

Reduction of H_xMoO_3 with different amounts of hydrogen to high surface area molybdenum oxides

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Abstract

The effect of the amounts of hydrogen in molybdenum bronze on the surface area of its reduction product was studied. H_2 reduction of molybdenum bronze induced an increase in the surface area. Molybdenum bronze with the larger amount of hydrogen exhibited the higher surface area after H_2 reduction. The reduction process varied with the amount of hydrogen in molybdenum bronze. The formation of MoO_2 was suppressed and that of molybdenum oxyhydride, MoO_xH_y , was promoted by an increase in the amount of hydrogen. Molybdenum bronze decomposed to Mo_4O_{11} and MoO_2 on thermal treatment at 400 °C in a flow of N_2 . The surface area of the thermally treated bronze changed very little with H_2 reduction. We conclude from these results that the reduction of molybdenum bronze to MoO_xH_y , of which the formation was dominated by the amount of hydrogen in molybdenum bronze, involved an enlargement in the surface area.

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1. Introduction

Inorganic materials with high specific surface area have a great utility as catalysts and adsorbents. Synthesis and characteristics of Mo- and W-based materials with high specific surface area have been reported. Volpe and Boudart [1] have reported that temperature-programmed reaction between MoO_3 or WO_3 with NH_3 provided a new way to prepare Mo_2N and W_2N powders with surface areas as high as 220 and 91 m^2/g , respectively. The Mo_2N and W_2N were transformed to MoC_x and WC_x with surface areas of 185 and 55 m^2/g , respectively, by temperature-programmed carburization in a mixture of CH_4 and H_2 [2,3]. Temperature-programmed carburization of MoO_3 in a CH_4 – H_2 mixture also led to the formation of MoC_x with high surface area [4]. Ledoux and co-workers have shown that the reaction of MoO_3 with a mixture of H_2 and hydrocarbon at 350 °C yielded molybdenum oxycarbide, MoO_xC_y , with a surface area of about 150 m^2/g [5–7].

We showed in previous papers [8,9] that H_2 reduction of MoO_3 at 350 °C was accompanied by a significant increase in

the surface area. The reduced MoO_3 exhibited a surface area of 180 m^2/g when its average valence of Mo was in the range of 2.5–3.5. The enlargement of surface area was found to result from the formation of pores with diameters of 0.6–3.0 nm. MoO_3 became an active and selective catalyst for heptane isomerization after H_2 reduction at 350 °C [10,11]. Furthermore, the reduced MoO_3 catalyzed the dehydrogenation and the dehydration of propan-2-ol simultaneously [11,12]. We have suggested from these results that MoO_3 reduced at 350 °C is a porous transition metal oxide with the bifunctional property.

The physical and catalytic properties of H_2 -reduced MoO_3 were strongly dependent on reduction temperature [13,14]. When the samples reduced at different temperatures were compared at a certain average valence of Mo, MoO_3 reduced at 350 °C had much higher surface area than MoO_3 reduced at 400 °C and above. Similar results were obtained in heptane isomerization. Since the formation of hydrogen molybdenum bronze, H_xMoO_3 , was observed during reduction at 350 °C, but not at 400 °C, we have suggested that the surface area and the isomerization activity can be enlarged when reduction involves the formation of H_xMoO_3 . Wehrer et al. reported the strong influence of reduction conditions of MoO_3 on its isomerizing property for hexane, and they have proposed that H_xMoO_3 can be the precursor of the active phase for alkane isomerization

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[15–17]. The important role of H_xMoO_3 was also observed in preparation of molybdenum oxycarbide; MoO_xC_y was formed as a pure phase without the presence of MoO_2 by starting from H_xMoO_3 , while carburization of MoO_3 yielded a mixture of MoO_xC_y and MoO_2 [18].

The dependency of the surface area on reduction temperature was not observed when temperature-programmed reduction of MoO_3 was conducted in the presence of noble metal, such as Pt and Pd [19–21]. It is well known that MoO_3 with a noble metal absorbs a large amount of atomic hydrogen at room temperature without an equivalent amount of water being generated [22–24]. This phenomenon is understood as follows: H_2 molecules are dissociatively adsorbed on noble metal, and the dissociated species migrate onto MoO_3 , and then insert into the MoO_3 lattice, leading to the formation of H_xMoO_3 . When reduction of Pt/ MoO_3 was performed at 400 °C after heating in a stream of N_2 , the reduction proceeded without the formation of H_xMoO_3 . In this case, the surface area did not change at all [25]. We reported in previous papers [26,27] that the effects of H_2 reduction on the surface area of H_xMoO_3 that were prepared from a mixture of MoO_3 , Zn, and HCl solution was similar to those on Pt/ MoO_3 , but differed from those on MoO_3 . We have suggested from these results that the enlargement of surface area can originate from reduction of H_xMoO_3 . However, the roles of H_xMoO_3 in the enlargement of surface area are still under investigation. The main purpose of this paper is to describe the effect of the amounts of hydrogen in H_xMoO_3 on the surface area of its reduction product.

