadsorbed CO or  $\text{C}_2\text{H}_2$  and this fact implies that about 40% of the total Ta atoms on surface take part in the active site, provided that the surface is mainly composed of such low index planes as (111), (100), and (110) and that a poisoning molecule occupies a surface atom. As shown in Fig. 10, the above three planes can be divided into two groups; the (111) plane exposes alternately Ta and C atom layers, whereas the other two planes include both Ta and C atoms with periodical orientation. Tardif *et al.* (15) presumed that the carbon-deficient part of TaC(111) plane forms active sites, since the catalytic activity of nonstoichiometric compound  $\text{TaC}_x$  increased as  $x$  decreased from 1.0 to 0.8. Schulz-Ekloff *et al.* (16) assumed that the  $(10\bar{1}0)$ ,  $(\bar{1}100)$  and  $(0\bar{1}10)$  planes of WC expose only W atoms forming active sites for ammonia synthesis. A recent study by Oshima *et al.* (17) on the (100) and (111) faces of TiC revealed that the (111) face exposes Ti atoms on the uppermost layer and the adsorption of oxygen on the (111) face is 100 times larger than that on the (100) face. In analogy to TiC, Ta metal atoms are likely exposed on the surface of TaC(111) plane, suggesting that the face is catalytically the most active. The

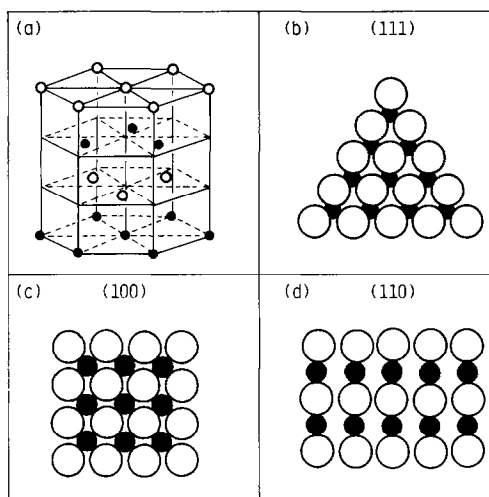


FIG. 10. (a) Crystal structure of TaC; structures of (b) (111); (c) (100); and (d) (110) faces.  $\circ$ , Ta atom;  $\bullet$ , C atom.

effect of oxygen admitted (5, 6) as a strong poison also supports this view.

The hydrogenation rate on the thermally activated TaC,  $1.2 \times 10^{14}$  molecule  $\text{cm}^{-2} \text{s}^{-1}$  at 273 K ( $P_h = 20$  Torr and  $P_e = 10$  Torr), is compatible to that on an evaporated nickel film,  $2 \times 10^{14}$  molecule  $\text{cm}^{-2} \text{s}^{-1}$ , which was estimated by the correction of the data obtained by Alexander *et al.* (18) to the present reaction conditions. Referring the finding by Beeck (19) that the evaporated nickel film is 100 times or more as active as the evaporated Ta one, it will be noted that with alloying to carbon, Ta metal is catalytically activated by about two orders of magnitude. Such an enhanced activity of TaC will be associated with the characteristic electronic states of Ta and C atoms; the lower binding energy of C 1s level of TaC indicates that an electron transfer occurs from Ta atom to carbon atom (20). Further evidence for the distinct feature of carbon atom in the carbide was obtained from the results for the heat treatment in a  $\text{C}_2\text{H}_4$  atmosphere; the accumulation of graphite-like carbon during the treatment brought about the depression of catalytic activity. An APW calculation of TaC shows that the electronic states near

the Fermi level is composed of  $t_{2g}$ -electrons which are localized on a Ta atom but partly are involved in a Ta-Ta bond (21). A DV- $X_\alpha$  calculation of  $Ti_{14}C_{13}$  cluster suggests that the  $d$ -electron density of states near the Fermi level is increased on the uppermost surface layer (22). The evacuation of TaC at 1370 K promoted evidently the intensity due to valence band electrons near the Fermi level as is seen from the spectra in Fig. 8. Thus produced valence electrons on the surface layer will interact with ethylene  $2p\pi^*$  antibonding orbital, which would cause a back donation of electrons from TaC to ethylene. Such electron donation may facilitate the rupture of the double bond of the adsorbed ethylene at high temperatures, resulting in the formation of the graphite-like carbon residues on the surface.

## REFERENCES

- Toth, L. E., in "Transition Metal Carbides and Nitrides," Academic Press, New York/London, 1971.
- McCarty, J. G., and Madix, R. J., *J. Catal.* **38**, 402 (1975).
- Levy, R. B., and Boudart, M., *Science* **181**, 547 (1973).
- Boudart, M., Oyama, S. T., and Leclercq, L., in "Proceedings, 7th Intern. Congr. Catalysis," Part A, p. 578, 1980.
- Miyazaki, E., and Fuse, K., *Nippon Kagaku Kaishi*, 815 (1972); 1388 (1973).
- Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **59**, 472 (1979).
- Kojima, I., Miyazaki, E., and Yasumori, I., *J. Chem. Soc. Comm.*, 573 (1980).
- Yasumori, I., Ohno, S., and Miyazaki, E., *Bull. Chem. Soc. Japan* **40**, 769 (1967).
- Yasumori, I., and Ohno, S., *Bull. Chem. Soc. Japan* **39**, 1302 (1966).
- Turkevich, J., Schissler, D., and Irsa, P., *J. Phys. Colloid Chem.* **55**, 1078 (1951).
- Bond, G. C., Phillipson, J. J., Wells, P. B., and Winterbottom, J. M., *Trans. Faraday Soc.* **62**, 443 (1966).
- Bond, G. C., Webb, G., and Wells, P. B., *Trans. Faraday Soc.* **61**, 999 (1965).
- Bond, G. C., Phillipson, J. J., Wells, P. B., and Winterbottom, J. M., *Trans. Faraday Soc.* **60**, 1847 (1964).
- Horiuti, J., and Polanyi, M., *Trans. Faraday Soc.* **30**, 1164 (1934).
- Tardif, A., Michel, J. M., and Wach, J., *Surface Sci.* **26**, 255 (1971).
- Schulz-Ekloff, G., Baresel, D., and Sarholz, W., *J. Catal.* **43**, 353 (1976).
- Oshima, C., Tanaka, T., Aono, M., Nishitani, R., Kawai, S., and Yajima, F., *Appl. Phys. Lett.* **35**, 822 (1979).
- Alexander, E. G., and Russell, W. W., *J. Catal.* **4**, 184 (1965).
- Beeck, O., *Discuss. Faraday Soc.*, No. 8, 118 (1950).
- Ramqvist, L., Hamrin, K., Johansson, G., Fahlman, A., and Nordling, C., *J. Phys. Chem. Solids* **30**, 1835 (1969); Ramqvist, L., Hamrin, K., Johansson, G., Gelius, U., and Nordling, C., *J. Phys. Chem. Solids* **31**, 2669 (1970).
- Ihara, H., Hirabayashi, M., and Nakagawa, H., *Phys. Rev. B* **14**, 1707 (1976).
- Hori, T., Adachi, H., and Imoto, S., *Trans. Japan Inst. Met.* **18**, 31 (1977).