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Catalysis by Transition Metal Carbides. VI. Hydrogenation of Carbon Monoxide over WC, W_2C, and W Powder Catalysts

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WC, W_2C, and W were comparatively studied for CO hydrogenation to reveal the catalytic role of carbon alloyed with metals. The main products of the reaction were CH_4, CO_2, and H_2O on these catalysts, but the kinetic data obtained for WC catalyst were different from those for W_2C and W catalysts: *i.e.*, the apparent activation energies for CO consumption and for CH_4 formation on WC were found to be about three times larger than those on W_2C or W. Furthermore, the catalytic activity of WC was about 20 times larger than that of W_2C and W. It was suggested that the hydrogenation of CO on WC proceeds *via* direct hydrogenation of adsorbed CO forming a CHO adsorbed species as an intermediate, whereas on W_2C and W catalysts, dissociation of CO occurs in the initial step, followed by further hydrogenation of adsorbed carbon to form CH_4. X-ray photoelectron spectroscopic (XPS) studies on WC and W_2C showed that the WC surface catalytically activated was almost free from graphite carbon and oxygen as poison, but W_2C surface was largely covered with graphite carbon. These distinctive catalytic behavior differences between the carbide catalysts are discussed on the basis of the structure of the active surfaces.

The hydrogenation of carbon monoxide is a current problem in research on heterogeneous catalysis, and has been studied by many investigators on supported and unsupported metal catalysts.[1,2,3] Recently, it has been shown that the transition metal carbides form a new group of catalysts for the hydrogenation of benzene,[4] ethylene,[5,6] and carbon monoxide.[7,8] For the hydrogenation of carbon monoxide, the metal carbides were found to produce higher molecular weight hydrocarbons involving olefins other than methane.[7] A subsequent kinetic study suggested that the adsorbed CO and H atoms form an intermediate of CH_xO type prior to the C–O bond rupture.[8]

From the point of view of catalyst modification by alloying metals with carbon, the states of the carbon species are of importance in understanding the difference in the catalytic properties between metal carbides and the original pure metals. For example, McCarty and Madix found that the carbide-carbon on the Ni(110) plane changes its catalytic properties like those of copper metal for the decomposition of formic acid.[9] Boudart and coworkers reported that W and Mo catalysts modified by C and O atoms exhibit activity and selectivity resembling those of Group VIII transition metals.[10,11] Ross and Stonheart reported that the electrocatalytic activity of tungsten carbide was sensitive to surface composition.[12,13] The unique physical properties such as extremely high melting point, metal-like thermal and electronic conductivities, superconductivity *etc.* of transition metal carbides can be closely related to their electronic structure derived from the coexistence of covalent, metallic and ionic bonds. They have been extensively studied both experimentally and theoretically.[14] However, little effort has been devoted to understanding their chemical reactivity and catalysis. In particular, the question as to how the carbon incorporated in metals affects the catalytic activity still remains open.

In the present study, the hydrogenation of CO was investigated on WC, W_2C, and W in order to reveal the catalytic behavior of the transition metal carbides. Attention was focused on the reaction mechanisms over these catalysts and on the structure of active sites which are responsible for the catalysis. By the use of computer aided analysis of pressure dependencies, a surface intermediate of CHO species was concluded to be formed during the reaction on WC, whereas, it was expected on W_2C and W that CO first dissociates into C and O atoms on the surface, followed by hydrogenation to produce methane. XPS technique was used to examine the surface states of the catalysts.

Experimental

The kinetic measurements of the reaction 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. The powdered materials, WC, W_2C, and W (≈300 mesh) of high purity (>99%) were purchased from Fru-uchi Chemicals Co. X-ray diffraction measurement of WC exhibited only the peaks due to monocarbide, but the diffraction peaks of W_2C catalyst showed a slight trace of metallic tungsten. Before the kinetic measurements, WC was catalytically activated by heating *in vacuo* at 700 °C as described elsewhere.[5] W_2C and W were reduced at 600 °C in an atmosphere of hydrogen at 100 Torr (1 Torr=133.322 Pa) until there was no further formation of H_2O, and subsequently evacuated at 700 °C. The material balance of carbon in the reaction system was maintained within ±5%. The BET surface area of WC measured by Kr adsorption was 1.5 $m^2 g^{-1}$, which was almost identical to the area of the other powdered carbide catalysts. XPS spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer using monochromatic Al *Kα* exciting radiation. The samples pressed into discs were transferred into the preparation chamber of the spectrometer and subjected to *in situ* heat-treatment *in vacuo* or in hydrogen at 700 °C.

