# METAL-CATALYZED GASIFICATION OF CARBON

Young-Woo Nam[†] and Jae Sung Lee*

Dept. of Chem. Eng., Soong Sil University, Seoul 156-743, Korea
*Dept. of Chem. Eng., Pohang University of Science and Technology, Pohang 790-784, Korea
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**Abstract**—The catalytic hydrogenolysis(gasification) of carbon by dihydrogen in the presence of molybdenum carbide and platinum has been studied around 900 K. As indicated by X-ray absorption, the catalytic phases during the reaction were stable molybdenum carbide or slightly electron-deficient platinum. The rates of hydrogenolysis with molybdenum carbide were only slightly less than those with platinum, one of the most active metals for the reaction. However, these two types of catalyst showed different kinetic parameters and different behavior of catalyst particles during the reaction.
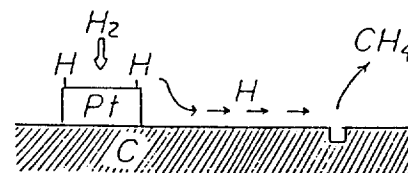
## INTRODUCTION

The group VIII metals are well known to be active catalysts for hydrogenolysis (commonly called hydrogenation or gasification) of carbon [McKee, 1980]. In the case of platinum, Rewick et al. [1974] have proposed that the catalyst serves as a source of adsorbed hydrogen atoms which spill over to the carbon and react with it. By contrast, Holstein and Boudart [1981, 1983] have suggested that carbon reacts with platinum with breakage of carbon-carbon bonds and the removal of a carbon atom from the carbon lattice to the platinum surface where carbidic carbon reacts readily with $H_2$. Two mechanisms are schematically compared in Fig. 1.

In recent studies concerning the catalysis by molybdenum carbides, it was observed that polymeric carbon deposited during preparation on the top of carbide surface reacts much more rapidly with dihydrogen to form methane than bulk carbon alone [Boudart et al., 1987]. Also, molybdenum carbide is a good catalyst for making and breaking carbon-carbon bonds [Lee et al., 1990; Leclercq et al., 1978]. These observations have lead us to investigate molybdenum carbide as a catalyst for the hydrogenolysis of carbon. A study of molybdenum carbide with its stable metal-carbon bond might also shed a light on the nature of platinum-carbon bond which has been suggested to be formed during Pt-catalyzed hydrogenolysis of carbon [Holstein and Boudart, 1981].

A very few has been known about the catalysis by metal carbides in the hydrogenolysis of carbon. Using Auger electron spectroscopy, Bliznakov et al. [1983] showed the formation of carbide phases during the hydrogenolysis of polycrystalline graphite around 850 K in the presence of nickel or tungsten. Yang and Wong [1984], by means of the etch decoration/ transmission electron microscopy, observed that, unlike group VIII metals, metal carbides WC, TaC, and $Mo_2C$ did not form pits or channels on carbon substrate during catalytic oxidation of single-crystal graphite. Furthermore, carbides catalyzed the reaction at the edges which were distant from the catalysts by apparently a long-range action.

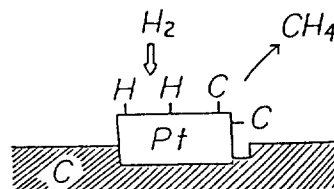Rewick et al. (1974)



Holstein and Boudart (1981)



**Fig. 1. Mechanism of Pt-catalyzed hydrogenolysis of carbon.**

The present study compares the catalytic hydrogenolysis of carbon with molybdenum carbide and with platinum. In addition to the measurement of reaction rates in a flow system, catalysts are characterized by X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS) in order to monitor chemical or structural changes which the catalyst might undergo during the reaction.

## EXPERIMENTAL

The samples employed in this study are described in Table 1. The carbon selected was Spheron 6, a high purity (99.95%) channel black made by Godfrey Cabot Corp. Spheron 6 was selected because of its purity and high specific surface area (102 $m^2$/g). It consists of almost sherical, nonporous particles 30 nm in diameter. The weight of a sample charged into the reactor was decided such that the weight of Spheron 6 of 70 mg was maintained in all runs. Hydrogenolysis of carbon was carried out by flowing $H_2$/He mixtures of known composition at a rate of 90 $\mu mol \cdot s^{-1}$

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[†]To whom all correspondence should be addressed.

