Characteristics of MoO_3 Reduced with H_2 at the Different Flow Rates of H_2

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MoO_3 was treated with H_2 at 623 K for 12 h. The degree of reduction and the specific surface area of H_2-reduced MoO_3 were dependent on the flow rate of H_2 in the reduction process. MoO_3 with a surface area of about 5 $m^2 g^{-1}$ was transformed to a porous MoO_x with a surface area of 180 $m^2 g^{-1}$ after reduction at a flow rate of H_2 larger than 600 ml min^{-1} g^{-1}. The MoO_x was found to be stable at 623 K, even in the presence of H_2O vapor. A study of reduction with a mixture of H_2 and H_2O showed that the degree of reduction and the surface area decreased with increasing partial pressure of H_2O in the reduction process. We conclude from these results that the reduction of MoO_3 to porous MoO_x with a large surface area was prohibited by the action of H_2O produced by the reduction.

Micro and mesoporous inorganic materials have found to be a great utility as catalysts and absorbents due to their large internal surface. Typical microporous materials are zeolites. Zeolites and related crystalline molecular sieves possess not only catalytically active sites, but also uniformly sized pores, which allow their industrial application as shape-selective catalysts. Since the discovery of MCM-41 by Mobil Oil Corporation,[1,2] the preparation of nanostructured porous materials has attracted great interest in materials science. The synthesis and characteristics of Si-based micro and mesoporous materials have been extensively investigated by many research groups. Although the preparation of mesoporous transition metal oxides from a cooperative assembly of a periodic inorganic and surfactant-based structure has recently been reported,[3,4] there have been few studies concerning microporous transition metal oxides. Nanostructured transition metal oxides are expected to have some advantages over Si-based materials for applications in electromagnetics, photoelectronics, and catalysis because transition metals can exist in various oxidation states.

Mo is an important catalytic component, and its physical and catalytic properties have been investigated in detail. In practice, Mo-based materials have been used as catalysts for the hydrodesulfurization of petroleum feed stocks and the selective oxidation of alkenes in industrial processes. Unique catalytic functions of Mo-based materials have recently been reported. Katrib and co-workers[5,6] showed by systematic studies using catalytic reactions in association with spectroscopic techniques that the MoO_2 phase was capable of catalyzing the isomerization of alkane without cyclization and excessive hydrocracking. It was shown in our previous papers[7—9] that MoO_3 reduced with H_2 at 623 K was active for the isomerization of heptane and for the dehydration and dehydrogenation of 2-propanol. After reduction for 48 h, MoO_3 exhibited high dehydration activity compared with that of zeolite catalysts. The H_2 reduction of MoO_3 at 623 K was accompanied by an increase in the surface area: the MoO_3 reduced for 12 h or longer had a surface area of 180 $m^2 g^{-1}$. Furthermore, reduced MoO_3 with a large surface area was found to have micropores, of which the diameter was in the range from 6 to 30 Å.[10] We showed in a previous paper[11] that the catalytic activities for the conversions of heptane and 2-propanol and the surface area of H_2-reduced MoO_3 were markedly affected by the flow rate of H_2 in the reduction process. The main purpose of the present work is to describe the effect of the flow rate of H_2 in the reduction process on the transformation of MoO_3 to MoO_x with a large surface area.

Experimental

H_2 and N_2 were purified by passing through a molecular sieve and a Mn/SiO_2 oxygen trap. The MoO_3 used in this study was obtained by calcination of $H_2MoO_4 \cdot H_2O$ (Kanto Chemical Inc.) at 673 K for 3 h. The powder was made into pellets, crushed, and then sieved (30—60 mesh) for charging into a cell.

A prescribed amount of MoO_3 (0.1—0.5 g) was packed at the central position of a cell, which was made of a pyrex glass tube with an inner diameter of 6 mm. The sample was heated to 623 K at a rate of 5 K min^{-1} in a stream of H_2, and was kept for a desired period, typically for 12 h. The flow rate of H_2 was varied from 60 to 1200 ml min^{-1} g-MoO_3 $^{-1}$. The reduced MoO_3 samples are denoted here by MoO_3 (60), MoO_3 (1200), etc. The values in parentheses represent the flow rate of H_2 in the reduction process. Water vapor was added to the gas stream by passing H_2 or N_2 through a water saturator in a constant temperature bath.