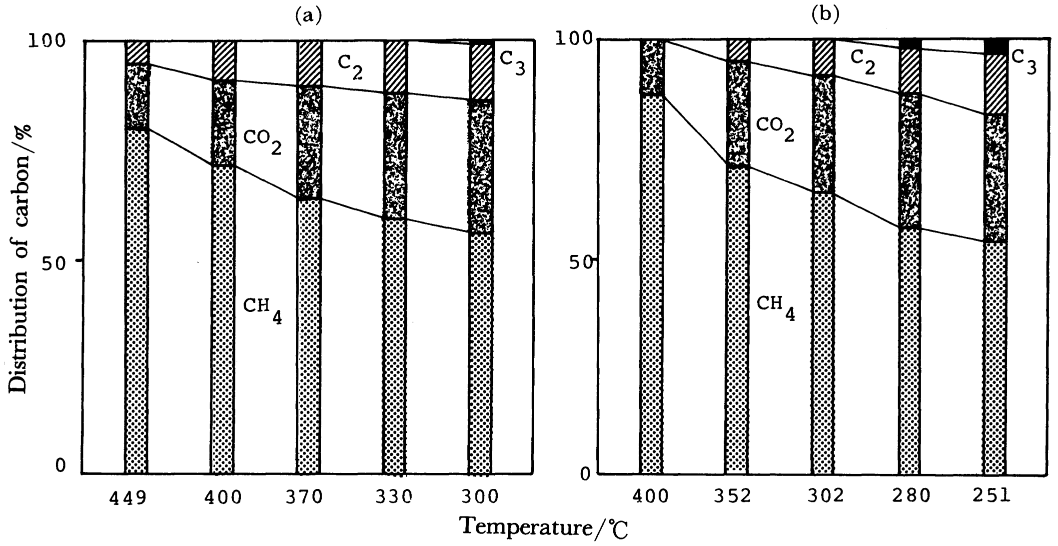

Fig. 1. %-Distribution of carbon containing products for the CO hydrogenation by (a) W_2C and (b) WC.

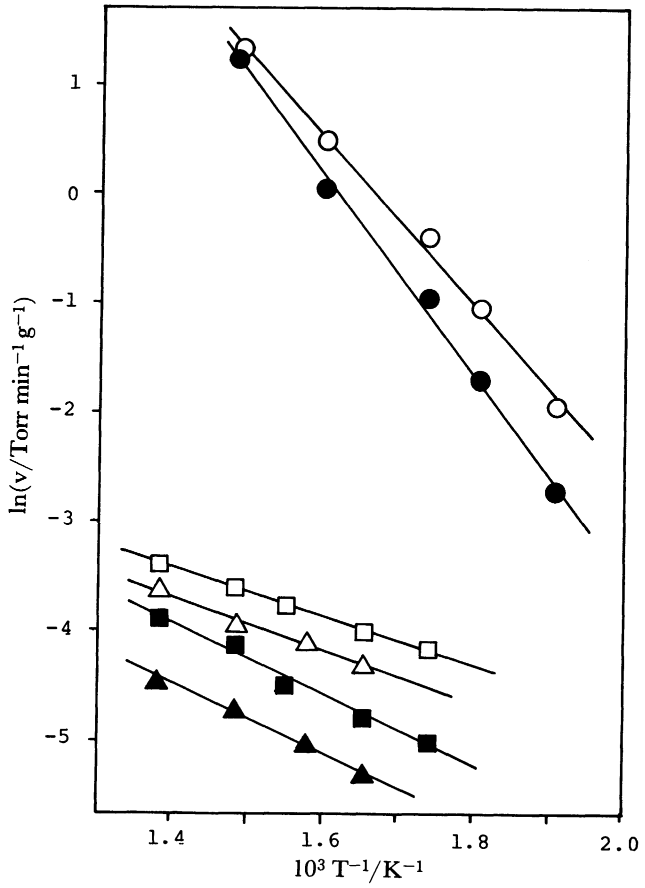

Fig. 2. Dependence of catalytic activities on reaction temperatures for the CO hydrogenation by WC, W_2C, and W.

○, ●: WC, □, ■: W_2C, and △, ▲: W.

Open and close symbols are for the rates of CO consumption and CH_4 formation, respectively.

Result

Figure 1 shows the variation of product distributions with reaction temperature on WC and W_2C. The main products were CH_4, CO_2, and H_2O on WC catalyst at temperatures above 400 °C, and the formation of hydrocarbons of higher molecular weight became appreciable at lower temperatures even at high values of the H_2/CO ratio. Among the metal carbide catalysts investigated here and elsewhere,[7,8] WC is most liable to produce methane. The distribution of products on W catalyst was almost identical to that on W_2C.