**Table 1. Sample preparation, pretreatments, and chemisorption of CO**

| Sample | Preparation | Pretreatment | CO chemisorption[1] |
|---|---|---|---|
| C | Spheron 6 | In He at 1070 K for 1 h | None |
| 1% Pt/C | Impregnation of Spheron 6 with $H_2PtCl_6 \cdot 6H_2O$(Aldrich). Dried at 343 K | In He at 1070 K for 1 h, and then reduced at 570 K in $H_2$ | Negligible |
| 1% $Mo_2C$/C | Impregnation of Spheron 6 with $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. Dried at 343 K | In 20% $CH_4/H_2$ at 950 K for 3 h | Negligible |
| 25% $Mo_2C$+C | Physical mixture of $MoO_3$(Alfa) and Spheron 6 | TPR with 20% $CH_4/H_2$ between 670 K and 930 K | 270 $\mu$mol/g-$Mo_2C$ |
| 25% Mo+C | Physical mixture of $MoO_3$ and Spheron 6 | Reduced at 770 K in $H_2$ for 30 h | 24 $\mu$mol/g-Mo |

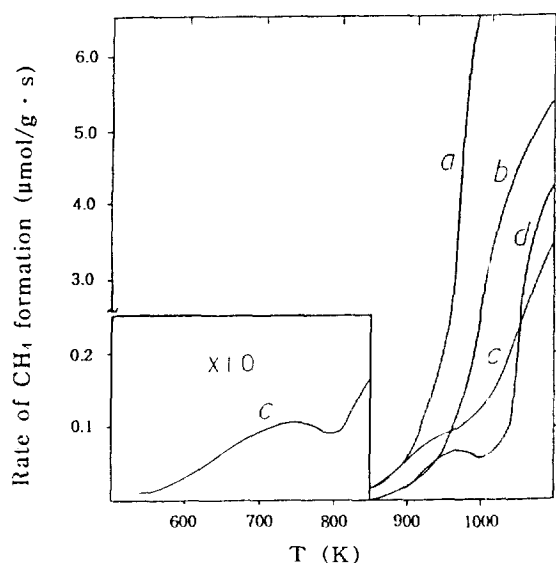[1]Irreversibly chemisorbed CO at room temperature.



Fig. 2. TPR profiles of catalytic hydrogenolysis of Spheron 6 with atmospheric dihydrogen. The rate of heating was 0.12 K s$^{-1}$. (a) 1% Pt/C, (b) 1% $Mo_2C$/C, (c) 25% $Mo_2C$+C, (d) 25% Mo+C

through the packed bed of carbon. The concentration of methane in the gas leaving the reactor was measured with a gas chromatograph.

The phases present in mixture samples were determined by powder XRD using $CuK_\alpha$ radiation. Samples were passivated with 1% $O_2$ in He at room temperature before removal from the treatment cell. For impregnated samples, the XAS data were collected at Photon Factory BL-10B (Tsukuba Japan). Spectra at the Mo K-edge and the Pt $L_{III}$-edge were taken in the transmisson mode. Where the absorbance was obtained by measuring intensities of incident and transmitted beams as a function of beam energy. Measurements were done on sample powders at room temperature in a controlled atmosphere cell under the same gas atmosphere as used during previous sample treatments. Foils of Mo and Pt, and $Mo_2C$ powders with a particles size of ca. 0.5 $\mu$m mixed with Spheron 6 were used as references. The XAS data were analyzed according to standard procedures [Choi, 1995].