The surface area was determined from a N_2 adsorption isotherm, which was obtained on the sample without exposure to air. The reduced sample was cooled to room temperature with H_2 still flowing. After evacuation for 0.5 h at room temperature, the adsorption of N_2 was measured at 77 K using a conventional high-vacuum static system. To determine the pore-size distribution, adsorption-desorption isotherms of N_2 were measured with an automatic gas-

adsorption apparatus (Sorptomatic 1990, Carlo Erba) after evacuation at 573 K for 2 h. Pore-size distribution curves were obtained by analyzing the adsorption data using the Horvath–Kawazoe method.

The average oxidation state of Mo was determined by measuring the amount of O_2 consumption required for complete reoxidation to MoO_3 after the reduction procedure. A pulse technique was employed. The procedures for reoxidation were described in detail elsewhere.[9]

Crystalline phases of H_2-reduced MoO_3 were determined by X-ray diffraction using Ni-filtered Cu $K\alpha$ radiation. The sample for XRD measurements was obtained as follows: MoO_3 was subjected to H_2 reduction at 623 K for 12 h, followed by flowing N_2 for 0.5 h at the same temperature. After cooling to room temperature under a N_2 atmosphere, the sample was passivated for 1 h with a 1% O_2–99% N_2 gas mixture to avoid any strong bulk oxidation.

Results and Discussion

We showed in a previous paper[9] that the physical and catalytic properties of MoO_3 were dependent on the period of H_2 reduction at 623 K: The catalytic activities for the conversions of heptane and 2-propanol and the surface area increased for longer periods of reduction. It was found that the surface area of H_2-reduced MoO_3 was affected not only by the reduction period, but also by the flow rate of H_2. Figure 1 shows the surface area of reduced MoO_3 as a function of the flow rate of H_2 in the reduction process, which was performed at 623 K for 12 h. The parent MoO_3 had a surface area of about 5 $m^2\,g^{-1}$. H_2 reduction enlarged the surface area remarkably. A change in the surface area was induced when the reduction condition differed only in the flow rate of H_2. The surface area increased in proportion to the flow rate of H_2, and reached a constant value of about 180 $m^2\,g^{-1}$ at a flow rate of H_2 larger than 600 ml $min^{-1}\,g^{-1}$. XRD patterns of the MoO_3 reduced for 12 h are demonstrated in Fig. 2. The diffraction lines corresponding to the MoO_3 phase completely disappeared after reduction for 12 h, irrespective of the flow rate of H_2. MoO_3 (60) provided only the diffraction

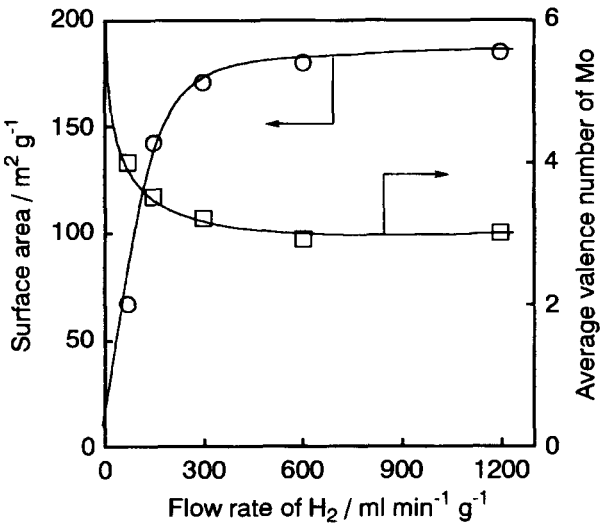

Fig. 1. Effect of the flow rate of H_2 in the reduction process on the surface area of reduced MoO_3. MoO_3 was reduced at 623 K for 12 h.