Figure 2 shows the dependence of the initial rates of CO consumption and of CH_4 formation on the reaction temperature during the CO hydrogenation under the initial pressures of H_2 at 100 Torr and CO at 10 Torr. The apparent activation energies for CO consumption and CH_4 formation were respectively 64.4 and 76.1 kJ mol^{-1} on WC, 18.4 and 26.8 kJ mol^{-1} on W_2C, and 20.1 and 25.9 kJ mol^{-1} on W catalysts. It is noted that the two values for W_2C and W catalysts are very close in both processes and the values for WC are about three times larger than for W or W_2C catalyst. The catalytic activity ratio of WC, W_2C, and W per unit weight were 200:1.4:1 at 400 °C. The amounts of CO chemisorbed at 0 °C were determined to be 4×10^{14} and 5×10^{13} mol cm^{-2} on the activated WC and W_2C, respectively. This finding indicates that the WC catalyst is roughly 20 times more active per CO-site than W_2C catalyst.

The pressure dependence of the reaction rates was investigated on WC and W_2C at the reaction temperature of 400 °C, where the main products were CH_4, H_2O, and CO_2. The results are shown in Figs. 3 to 5, and they are summarized in Table 1. The reaction orders of the rates of CO consumption and CH_4 formation are similar to those on the transition metals such as Ni, Pd, Rh, Ru *etc.*[15] However, characteristic features on the carbide catalysts can be seen in the reaction orders for the formation of H_2O and CO_2 on WC; *i.e.*, the order for H_2O formation exceeds unity with respect to H_2 pressure, but is negative with respect to CO pressure. Furthermore, the order for CO_2

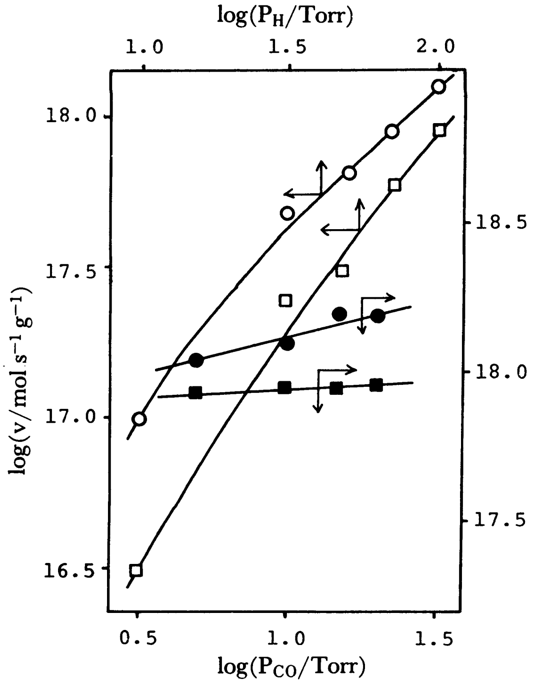

Fig. 3. Dependence of reaction rates of CO consumption (○, ●) and of CH_4 formation (□, ■) on the pressure of CO (open) and H_2 (close) for the CO hydrogenation by WC.

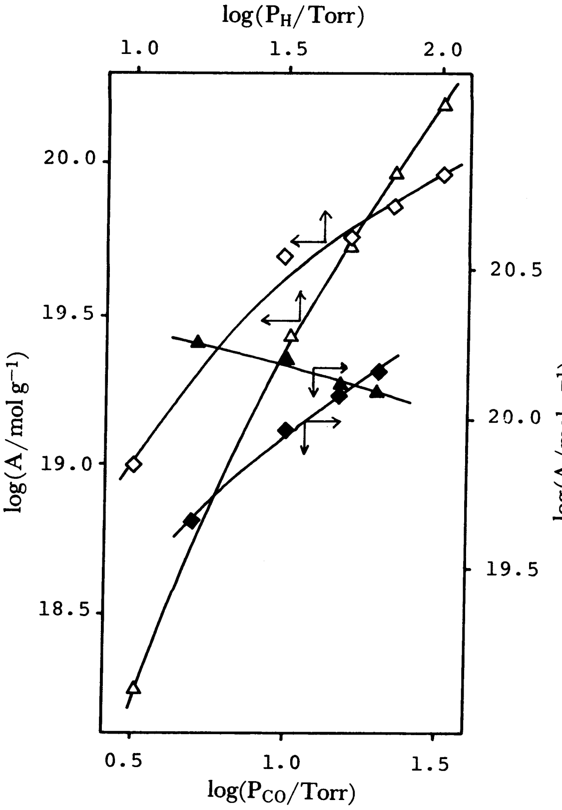

Fig. 4. Dependence of reaction rates of CO_2 formation (◇, ◆) and of H_2O formation (△, ▲) on the pressure of CO (open) and H_2 (close) for the CO hydrogenation by WC.