## RESULTS

The amounts of CO chemisorbed on pretreated samples prior to rate measurements are shown in Table 1. No chemisorption

**Table 2. Steady-state rates of the hydrogenolysis of carbon with dihydrogen at 1000 K**

| Sample | r ($\mu$mol/g-carbon$\cdot$s) | v$\times 10^3$ (s$^{-1}$) |
|---|---|---|
| C | 0 | - |
| 1% Pt/C | 6.5 | - |
| 1% $Mo_2C$ | 1.0 | - |
| 25% $Mo_2C$+C | 1.65 | 18.3 |
| 25% Mo+C | 0.75 | 93.7 |

of CO was observed for carbon alone. The adsorption of CO on Pt/C and $Mo_2C$/C was also negligible. Two mixture samples, however, chemisorbed the same amount of CO expected for pure $Mo_2C$ or Mo prepared by similar procedures without bulk carbon [Boudart et al., 1987; Lee et al., 1990].

Fig. 2 compares the rates of methane formation for temperature-programed reaction (TPR) of each sample with $H_2$ at atmospheric pressure. The temperature of the reactor was increased at the rate of 0.12 K/s while the product was analyzed every 120 s with a gas chromatograph. The catalytic hydrogenolysis of carbon was observed from 800 K for all samples. The Pt/C showed the highest reactivity. Carbon alone did not react at an appreciable rate below 1100 K. A sample peak between 650 K and 800 K in TPR profile of ($Mo_2C$+C), magnified in an insert, was due to the hydrogenation of carbidic carbon of $Mo_2C$. The carbidic carbon on the surface of $Mo_2C$ also reacted at these temperatures [Boudart et al., 1987]. From the crystal size determined by XRD (Table 3), the surface area of $Mo_2C$ were estimated assuming spherical particles. Further assuming that 1 m$^2$ of surface area contained 10$^{19}$ surface atoms of molybdenum, the number of carbon atoms hydrogenated off the surface in this early stage of TPR corresponded to ca. 0.5 monolayer of $Mo_2C$ surface. This indicated that only surface carbidic carbon reacted, being consistent with the study of $Mo_2C$ alone [Boudart et al., 1987].

Table 2 lists steady-state rates of hydrogenolysis of carbon with atmospheric pressure of $H_2$ at 1000 K. The rates were expressed either per gram of initial carbon (r) or per number of CO molecule chemisorbed at room temperature for the unreacted sample (v). The rate of Pt/C. $Mo_2$/C, and (Mo+C) decreased rapidly to 50-70% of initial values in the first 1 h on stream, and then showed fairly constant values. Mean while, the initial rate of ($Mo_2C$+C) was only 10% of the steady-state rate which was also reached in 1 h on stream.

The effect of $H_2$ concentration [$H_2$] on the reaction rate (Fig. 3) was determined at two temperatures each for Pt/C and $Mo_2$-C/C. As in the previous work [Holstein and Boudart, 1981], the rates on Pt/C showed approximately zero-order dependence on
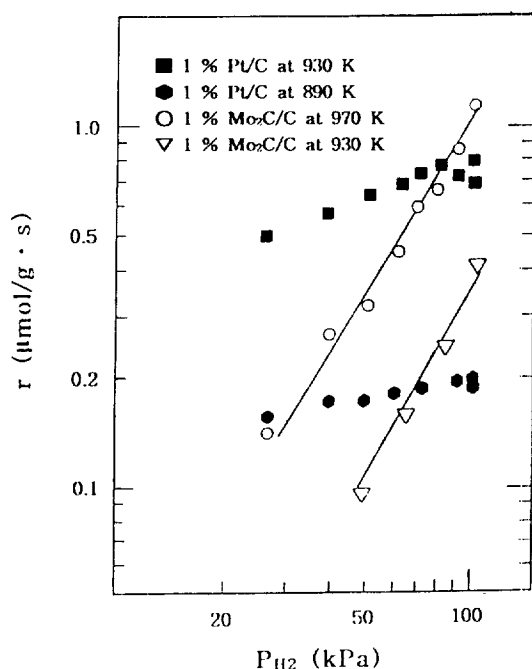
Fig. 3. The dependence of the reaction rate of carbon on the concentration of $H_2$.