2. Experimental

2.1. Materials

H_2 , N_2 , and Ar were purified by passage through a molecular sieve and an Mn/SiO₂ oxygen trap. H_2MoO_4 of purity 98% was purchased from Kanto Chemical Co. Inc. The MoO_3 used in this study was obtained by calcination of H_2MoO_4 at 400 °C for 3 h. Hydrogen molybdenum bronze, H_xMoO_3 , was prepared at room temperature according to the method described by Glemser and Lutz [28]. MoO_3 powder (10 g) was mixed with chips of Zn, and then an aqueous solution of 4 M HCl was added. H_xMoO_3 with the different amounts of hydrogen was obtained by changing the amounts of Zn and HCl solution, namely the molar ratio of MoO_3 and H_2 that was evolved from the reaction of Zn and HCl. H_xMoO_3 samples were prepared at the H_2/Mo ratios of 0.5, 1.0, and 2.0. The reaction mixture was filtered and washed many times in water to eliminate $ZnCl_2$ and HCl. After filtration, the product was dried in vacuo, and was then stored under Ar atmosphere.

2.2. Reduction and characterization methods

A sample weighing 0.1 g was heated to 200–500 °C at a rate of 5 °C/min in a stream of H_2 (60 mL/min), and was kept for 12 h. For comparison, H_2 reduction was conducted at 400 °C for a desired period, typically for 12 h, on H_xMoO_3 that was treated in a flow of N_2 at 200–400 °C for 2 h prior to reduction.

After reduction and evacuation at room temperature, the adsorption isotherm of N_2 was measured at –196 °C using a conventional high vacuum static system to determine the surface area. After the adsorption measurement, the sample was heated in vacuo to 500 °C, and then was oxidized by introducing prescribed amounts of O_2 . The average valence of Mo was calculated from the amounts of O_2 consumed in the reoxidation to MoO_3 . The pore-size distribution and the pore volume were determined with an automatic gas adsorption apparatus (Sorpmatic 1990, Carlo Erba) using the Horvath–Kawazoe method.

X-ray diffraction analyses were carried out on a Rigaku Model Rint 1200 diffractometer with the Ni-filtered $Cu K\alpha$ radiation. H_2 -reduced samples for XRD measurements were obtained as follows: a sample was subjected to H_2 reduction at temperature in the range of 200–500 °C for a desired period, followed by flowing N_2 for 0.5 h at the same temperature. After cooling to room temperature under a flow of N_2 , the reduced sample was transferred to a glove box without exposure to air, and was dispersed in a solution of heptane to avoid any bulk oxidation.

Temperature-programmed reduction (TPR) was conducted to study the reduction process of H_xMoO_3 . A sample weighing 0.4 g was heated from 25 to 900 °C at a rate of 5 °C/min in a stream of 20% H_2 –Ar (20 mL/min). The concentrations of H_2 and H_2O were monitored with TCD gas chromatography using a Poropak N separation column at 140 °C. Temperature-programmed decomposition (TPD) was carried out using Ar as a carrier gas to determine the amounts of hydrogen in H_xMoO_3 samples.

3. Results and discussion

3.1. Characteristics of H_xMoO_3

Fig. 1 demonstrates the XRD patterns of H_xMoO_3 samples prepared using Zn metal and an aqueous solution of HCl. The H_xMoO_3 prepared at the H_2/Mo molar ratio of 0.5 provided no diffraction lines due to the MoO_3 phase; the lines corresponding to the $H_{0.34}MoO_3$ phase were observed at $2\theta = 12.6^\circ$, 23.7° , 27.0° , 29.8° , 33.8° , and 38.5° , and those to the $H_{0.93}MoO_3$ phase appeared at $2\theta = 12.2^\circ$, 24.2° , 25.5° , 37.2° , and 39.1° . The mixture of the $H_{0.34}MoO_3$, the $H_{0.93}MoO_3$, and the $H_{1.68}MoO_3$ phases was obtained at the H_2/Mo ratio of 1.0. The H_xMoO_3 prepared at the H_2/Mo ratio of 2.0 gave no diffraction lines due to the $H_{0.34}MoO_3$ and $H_{0.93}MoO_3$ phases; the lines were observed at $2\theta = 12.7^\circ$, 24.4° and 38.7° , which were assigned to $d(2\ 0\ 0)$, $d(1\ 1\ 0)$, and $d(6\ 0\ 0)$ diffraction of the $H_{1.68}MoO_3$ phase.

Temperature-programmed decomposition (TPD) and reoxidation of H_xMoO_3 were performed to determine the x value of H_xMoO_3 . Results are summarized in Table 1. TPD of H_xMoO_3 in an Ar flow yielded H_2O only. The amounts of H_2O evolved from H_xMoO_3 prepared at the H_2/Mo ratios of 0.5, 1.0, and 2.0 in temperatures of 25–500 °C were 5.63×10^{-2} , 6.88×10^{-2} , and 9.34×10^{-2} g/g H_xMoO_3 , respectively, from which the x values of the H_xMoO_3 samples were determined to be 0.9, 1.1,

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