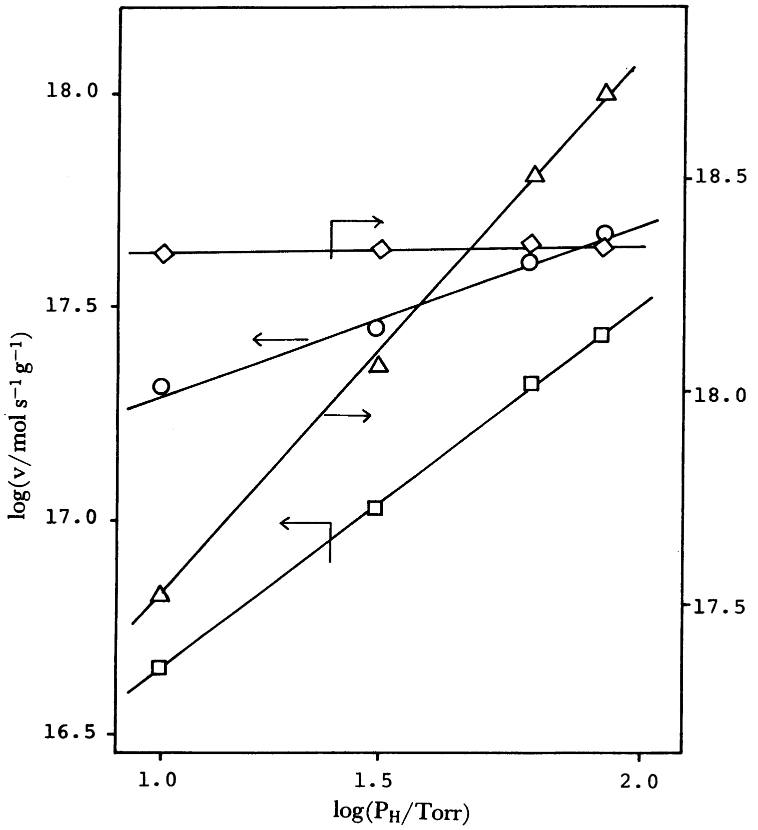

Fig. 5. Dependence of reaction rates on the pressure of H_2 for the CO hydrogenation by W_2C. ○: CO consumption, □: CH_4 formation, ◇: CO_2 formation, and △: H_2O formation.

TABLE 1. PRESSURE DEPENDENCE OF REACTION RATES ON WC AND W_2C

	r_{CO}		r_{CH_4}		$\bar{r}_{H_2O}$		$\bar{r}_{CO_2}$	
	x	y	x	y	x	y	x	y
WC	0.9	0.3	1.2	0.1	1.5	−0.3	0.6	0.7
W_2C	0.4	—	0.8	—	1.0	—	0.0	—

r (or $\bar{r}$)$=k P_H^x P_{CO}^y$, where r represents the initial rate, and $\bar{r}$ is the average rate estimated from the amount produced in a constant initial period of reaction, 10 min.

formation is positive with respect to H_2 pressure. These characteristics of pressure dependence are in common with those on other metal carbides such as TiC, TaC, and Mo_2C. While, on W_2C, the orders of H_2O and CO_2 with respect to H_2 pressure are 1.0 and nearly zero, respectively.

In a previous XPS study on TaC and WC,[5] the peaks assigned only to the pure state of the respective metal monocarbide were observed when the samples were heated *in vacuo* at temperatures higher than the temperatures required for activation, while the oxidized states of the metals were observed in the lower temperatures. In the present case of WC and W_2C, the characteristic peaks due to the oxides disappeared after the activation treatments were made (Figs. 6 and 7). As shown in Fig. 7(a), the catalytically activated WC exhibited a typical peak only at 283.2 eV which can be attributed to carbide carbon, indicating that the surface was almost free from graphite-like contaminant. However, the superimposed peaks were observed with almost equal intensity at 284.8 and 283.5 eV for the activated W_2C (Fig. 7(c)). The existence of the former peak indicates that the surface of W_2C is largely covered with graphite-like carbon. The C 1s peak of WC was found to shift toward lower binding energy relative to that of graphite carbon by 1.6 eV, suggesting that the electrons are transferred from the W to C atoms. It is of note that the observed shift of W_2C, 1.4 eV was smaller than that of WC.