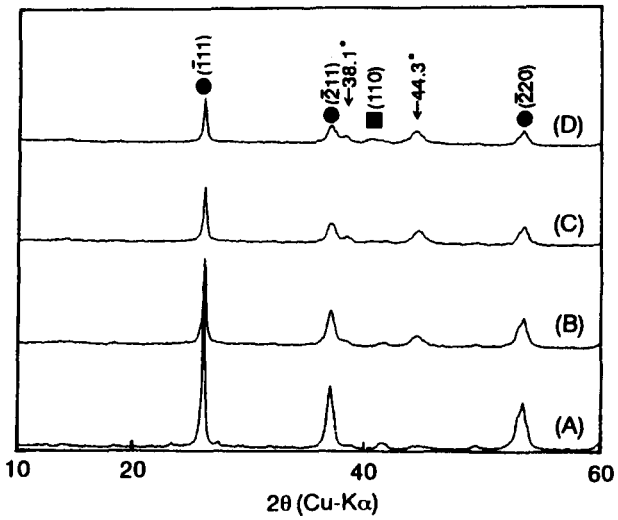

Fig. 2. XRD patterns of MoO_3 reduced with H_2 at 623 K for 12 h. Flow rate of H_2/ml $min^{-1}\,g^{-1}$: (A), 60; (B), 300; (C), 600; (D), 1200. ●, MoO_2; ■, Mo metal.

lines corresponding to the MoO_2 phase. The intensity of these peaks was weakened by an increase in the flow rate of H_2, after which new peaks appeared at 2θ = 38.1° and 44.3°. In the case of MoO_3 (1200), the d (110) diffraction of Mo metal was observed at 2θ = 40.5°. As shown in Fig. 1, MoO_3 was more deeply reduced at a larger flow rate of H_2. This is in accordance with the XRD results.

Hydrogen molybdenum bronze, H_2MoO_3, provides the diffraction line of d (600) at 40.0°. This line appears at a lower angle when the content of H_2 decreases: the d (600) diffraction line of $H_{0.93}MoO_3$ is observed at 2θ = 37.2°. Thus, the diffraction line appearing at 2θ = 38.1° seems to be related to hydrogen molybdenum bronze, H_xMoO_3. Delporte and co-workes[12] showed that a treatment of MoO_3 with a mixture of H_2 and hydrocarbon at 623 K yielded molybdenum oxicarbide, MoO_xC_y, where carbon atoms were substituted for some of oxygen atoms. This phase gave the diffraction line at 2θ = 44.3°. They stated that H or H_2 was able to act like C atoms to form MoO_xH_y, of which the diffraction line appeared at 2θ = 44.5°. We deduce from the reported results that the line at 2θ = 44.3° reflected the formation of the MoO_xH_y phase.

The surface area of MoO_3 has already been reported to be enlarged in a temperature- programmed reaction with NH_3,[13,14] in carburization under a H_2 and CH_4 mixture,[15–17] and in H_2 reduction.[12] The following mechanism has been proposed to explain this phenomenon:[18] The reduction of MoO_3 begins preferentially at the shear planes, which are crystallographic defects created by the aggregation of oxygen vacancies to form planes of molybdenum bound to a tetrahedron of oxygen atoms instead of the octahedrally bound molybdenum of bulk MoO_3. As reduction proceeds in these planes, the metal lattice contracts and fractures the crystal to generate a large surface area.