Table 3. Characterization results by X-ray diffraction

| | Before reaction | | After reaction[1] | |
|---|---|---|---|---|
| | Phase | Dc[2] (nm) | Phase | Dc[2] (nm) |
| 25% $Mo_2C$+C | $Mo_2C$ | 9 | $Mo_2C$ | 20 |
| 25% Mo+C | Mo | 25 | $Mo_2C$ | 40 |

[1]After 5 h of hydrogenolysis with dihydrogen at 1000 K and atmospheric pressure.

[2]$Dc = \lambda/(\beta \cos \theta)$, $\lambda$ = wavelength of X-ray radiation, $\beta$ = half-width of the diffraction peak at Bragg angle $\theta$, corrected for $K_\alpha$-doublet separation and instrumental broadening.

[$H_2$] at 890 K, and became only slightly positive-order dependent at 930 K. On the other hand, the rates on $Mo_2C$ were strongly dependent on [$H_2$], exhibiting $H_2$ order of ca. +1.7.

Results of powder XRD study are summarized in Table 3 for two mixture samples. Initially samples showed only peaks corresponding to pure phases of hexagonal $Mo_2C$ and Mo, respectively. The X-ray patterns taken after 5 h of hydrogenolysis at 1000 K indicated that Mo phase in (Mo + C) changed to $Mo_2C$, while $Mo_2C$ in ($Mo_2C$ + C) remained unaltered. A significant growth of crystal during the reaction was observed in both samples.

Fig. 4 compares the normalized X-ray absorption edge (XAE) spectra near the Mo K-edge recorded for four cases: a) molybdenum foil, b) the sample obtained by treating the molybdenum precursor (carbon impregnated with ammonium heptamolybdate and then dried) in He at 1170 K for 1 h, c) after treating b in $H_2$ at 970 K for 1.5 h, and d) after treating b in 20% $CH_4/H_2$ at 950 K for 3 h. It should be noted that these treatments represented the conditions employed for the pretreatment of the sample (b and d), and the hydrogenolysis (c). The edge position of Mo foil, the first inflection point in the rise of the absorption edge, was assigned an energy of 20003.9 eV. All the sample had the edge positions similar to that of Mo foil within ± 0.5 eV. This
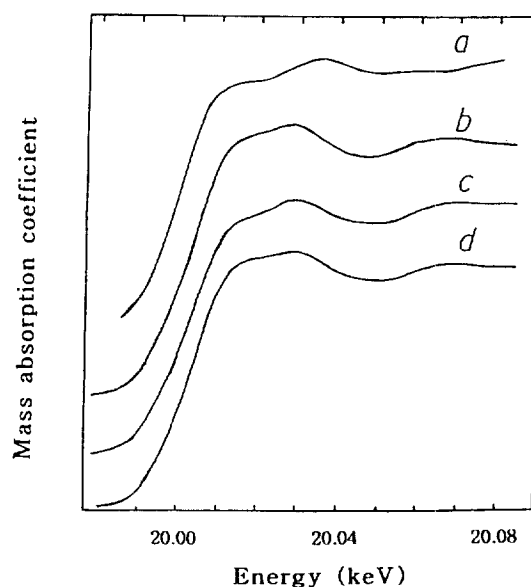


Fig. 4. The X-ray absorption edge near Mo K-edge.
(a) Mo foil
(b) $Mo_2C$/C, treated in He at 1070 K for 1 h
(c) After treating b in $H_2$ at 970 K for 1.5 h
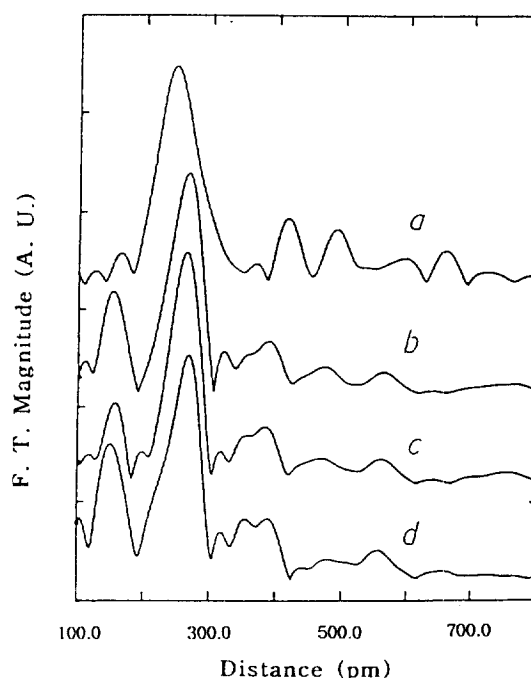(d) After treating b in 20% $CH_4/H_2$ at 950 K for 3 h