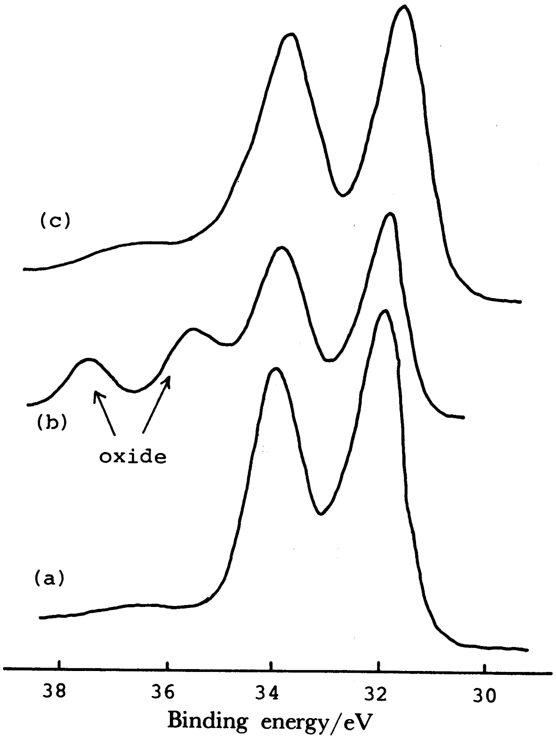

Fig. 6. XPS spectra of W 4f region for WC and W_2C. (a) activated WC, (b) untreated WC, and (c) activated W_2C.

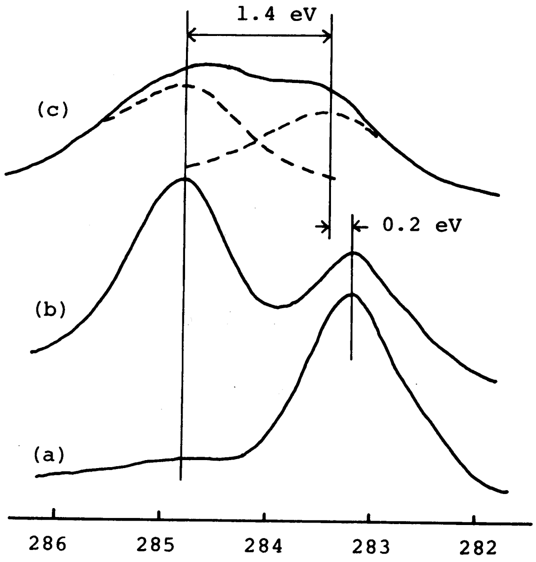

Fig. 7. XPS spectra of C 1s region for WC and W_2C. (a) activated WC, (b) untreated WC, and (c) activated W_2C.

Discussion

Structure of Active Sites. The present kinetic measurements of CO hydrogenation showed a remarkable difference among the WC, W_2C, and W catalysts. The latter two catalysts exhibited very similar activation energies, specific activities and product distributions. WC, on the contrary, exhibited a marked catalytic activity; the activation energies for CH_4 formation and CO consumption were about three times larger than those on W_2C and W, and the specific activities were larger by about 20 times. This different catalytic behavior among the catalysts may arise from the different states of the active sites distributed on the surfaces. Figure 8 shows the crystal structures of WC and W_2C and the periodic arrangement of constituent atoms for $(10\bar{1}0)$ and (0001) planes. These carbides have similar hexagonal structures: The monocarbide consists of an alternate stacking of W- and C-layers along the c-axis direction, whereas W_2C has a series of a unit consisting of two W-layers and a C-layer.[14] As for the $(10\bar{1}0)$ plane of these carbides, both W and C atoms compose the uppermost layer in contact with each other, whereas either of W- or C-atoms compose the uppermost layer for the (0001) plane. Although there is little knowledge concerning the surface structure of WC, an ISS study on the single crystal faces of TiC by