According to this mechanism, reduction at the larger flow rate of H_2 provides smaller particles. Hence, the particle size

of the reduced MoO_3 was calculated from the d ($\bar{1}11$) line of the MoO_2 phase using the Sherrer equation. The results are given in Table 1. Particles of the parent MoO_3 had an average size of about 500 Å which was determined from the d (020) diffraction line of the MoO_3 phase. The size of the produced MoO_2 particles was small compared with that of the parent MoO_3. This is consistent with the reported results. The particle size of MoO_2, however, increased in proportion to the flow rate of H_2. The surface area was calculated from the particle size by assuming spherical particles. The calculated surface areas of reduced MoO_3 were much smaller than the surface areas determined from the adsorption isotherms of N_2. These results indicate that the enlargement of the surface area cannot be attributed to the formation of MoO_2 particles with smaller size. A treatment of MoO_3 with a mixture of H_2 and hexane at 623 K was reported to produce a mixture of MoO_2 and MoO_xC_y phases, of which the surface area was about 150 $m^2\,g^{-1}$.[12] As mentioned above (Fig. 2), H_2-reduced MoO_3 with a large surface area gives a diffraction line at $2\theta = 44.3°$, while that with a small surface area, such as MoO_3 (60), does not. We deduce from these results that the large surface area of H_2-reduced MoO_3 is related to the formation of the MoO_xH_y phase.

The type of N_2 adsorption isotherm was found to be dependent on the flow rate of H_2. The BET isotherm gave a better fit of the N_2 adsorption data on the parent MoO_3 and MoO_3 (75) than the Langmuir isotherm. For reduced MoO_3 with large surface areas, such as MoO_3 (600), however, the Langmuir equation provided a satisfactory linear fit of the N_2 adsorption data, while the BET did not. These results suggest the presence of micropores in the reduced MoO_3 with large surface areas. In order to confirm this, N_2 adsorption–desorption isotherms and the corresponding pore size distribution curves were determined. Figure 3 shows the adsorption-desorption isotherms of N_2 on MoO_3 (75) and MoO_3 (600). MoO_3 (600) gave no hysterisis, and the amount of N_2 adsorption increased sharply at very low pressures, and changed little at intermediate pressures. These phenomena are characteristics of microporous materials. In contrast, the amount of N_2 adsorption on MoO_3 (75) increased slightly in keeping with the pressure. Pore-size distribution curves determined by the Horvath–Kawazoe method are demonstrated in Fig. 4. MoO_3 (600) was found to possess micropores, of which the diameter was in the range from 6 to 30 Å. The value of Dv/Dr was enlarged by an increase in the flow rate of H_2, suggesting the progression of a porous structure. It is obvious from these results that the reduction of MoO_3 at the larger flow rate of H_2 yielded a microporous MoO_x with a larger surface area. The large surface area of H_2-reduced MoO_3 seems to be caused by the formation of micropores. We reported in a previous paper that the surface area and porosity of the reduced MoO_3 were dependent on the period of H_2 reduction.[10] The effect of the H_2 flow rate on the characteristics of reduced MoO_3 are very similar to that of the reduction period.

Table 1. Average Particle Size of H_2-Reduced MoO_3

Sample	Particle size	Surface area/$m^2\,g^{-1}$	
	Å	Calcd	Measured
MoO_3 (60)	272	34	67
MoO_3 (300)	340	27	170
MoO_3 (600)	388	24	180

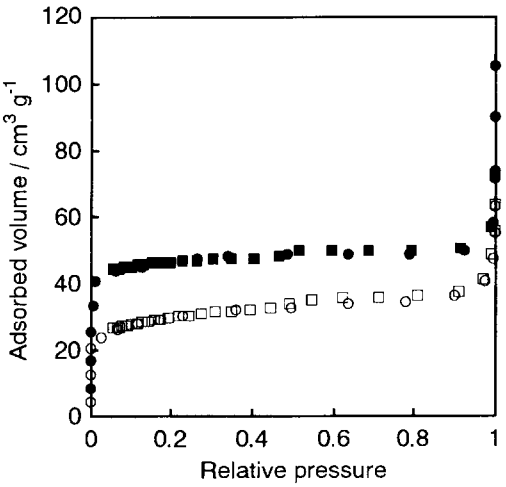

Fig. 3. Adsorption–desorption isotherm of N_2 on MoO_3 reduced at 623 K for 12 h. Flow rate of H_2/ml min^{-1} g^{-1}: open symbols, 75; solid symbols, 600. Isotherm: circles, adsorption; squares, desorption.