Fig. 5. Radial structure functions of Mo K-edge EXAFS.
(a) Mo foil
(b) $Mo_2C$/C, treated in He at 1070 K for 1 h
(c) After treating b in He at 970 K for 1.5 h
(d) After treating b in 20% $CH_4/H_2$ at 950 K for 3 h

indicates that molybdenum in all samples were completely reduced [Cramer et al., 1976]. Spectra b-d were indistinguishable from each other, but were distinct from the spectrum of Mo foil in that they had a smaller separation between two broad peaks above the absorption edge. This is the characteristics of XAE
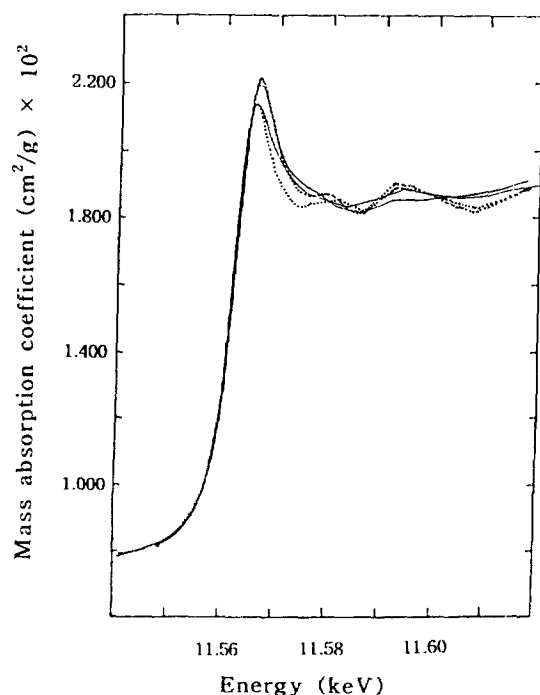
Fig. 6. The X-ray absorption edge near Pt L$_{III}$-edge.

· Solid curve with a larger threshold peak: Pt/C, from treatment of precursor in He at 1070 K for 1 h

· Dotted curve with a larger threshold peak: After treating the above in H$_2$ at 920 K for 2 h

· Solid curve with a smaller threshold peak: Pt/C, treated in H$_2$ at 570 K for 3 h

· Dotted curve with a smaller threshold peak: Pt foil



Fig. 7. The radial structure function from Pt L$_{III}$-edge EXAFS.

(a) Pt foil

(b) Pt/C, from treatment of precursor in He at 1070 K for 1 h

(c) After treating b in H$_2$ at 920 K for 2 h

(d) Pt/C, treated in H$_2$ at 570 K for 3 h

spectrum of bulk molybdenum carbide [Leclercq et al., 1978].

Fig. 5 shows the Fourier transforms of the weighted extended X-ray absorption fine structure (EXAFS) of the same samples. These are called a radial structure function (RSF) where the position of major peaks corresponds to the important interatomic distance shifted from true distance by phase shift. The phase shift could be determined from the spectrum of reference material with a known structure. Again, catalyst samples (Spectra b-d) showed the RSF characteristic of molybdenum carbide with two major peaks at 154± 2 pm and 264± 2 pm, corresponding to Mo-C and Mo-Mo distances, respectively, without the correction for phase shift. These are different from the spectrum of Mo foil (Spectrum a) which showed only Mo-Mo peak at the distance 24 pm shorter than the Mo-Mo distance in molybdenum carbide. Thus both XAE and RSF consistently indicate that three different treatments of precursor yielded an identical molybdenum carbide phase.