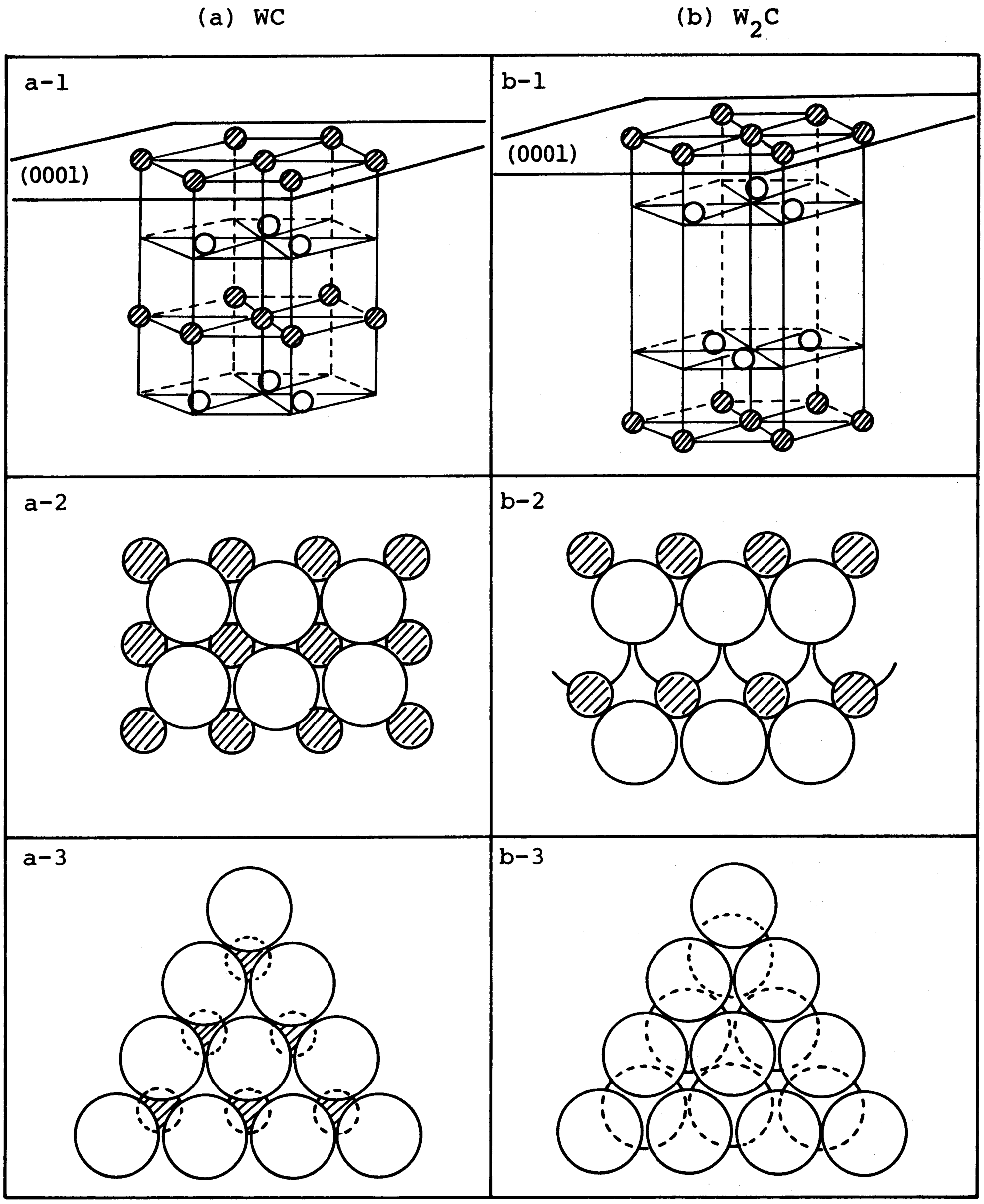

Fig. 8. Structures of (a) WC and (b) W_2C.
1: crystal structure, 2: $(10\bar{1}0)$ face, and 3: (0001) face.
○: W atom, and ▨: C atom.

Oshima *et al.*[16] gives some assistance for describing the behavior of the WC surface. It revealed that with the TiC (111) face Ti atoms compose the uppermost layer and the adsorption rate of oxygen on the (111) face is 100 times larger than that on the (100) face.[16] It is of note that the structures of the (0001) and $(10\bar{1}0)$ faces of WC resemble those of the (111) and (001) faces of TiC, respectively. More recently, Aono *et al.* reported that the carbon vacancies on the TiC (100) plane were very active for the adsorption of oxygen.[17] If carbon vacancies are formed on the WC surface during the activation treatments and are responsible for the catalytic reaction, the catalytic behavior of WC is expected to become closer to that of W_2C, which is opposed to the experimental facts obtained here. Furthermore, considering the uptake of CO adsorption, 30—40 percent of the total surface atoms of WC are estimated to be catalytically effective. This suggests that the surface vacancies are less likely to contribute to the hydrogenation of CO.

It is found that the surface of activated WC is free from contaminants such as oxygen and graphite-like carbon. However, a large amount of graphite residues remains on W_2C even after the high temperature treatment *in vacuo*, and the adsorption amount of CO on W_2C is very small in comparison with that on WC. From the previous study on TaC, the surface graphite acts as a strong poison for the catalytic reaction of ethylene hydrogenation. Assuming that the metal atoms are exposed as the uppermost surface layer of WC (0001) and W_2C (0001) faces as in TiC, the (0001) faces are expected to be catalytically more active than the $(10\bar{1}0)$ faces. With WC (0001) surface, the electronic state of the uppermost W atoms should be strongly modified by the underlying C atoms. This effect is thought to be responsible for the suitable modification of the catalytic properties of surface-exposed W atoms. On the other hand, the nature of the W_2C (0001) surface might be similar to the pure W metal because the second layer also consists of W atoms. Therefore, metallic atoms of the W_2C (0001) surface with high chemical reactivity may strongly bind with contaminants such as graphite carbon or oxygen atoms, resulting in a reduction of the catalytically effective area to only a few per cent of the total surface.