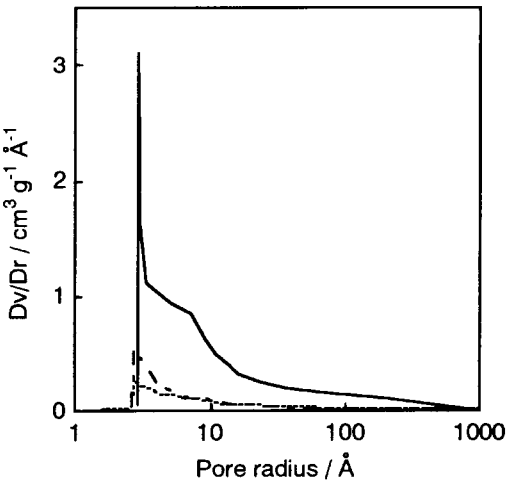

Fig. 4. Pore size distribution in MoO_3 reduced at 623 K for 12 h. Flow rate of H_2/ml min^{-1} g^{-1}: ····, 75; –·–, 150; —, 600.

It was reported that Mo_2N with a larger surface area was produced at a greater space velocity of NH_3 in a temperature-programmed reaction of MoO_3 and NH_3.[18,19] The resultant high surface area was achieved only when the reaction took place at a slow, controlled rate, so that oxygen could be removed and replaced with nitrogen without any substantial reorganization of the metal lattice. The concentration gradient of NH_3 in a MoO_3 bed was thus suggested to affect the surface area of the resultant Mo_2N. The importance of the space velocity was also stated in the synthesis of Mo_2C by the temperature-programmed reduction of MoO_3 with a gas

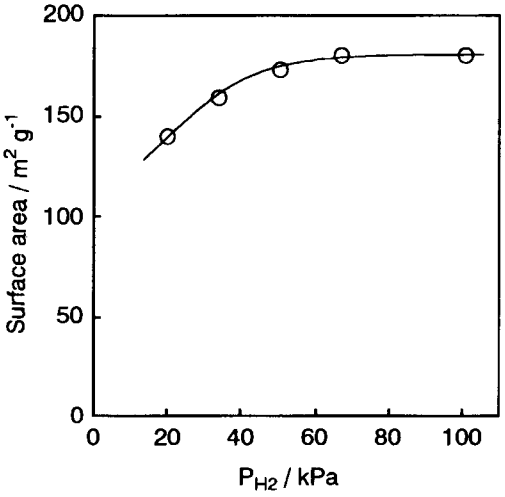

Fig. 5. Effect of partial pressure of H_2 on the surface area of MoO_3 reduced for 12 h at the H_2 flow rate of 600 ml min^{-1} g^{-1}.

mixture of H_2 and CH_4.[19] Figure 5 shows the surface area of reduced MoO_3 as a function of the partial pressure of H_2. Here, the flow rate of H_2 was adjusted to be 600 ml min^{-1} g^{-1}. The surface area was slightly dependent on the partial pressure of H_2. Reduction with a gas mixture of 20% H_2 and 80% N_2, however, yielded MoO_x with a surface area of 140 m^2 g^{-1}, indicating that the effect of the concentration gradient of H_2 was small.

The presence of H_2O vapor has been shown to cause hydrothermal sintering.[20] The most likely reason for the positive effect of the reactive gas flow rate on the surface areas of Mo_2N and Mo_2C was suggested by Oyama and co-workers:[19] The H_2O vapor produced by reduction was rapidly removed from the vicinity of MoO_3 particles, and its partial pressure was lowered at a large flow rate of reactive gas, leading to a suppression of sintering. Figure 6 shows the stability of H_2-reduced MoO_3 (600) in the presence of H_2O vapor. A treatment at 623 K in a pure N_2 atmosphere had no effect on the surface area of MoO_3 (600). When treated in a stream of the N_2–H_2O gas mixture (P_{H2O} = 1226 Pa), the surface area declined. After a treatment for 12 h, the MoO_3 (600) exhibited a surface area of 150 m^2 g^{-1}. This result indicates that a high surface area can be retained even in the presence of H_2O.

