CVD Synthesis of Alumina-supported Molybdenum Carbide Catalyst

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The alumina-supported Mo carbide catalyst was synthesized using a chemical vapor deposition (CVD) technique. The CVD carbide exhibited an extremely high activity for the reduction of CO_2, compared to the alumina-impregnated carbide. The XPS and XRD analyses showed the formation of Mo carbide on the alumina. The increase in the BET surface area of the CVD carbide with increasing Mo loading suggested that very fine particles of Mo carbide were formed on the alumina.

Mo carbide is known to be a very active catalyst for a variety of reactions, such as alkane isomerization,[1] CO hydrogenation,[2] and CO_2 hydrogenation.[3] Boudart et al.[4] reported that Mo carbide with high specific surface area (>100 m^2/g) was prepared by the temperature-programmed reaction (TPR) of MoO_3 with a mixture of CH_4/H_2. Preparation of supported Mo carbides is more difficult than that of unsupported carbides, because of a strong interaction between Mo oxide and the supported alumina material. The authors[5] reported the formation of Mo carbides on the surface of an alumina pellet in the CVD method at a relatively low temperature (500 ℃) and for a shorter deposition time (<60 min) than the TPR method.

Here we wish to report that the activity of the CVD carbide catalyst was extremely higher than that of the TPR carbide. Furthermore, very fine particles of active carbide species on the alumina surface were able to be synthesized using the CVD technique. For catalytic activity measurements in this study, the hydrogenation of CO_2 was chosen because of a recycling technology for emitted CO_2.

The Mo carbide was deposited on alumina particles (10-20 mesh; Japan Reference Catalyst, JRCALO4) using the CVD technique in a gas mixture of $MoCl_5$-C_6H_6-H_2 at a total pressure of 0.12 kPa. The $MoCl_5$ and C_6H_6 were introduced to the reactor by vaporization at 150 ℃ and 30 ℃, respectively. For comparison of the CVD Mo carbides, alumina-supported Mo carbides (TPR carbide) were prepared by impregnating of γ -alumina with ammonium paramolybdate and carburizing of molybdena-alumina according to the procedure reported by Boudart et al.[1] as follows: 12.5 wt% MoO_3/Al_2O_3 was carburized in a gas mixture of 20 % CH_4/H_2 at a flow rate of 4 l/h from 300 ℃ to 700 ℃ and held at 700 ℃ for 3 h, and then cooled to room temperature followed by passivation in 1 % O_2/He for 12 h. These samples were characterized by BET, XRD and X-ray photoelectron spectroscopy (XPS) analyses. Overlapping peaks were deconvoluted by using an ESPAC curve fitting software of a Shimazu ESCA850. The activity measurement for the reduction of CO_2 was carried out using a fixed-bed microreactor at 400 ℃ and atmospheric pressure. Before catalytic measurement, both CVD and TPR carbides were reduced in flowing H_2 for 1 h at 650 ℃. The reactor feed gas, consisting of CO_2/H_2 (1/3), was introduced at a flow rate of 20 ml/min into the reactor. The catalytic activities of the Mo carbide catalysts were calculated on the basis of TOF determined by oxygen adsorption at room temperature after reducing treatment with H_2 at 650 ℃.

Figure 1 shows the activity of CVD carbide, compared with that of TPR carbide for the reduction of CO_2. The main products were CO and H_2O in the reaction. The reverse water gas shift reaction was occurred. The CVD carbide catalyst was 20 times more active than the TPR carbide. The catalytic activity of the CVD carbide was slightly decreased during 100 min of time on stream. Moreover, the oxidation treatment of the Mo carbide catalyst at room temperature in 1 % O_2/He for 12 h depressed the initial activity of the Mo carbide catalyst. Consequently, it is assumed that the deactivation of the Mo carbide catalysts in Figure 1 was caused by the oxidation of Mo carbide.

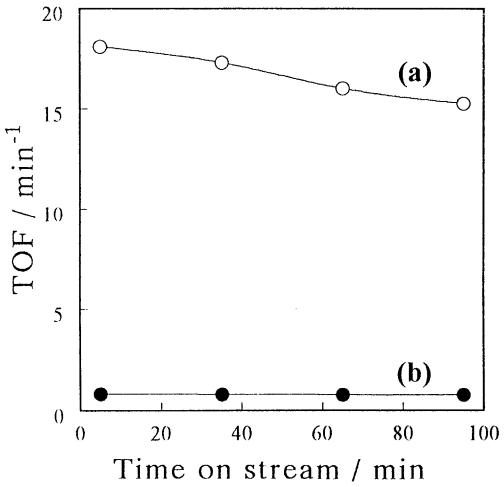

Figure 1. The catalytic activities of the CVD and TPR carbides for CO_2 reduction. (a)CVD carbide, (b)TPR carbide.

The XPS spectra of Mo_{3d}, C_{1s} and O_{1s} for the CVD carbide catalyst before(a) and after(b) Ar^+ ion etching for 10 min are shown in Figure 2. The peak of $Mo_{3d5/2}$ was observed at 228.0 eV. Two peaks of C_{1s} were observed at 284.5eV and 283.0 eV which were assigned to graphitic carbon and carbidic carbon with the bond of Mo and carbon, respectively.[6] The ratio of intensity of C_{1s} at 283.0 eV and $Mo_{3d5/2}$ for the catalyst after Ar^+ ion etching was 0.61 and 1.8 times greater than that before the etching, because oxygen was removed from the surface of the Mo carbide

catalyst. XPS analysis showed that the C_{1s}/ Mo_{3d} ratio of the carbide (0.61) was close to the stoichiometric value of η -Mo_3C_2 (0.67). Moreover, in a previous study,[5] the XRD analysis showed the presence of η -Mo_3C_2 crystal on a quartz glass plate. This result suggested the formation of η -Mo_3C_2 on the alumina support. The crystallite size of the Mo carbide was 12.6 nm from line broadening analysis of the diffraction spectrum. The plane spaceings [Å] and intensity of the XRD spectra are as follows: Found: 2.457 (intensity,100), 2.132(55), 1.503(30), 1.284(27). Reference (ASTM card: 42-890): 2.461(100), 2.125(100), 1.510(100), 1.285(100).