Bradshaw *et al.*[18] performed angle-resolved photoemission measurements of TiC (111) and TiC (100) surfaces. They found that TiC (111) yielded a Ti-terminated (1×1) structure after annealing at 1000 °C *in vacuo* and thus the prepared surface readily adsorbed hydrogen molecules, whereas TiC (100) showed no evidence of H_2 adsorption. These findings also suggest that metal-terminated polar surfaces are mainly responsible for the catalytic activities of refractory metal carbides.

Reaction Mechanisms. There is no general agreement of the nature of the reaction intermediates or of the reaction mechanism for CO hydrogenation on metallic catalyst surfaces: Some authors proposed that CO molecules first dissociate into carbon and oxygen atoms. This is followed by 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.[2,3,19,20] 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.[1,21,22] In a previous paper,[8] we proposed the latter mechanism for the CO hydrogenation on TaC, TiC, and Mo_2C catalyst mainly for the following reasons:

(i) The adsorbed oxygen atoms on these carbide catalysts are tightly bound to the surfaces and can not be eliminated near the reaction temperatures, regardless of the presence or absence of hydrogen in the gas phase.

(ii) The facts that the reaction order of H_2O formation with respect to the hydrogen pressure exceeds unity and that the formation of CO_2 is enhanced by an increase in H_2 pressure; this suggests the existence of some attractive interaction between chemisorbed CO and H atoms. Thus on WC catalyst, similar reaction mechanism to those proposed previously are likely to contribute to the hydrogenation of CO on WC as follows:

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

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

$$\mathrm{CO(a)} + x\mathrm{H(a)} \overset{K_3}{\rightleftharpoons} \mathrm{CH}_x\mathrm{O(a)} \tag{3}$$

$$\mathrm{CH}_x\mathrm{O(a)} + \mathrm{2H(a)} \xrightarrow{k_4} \mathrm{CH}_x\mathrm{(a)} + \mathrm{H_2O} \tag{4}$$

$$\mathrm{CH}_x\mathrm{O(a)} + \mathrm{CO(a)} \xrightarrow{k_5} \mathrm{CH}_x\mathrm{(a)} + \mathrm{CO_2} \tag{5}$$

$$\mathrm{CH}_x\mathrm{(a)} + (4-x)\mathrm{H(a)} \xrightarrow{k_6} \mathrm{CH_4} \tag{6}$$

where (a) denotes an adsorbed state, and K_i or k_i is the equilibrium or rate constant, respectively, of step i.

Assuming that the rate determining step exists in the elimination step of the oxygen atom in the CH_xO species to cause the C–O bond rupture and that all preceding steps are in quasi-equilibrium, the rates of the formation of H_2O and CO_2 are given respectively as

$$R_{\mathrm{H_2O}} = \frac{k_4K_1(K_2)^{1+x/2}K_3P_{\mathrm{H}}^{1+x/2}P_{\mathrm{CO}}}{(1+\sqrt{K_2P_{\mathrm{H}}}+K_1P_{\mathrm{CO}})^3} \tag{I}$$

$$R_{\mathrm{CO_2}} = \frac{k_5K_1^2(K_2)^{x/2}K_3P_{\mathrm{H}}^{x/2}P_{\mathrm{CO}}^2}{(1+\sqrt{K_2P_{\mathrm{H}}}+K_1P_{\mathrm{CO}})^2}. \tag{II}$$

From these rate expressions, one can estimate possible reaction orders with respect to H_2 and/or CO pressures. Comparing them with the experimental data,