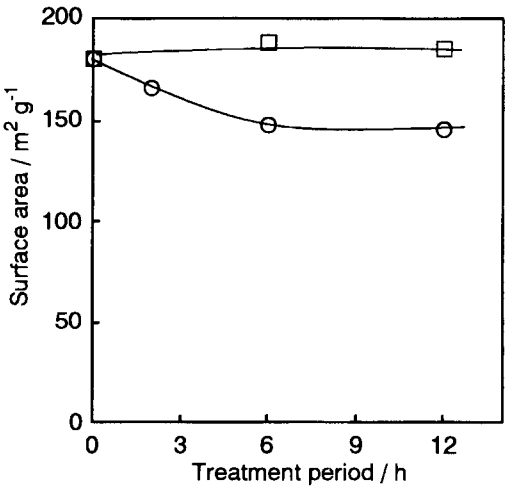

Fig. 6. Stability of the H_2-reduced MoO_3 (600) in the presence of H_2O. The reduced MoO_3 was treated at 623 K in N_2 (□) and in N_2+H_2O (1226 Pa) (○).

In order to study the effect of H_2O on the formation of MoO_x with a large surface area, reduction was performed in the presence of H_2O vapor. The surface area and average oxidation state of Mo as a function of the partial pressure of H_2O are shown in Fig. 7. The MoO_3 (600) reduced at P_{H2O} of 1226 Pa exhibited a surface area of 8 m^2 g^{-1}. This value is almost identical with that of the parent MoO_3. The surface area was enlarged from 8 to 180 m^2 g^{-1} by a decrease in P_{H2O} from 1226 Pa to zero. The Langmuir isotherm gave a better fit of N_2 adsorption data on the MoO_3 with a surface area larger than 100 m^2 g^{-1} than the BET isotherm. These results indicate the significant effect of H_2O vapor on the surface area and the formation of micropores. Figure 8 illustrates the XRD patterns of MoO_3 (600) reduced in the presence of H_2O. The diffraction peaks corresponding to MoO_3 were mainly detected in MoO_3 reduced at P_{H2O} of 1226 Pa. The reduction of MoO_3 was promoted by decreasing P_{H2O}. The diffraction lines corresponding to the MoO_3 phase disappeared completely, and those of the MoO_2 phase were mainly observed after reduction at P_{H2O} of 320 Pa. As shown in Fig. 7, the average oxidation state of Mo was lowered by decreasing P_{H2O}. This is in good agreement with the XRD results. There was a relationship between the surface area and the degree of reduction. This relationship is very similar to that described in Fig. 1. We suggest from these results that the H_2O vapor produced by reduction suppressed the reduction of MoO_3, resulting in the formation of a product with a small surface area.

The reduction of oxide to metal is thermodynamically re-

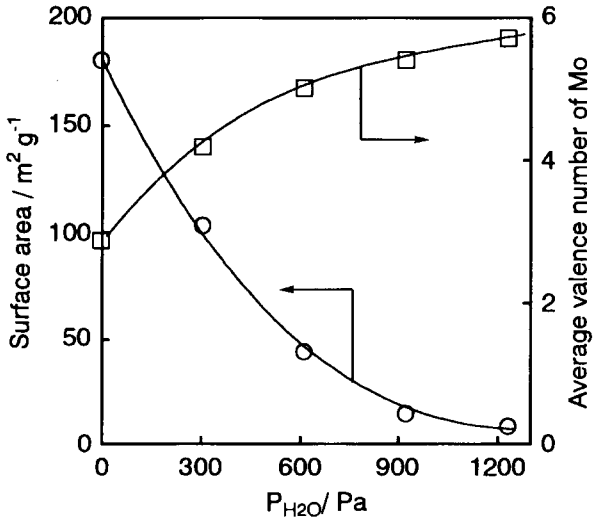

Fig. 7. Effect of partial pressure of H_2O on the surface area (○) and the average valence number of Mo (□). MoO_3 was reduced at 623 K for 12 h in a stream of H_2 (600 ml min^{-1} g^{-1}).