The X-ray absorption spectra were also collected near Pt L$_{III}$-edge for four cases: a) Pt foil, b) Pt/C treated in He at 1070 K for 1 h, c) after treating b in H$_2$ at 920 K for 2 h, and d) Pt/C treated in H$_2$ at 570 K for 3 h. The last treatment was done to obtain the sample representative of usual carbon-supported platinum catalyst without any high temperature treatment. All the XAE spectra shown in Fig. 6 exhibited an identical edge position, at 11562 eV within ±0.3 eV. However, they could be divided into two groups by their threshold peak areas determined by integrating the region under the spectral curves lying above the first minimum after the edge [Gallezot et al., 1978]. The Pt/C treated in He at 970 K (upper solid curve) and additionally in H$_2$ at 920
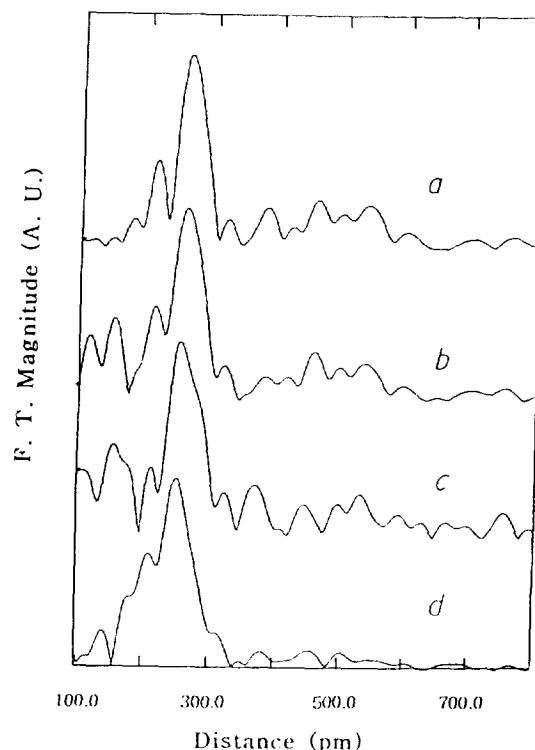
Table 4. Change in metal-metal coordination numbers during hydrogenolysis determined by X-ray absorption

| | |
|---|---|
| Mo$_2$C/C, treated in He at 1070 K for 3 h | 9 |
| Mo$_2$C/C, after hydrogenolysis at 970 K for 2 h | 11 |
| Pt/C, treated in He at 1070 K for 1 h | 8 |
| Pt/C, after hydrogenolysis at 920 K for 2 h | 5 |

*Coordination numbers of bulk molybdenum carbide and platinum metal are both 12.

K (upper dotted curve) had respectively ca. 15% and ca. 25% larger threshold areas than those for platinum foil (lower dotted curve) and Pt/C treated in H$_2$ at 570 K (lower solid curve). The threshold peak area of Pt L$_{III}$-edge together with edge position provides a physical measure of the electron density on the metal. These two quantities correlate each other [Cramer et al., 1976; Gallezot et al., 1978]. Namely, edge position moves to higher energy and threshold peak area increases as platinum is oxidized, i.e., as electron density is removed from the metal. It was reported that oxidized platinum with stoichiometry of Pt$_2$O, PtO, and PtO$_2$ had threshold peak areas relative to Pt foil of 2.0, 4.0, and 6.5, and positive shifts in edge position relative to Pt foil of 0.5, 1.1, 2.3 eV, respectively [Gallezot et al., 1978]. Thus with such small increases in the threshold peak area in our case, the shifts in edge position would not have been detected. In any case, platinum in our two samples treated at high temperatures appeared to be slightly electron-deficient. The RSF of the same samples are shown in Fig. 7. All the spectra had a major peak at 256± 2 pm,

orresponding to Pt-Pt distance of the bulk platinum metal.