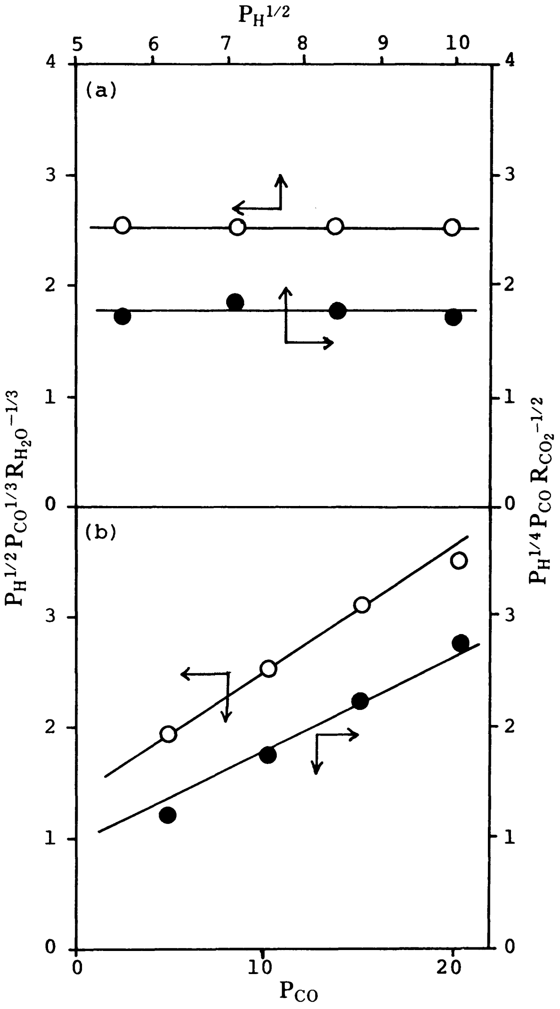

Fig. 9. Least square fitting of pressure dependency by applying the equations (I) and (II) with x=1.
(a) Dependency on H_2 pressure and (b) on CO. Open and closed circles are the experimental data for the formation of H_2O and CO_2 taken from Fig. 4, respectively.

as described in the previous paper, the value of x can be estimated to be 1 or 2. In order to choose a more restricted value, a least square fitting was achieved between the pressure dependencies given in Fig. 4 and the rate equations of (I) and (II). The best fit was attained when x was unity. Figures. 9(a) and (b) show the results and the optimized values of K_1 and K_2 are known to be 0.082 and 0.0, respectively. By using the value of 2 for the x, an unreasonable negative value for $\sqrt{K_2}$ was obtained.

On the other hand, as described above, the active surface of W_2C behaves like a metallic W surface. Since the dissociation of the C–O bond on a metallic W surface is known to be a non-activated process,[23] it is more likely on W_2C that CO molecules initially dissociate into adsorbed C and O atoms on the surface. Thus, the apparent activation energy of the CO hydrogenation is lower on W_2C and W than on WC. These considerations lead us to a dissociative reaction scheme on W_2C and W catalysts as follows:

$$\mathrm{CO} \overset{K_7}{\rightleftharpoons} \mathrm{C(a)} + \mathrm{O(a)} \tag{7}$$

$$\mathrm{H_2} \overset{K_8}{\rightleftharpoons} \mathrm{2H(a)} \tag{8}$$

$$\mathrm{O(a)} + \mathrm{2H(a)} \xrightarrow{k_9} \mathrm{H_2O} \tag{9}$$

$$\mathrm{O(a)} + \mathrm{CO(a)} \xrightarrow{k_{10}} \mathrm{CO_2} \tag{10}$$

$$\mathrm{C(a)} + \mathrm{4H(a)} \xrightarrow{k_{11}} \mathrm{CH_4} \tag{11}$$

Provided that the rate-determining step is the elimination of an adsorbed oxygen atom from the surface and that the preceding steps, (7) and (8) are in quasi-equilibrium, the rate equations for the formation of CO_2 and H_2O can be obtained as (III) and (IV).

$$R'_{\mathrm{H_2O}} = \frac{k_9 K_7{}^{1/2} K_8 P_{\mathrm{H}} P_{\mathrm{CO}}^{1/2}}{(1+\sqrt{K_7 P_{\mathrm{CO}}})^3} \tag{III}$$

$$R'_{\mathrm{CO_2}} = \frac{k_{10} k_7{}^{1/2} P_{\mathrm{CO}}^{3/2}}{(1+\sqrt{K_7 P_{\mathrm{CO}}})} \tag{IV}$$

Considering the material balance of carbon in the reaction system leads to the rate equation of (V) for the formation of CH_4.

$$R'_{\mathrm{CH_4}} = R'_{\mathrm{H_2O}} + R'_{\mathrm{CO_2}} \tag{V}$$

These rate equations are consistent with the experimental reaction orders shown in Table 1. A marked difference of the rate equations is seen between WC and W_2C; *i.e.*, formation of CO_2 depends on the hydrogen pressure on WC but does not depend on W_2C.

Bell *et al.*[3,19] investigated the reaction pathway involving CO dissociation on Ru catalyst in which they assumed the rate to be controlled in the step of the hydrogenation of the CH_x surface species. The present rate equations are not in accord with their mechanism, because the rate-determining step is different. Since the bonding energy of an oxygen atom to metals is stronger on a W surface (651 kJ mol^{-1}) than on a Ru surface (396 kJ mol^{-1}),[23] thereby the elimination of adsorbed oxygen atom from the surface may control the overall rate of CO hydrogenation on W_2C and W catalysts.

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