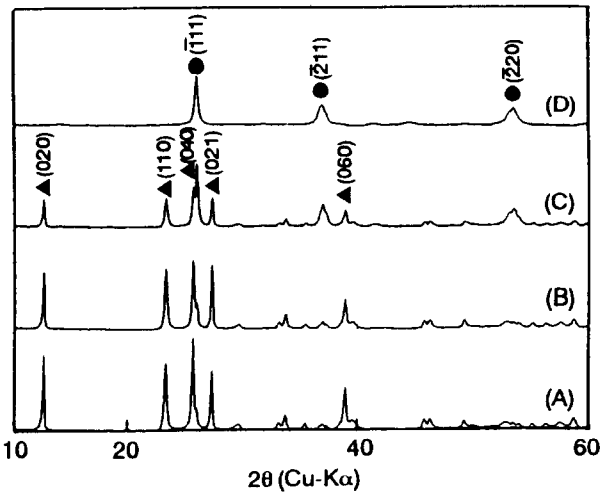

Fig. 8. XRD patterns of MoO_3 (600) reduced with H_2 at 623 K for 12 h in the presence of H_2O. Partial pressure of H_2O: (A), 1226 Pa; (B), 920 Pa; (C), 614 Pa; (D), 320 Pa. ▲, MoO_3; ●, MoO_2.

stricted in the presence of H_2O. The equilibrium constant for the H_2 reduction of MoO_3 to Mo metal at 623 K was calculated to be 2.6×10^4 from thermodynamic data. Therefore, the reduction of MoO_3 to Mo metal can not be thermodynamically limited at this temperature, even in the presence of large amounts of H_2O. Figure 9 shows the average valence number of Mo as a function of the reduction period. Here, MoO_3 was reduced at a H_2 flow rate of 600 ml min^{-1} g^{-1}. MoO_3 reduced for 2 h with pure H_2 had an average Mo valence number of 3.9. A H_2 treatment for a longer period gradually lowered the average valence number of Mo, which became 2.7 after reduction for 48 h. The reduction of MoO_3 proceeded progressively with increasing the reduction period, even in the presence of H_2O (P_{H2O} = 614 Pa). When compared at a definite reduction period, however, the MoO_3 reduced in the presence of H_2O exhibited a larger average valence number of Mo than the MoO_3 reduced with pure H_2.

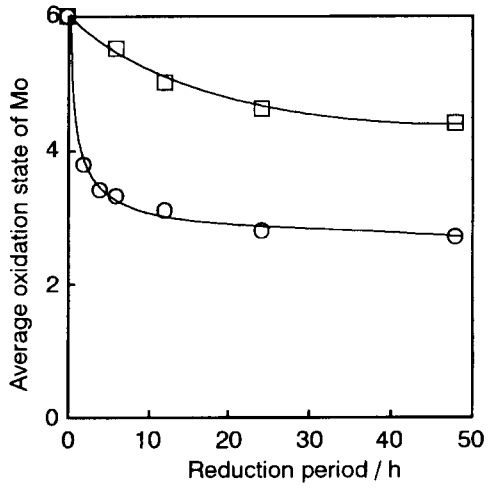

Fig. 9. Average valence number of Mo in the H_2-reduced MoO_3 (600) as a function of the reduction period. ○, H_2; □, H_2+H_2O (614 Pa).

It is obvious from these results that reduction of MoO_3 can be kinetically controlled in the presence of H_2O.