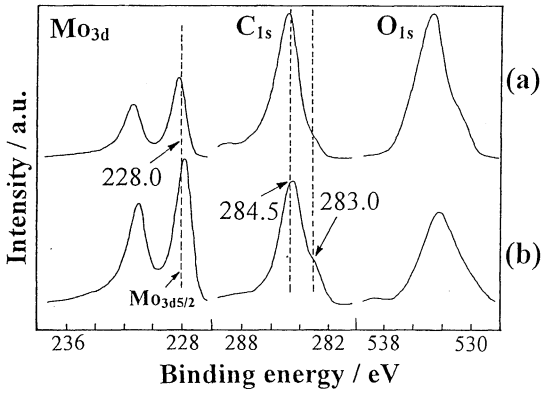

Figure 2. Mo_{3d} , O_{1s} and C_{1s} spectra of the CVD carbide catalyst. (a)as prepared, (b)after 10-min etching.

The Mo_{3d} and C_{1s} spectra of the TPR carbide are shown in Figure 3. The Mo_{3d} spectrum of the TPR carbide was observed at 229.8 eV, 1.8 eV higher than that of the CVD carbide. In a previous paper, Miyata et al.[7] reported that the $Mo_{3d5/2}$ peak at 228.5 eV was ascribed to Mo(Ⅱ～Ⅲ) for the 97.1 wt% MoO_3/Al_2O_3 nitrided at 700 ℃. These results suggested that the Mo valence in the TPR carbide was higher (e.g. Mo(Ⅳ); 229.6 eV[8]) than the Mo(～Ⅱ) in the CVD carbide. The peak of C_{1s} at 283.0 eV

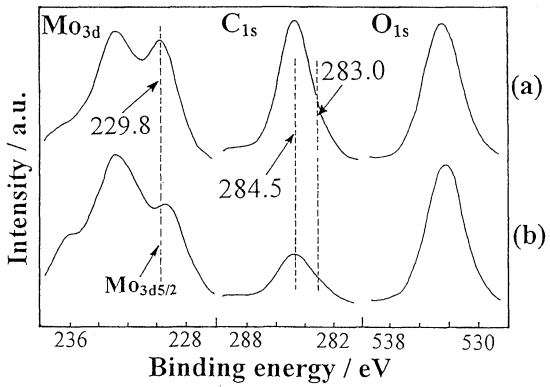

Figure 3. Mo_{3d}, C_{1s} and O_{1s} spectra of the TPR carbide catalyst. (a)as prepared, (b)after 10-min etching.

(carbidic carbon) was not observed before and after etching. This result showed that the bonding of molybdenum with carbon was not formed because of a strong interaction between Mo oxide and Al_2O_3 or possibly that graphitic carbon was much accumulated on Mo carbides and alumina. Consequently, the CVD carbide catalyst was more active than the TPR carbide catalyst due to the formation of η -Mo_3C_2 with a low Mo valence.

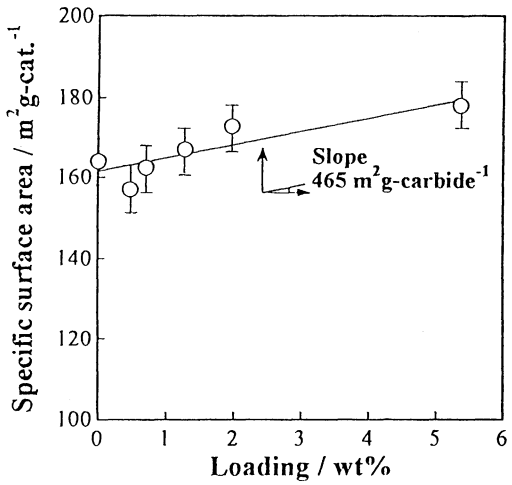

Figure 4. Change in the surface area of the CVD catalysts with carbide loading.

In order to calculated the intrinsic surface area of the Mo carbides supported on alumina, the specific surface area (BET) of the CVD catalysts were plotted against the loading of the Mo carbides in Figure 4. The plots followed a straight line with a slope of 465 m^2/g-carbide. The slope represented the average intrinsic surface area of the Mo carbide species supported on the alumina when the surface area of alumina did not change. Therefore, the calculated intrinsic surface area of the Mo carbide on the support was 465 m^2/g. The particle size of the Mo carbide was estimated from the calculated surface area using the equation of $D_p=6/\rho \cdot S_g$, where D_p is particle size, ρ is the density of the Mo carbide (9.1 g·cm^{-3}) and S_g is the calculated intrinsic surface area of the Mo carbide. From this calculation, the particle size of the CVD carbide was estimated to be 1.4 nm. Lee et al.[9] reported that the particle size of the unsupported TPR carbide was 8 nm. The Mo carbide during CVD synthesis, therefore, consists of very fine particles formed on the alumina pellet.

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