Table 4 lists the metal-metal coordination numbers estimated from comparison of RSF of Mo₂C/C and Pt/C samples with those of bulk Mo₂C powder and Pt foil, both having bulk coordination number of 12. These numbers are correlate with relative sizes of Mo₂C or Pt particles. The size of platinum particles appears to be reduced by reaction while that of Mo₂C was increased. The apparent coordination number of Pt after reaction was almost the same as that in Pt/C treated in H₂ at 570 K.

## DISCUSSION

### 1. Mechanism of Metal-catalyzed Hydrogenolysis of Carbon

In the hydrogenolysis of carbon catalyzed by a metal, Holstein and Boudart [1981, 1983] have proposed that the role of the metal catalyst is not merely to serve as a source of adsorbed hydrogen as proposed earlier by Rewick et al. [1974], but to interact strongly with carbon to break carbon-carbon bonds. This mechanism involves a reaction intermediate with metal-carbon bond. The rupture of carbon-carbon bonds may occur in the absence of a reactive gas as suggested in a study *in vacuo* of Pd-catalyzed conversion of amorphous carbon to graphite using *in-situ* electron microscopy [Holstein et al., 1982].

The X-ray absorption demonstrated that the pretreatment in He at 1170 K converted the molybdenum carbide (Fig. 3, 4-b). This observation could be rationalized by assuming that metal-carbon bond was formed by interaction of molybdenum and bulk carbon as suggested in the mechanism of Holstein and Boudart [1981]. However, the carbon surface, after exposure to oxygen, contains a large quantity of oxygenated groups which are evolved largely as CO upon evacuation or treatment in inert gas at temperatures between 870 K-1070 K [Anderson and Emett, 1952]. It was previously suggested that this CO disproportionated, with platinum acting as a catalyst, to carbon and CO₂, leaving carbon atoms on the platinum surface [Boudart et al., 1970]. Hence, it is not clear whether the carbon in Mo₂C was originated from bulk carbon because the same thing could have happened in our case with molybdenum as a catalyst.

X-ray absorption also showed that this molybdenum carbide phase formed during pretreatment was preserved during the reaction with H₂ (Fig. 4, 5-c). Furthermore, the bulk molybdenum metal in (Mo + C) converted completely to Mo₂C during the reaction (Table 3). The gas phase leaving the reactor during the reaction contained typically 0.5-1.5% of methane. When MoO₃ alone without bulk carbon was reduced with H₂ containing 1% CH₄ at 970 K, both Mo and Mo₂C were formed [Boudart et al., 1987]. Thus, molybdenum carbide phase is an active catalytic phase formed from the interaction of metal and bulk carbon during the reaction. It was hard to understand the nature of the suggested initial step of catalyzed hydrogenolysis occurring without participation of reacting gases [Holstein and Boudart, 1981] because of a possible interference of oxide groups on the surface of Spheron 6. However, identification of the active catalytic phase involving metal-carbon bonds supports the mechanism of Holstein and Boudart.

The pretreatment in He at 1070 K produced platinum which appeared to be slightly electron-deficient relative to bulk platinum metal (Fig. 6, 7). This cannot be due to the incomplete reduction since the same phase was preserved even under the highly reducing hydrogenolysis reaction conditions. Neither was it due to

the effect of particle size since smaller Pt particles in the Pt/C reduced in H₂ at 570 K showed X-ray absorption edge spectra indistinguishable from those of Pt foil. By analogy with the case of molybdenum, this electron-deficiency of platinum could be interpreted as due to the effect of elemental carbon formed on the surface as a result of interaction between platinum and bulk carbon. Again, because of the interference of oxide group on the carbon surface, the result of pretreatment in He does not provide any mechanistic information. An apparently small perturbation in the platinum may be partly due to the fact that X-ray absorption is not surface-sensitive and that Pt-C interaction is limited to surface. Similarly, a larger threshold area of Pt/C sample treated in H₂ at the high temperature than the sample treated in He could be attributed to the smaller particle sizes of the former sample (Table 4) which would have increased the contribution of the surface.