The effects of the reduction period on the surface area of the reduced MoO_3 are shown in Fig. 10. Under a pure H_2 atmosphere, the reduction of MoO_3 markedly enhanced the surface area, which reached a constant value of 180 m^2 g^{-1} after reduction for 12 h. The surface area of MoO_3 reduced in the presence of H_2O vapor was also dependent on the period of reduction. The degree of enlargement in the presence of H_2O, however, was much small compared with that in pure H_2. MoO_3 reduced for 48 h in the presence of H_2O exhibited a surface area of 62 m^2 g^{-1}. The BET isotherm gave a better fit of N_2 adsorption data on this sample than the Langmuir isotherm, indicating no formation of micropores. Figure 11 shows the relationship between the average valence number of Mo and the surface area. The surface area of H_2-reduced MoO_3 was highly related to the average valence number of

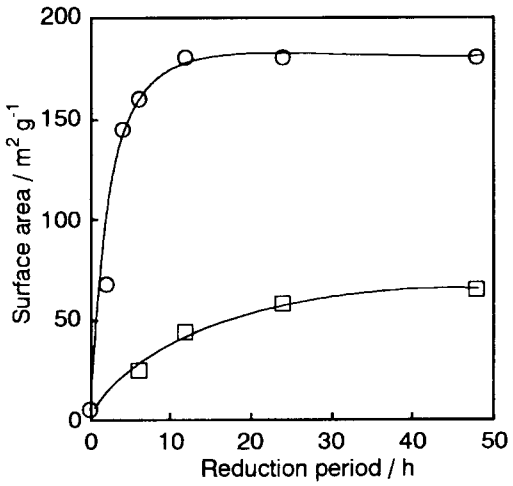

Fig. 10. Surface area of the H_2-reduced MoO_3 (600) as a function of the reduction period. ○, H_2; □, H_2+H_2O (614 Pa).

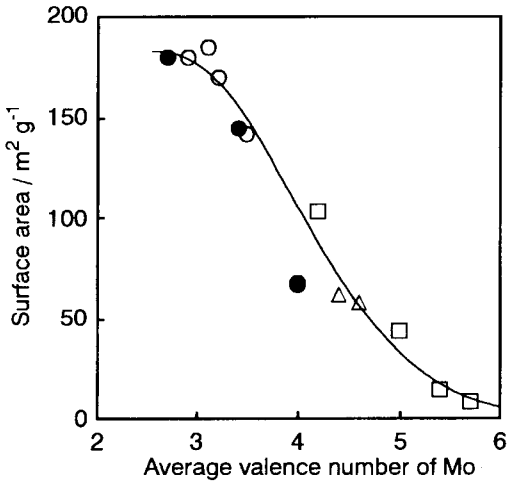

Fig. 11. Relation between the average valence number of Mo and the surface area. Variable: ○, flow rate of H_2; □, partial pressure of H_2O; △, reduction period in the presence of H_2O; ●, reduction period in pure H_2.

Mo, irrespective of the reduction conditions, such as the flow rate of H_2, the partial pressure of H_2O, and the reduction period. We conclude on the basis of these experimental results that the surface area and porosity of H_2-reduced MoO_3 was dependent on the degree of reduction.

Conclusion

The H_2 reduction of MoO_3 at 623 K yielded MoO_x with a large surface area. A change in the surface area was induced when the reduction condition differed only in the flow rate of H_2. The surface area increased in proportion to the flow rate of H_2, and reached a constant value of about 180 $m^2 g^{-1}$ at a flow rate of H_2 greater than 600 ml min^{-1} g^{-1}. The MoO_x was a mixture of MoO_2, H_xMoO_3, and MoO_xH_y phases. Although H_2 reduction of MoO_3 produced MoO_2 particles with a smaller size, the large surface area of reduced MoO_3 can not be explained by the particle size. An enlargement of the surface area was accompanied by the formation of micropores, of which the diameter was in the range from 6 to 30 Å. The microporous MoO_x with large surface area was stable at 623 K, even in the presence of H_2O. The degree of reduction and the surface area were lowered by an increase in the partial pressure of H_2O in the reduction process. There was a good relationship between the surface area and the average valence number of Mo, irrespective of the reduction conditions, such as the flow rate of H_2, the partial pressure of H_2O and the reduction period. We conclude from these results that the reduction of MoO_3 to porous MoO_x with a large surface area was prohibited by the action of H_2O produced by the reduction.

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