### 2. Molybdenum Carbide as a Catalyst for Hydrogenolysis of Carbon

Data on intrinsic rate of catalytic hydrogenolysis of carbon based on the number of reaction sites, i.e., turnover rates, have not been available primarily because the location of the reaction sites are not yet understood: on metal, on carbon, or at their interface? Even when the reaction site is assumed to be on the metal like many other catalytic reactions, it is often difficult to count the number of surface metal atoms using conventional selective chemisorption of simple gases since high temperature pretreatments suppress or eliminate the chemisorption. Furthermore, due to the severe reaction conditions of hydrogenolysis, the properties of the catalyst during the reaction might be quite different from those in fresh sample even when pretreatments at high temperatures have proceeded. Thus the rate of the hydrogenolysis of carbon has been conveniently reported on the basis of initial weight of carbon. Only relative rates are obtained for the same amount of carbon containing the same weight of metals.

Based on these relative rates of catalytic hydrogenolysis with group VIII metals, platinum belongs among the most active metals [McKee, 1980]. In order to evaluate the catalytic activity of Mo₂C, the rate on 1% Mo₂C should be compared to that of 1% Pt/C since they have the same amount of metal loading and have been prepared by similar methods. From both in TPR and at steady state, the rates of catalytic hydrogenolysis of carbon with Mo₂C are only slightly less than the rates with platinum.

Since (Mo₂C + C) and (Mo + C) samples exhibited usual chemisorption of CO, the rates v were calculated based on the amount of CO chemisorption in Table 2. The X-ray diffraction showed that in both samples Mo₂C was the phase of working catalysts with the particle size of (Mo₂C + C) being smaller than the size of (Mo + C) by a factor of 2. Thus much higher value of v for (Mo + C) suggests that the rate is not directly correlated with the number of surface metal atoms in the unreacted sample. It should also be noted that these v values are extremely small compared to other catalytic reactions, e.g., the hydrogenolysis of hydrocarbons, where the rate of 1 s⁻¹ could be easily achieved at much lower temperatures than those usually employed in the hydrogenolysis of carbon.

The hydrogenolysis of carbon with molybdenum carbide exhibited a strong positive-order dependence of rates on dihydrogen concentration in contrast to the zero-order dependence observed for Pt-catalyzed hydrogenolysis. Thus the details of reaction sequence for these two catalysts might be quite different.

Table 4 shows that the metal-metal coordination number of

Mo₂C, determined by X-ray absorption, increases during the reaction, indicating a growth of particles. Meanwhile, it was reduced in the case of platinum. The latter is consistent with the results of controlled atmosphere electron microscopy studies of Pt [Baker et al., 1980] and Ni [Keep et al., 1980] which showed that large catalyst particles broke up and redispersed on carbon substrates during catalytic hydrogenolysis. The same studies also demonstrated that the hydrogenolysis was accompanied either by the formation of pits in the vicinity of stationary metal particles or by channeling in the basal plane of graphite by mobile catalyst particles. The reaction of carbon was observed only in the vicinity of catalyst particles. Recently, however, Yang and Wong [1984] observed during catalytic oxidation of graphite that metal carbides including Mo₂C did not form pits or channels and that the reaction occurred at the edges distant from catalytic particles. These differences in the behavior of catalyst particles of Pt and Mo₂C might be relevant to those different kinetic parameters.

## CONCLUSIONS

The catalytic hydrogenolysis of carbon with platinum or molybdenum carbide appears to involve the intermediates with metal-carbon bonds. This reinforces the earlier conclusions of Holstein and Boudart [1981, 1983] that the role of metal catalysts is not merely to serve as a source of adsorbed hydrogen, but to interact strongly with carbon to break carbon-carbon bonds. However, the two types of catalyst exhibit different kinetic parameters and different behavior of catalyst particles during the reaction, suggesting the details of catalytic sequence are quite different. The rate of hydrogenolysis with molybdenum carbide is only slightly less than the rate with platinum. one of the most active metals for the reaction.

## ACKNOWLEDGEMENT

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