Acidity and catalytic properties of porous molybdenum oxyhydride obtained by H_2 reduction of MoO_3

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Abstract: H_2 reduction of Pt/MoO_3 yielded porous molybdenum oxyhydride (MoO_xH_y) with average Mo valences of 3.9-1.2. NH_3-TPD and TPO of MoO_xH_y used for NH_3-TPD were conducted to determine the acidity because of the formation of molybdenum oxynitride during NH_3-TPD. The acidity of MoO_xH_y depended on the Mo valence, and the most acidic catalyst was obtained at a Mo valence of near 3.0. MoO_xH_y was active for cyclopropane isomerization, and a good relationship was observed between the isomerization activity and the acidity, except for MoO_xH_y with a Mo valence of 3.9.

Keywords: Molybdenum oxide, Acidity, Isomerization

1. Introduction

Molybdenum is an important catalytic component, and Mo-based materials have been used as catalysts for hydrodesulfurization of petroleum feed stocks and selective oxidation of alkenes in industrial processes. Many research groups have extensively investigated the catalytic properties of these materials in association with their surface properties so as to develop more efficient catalysts. Unique physical and catalytic properties of molybdenum oxides have been reported [1,2]. We showed in the previous works that H_2 reduction of MoO_3 yielded an active and selective catalyst for alkane isomerization only when the reduction proceeded through the formation of hydrogen molybdenum bronze, and the activity depended on the extent of reduction. Although the reaction of alkane isomerization has been considered to proceed through the bifunctional mechanism, the acidity of the partially reduced MoO_3 is still under investigation. The main purpose of this work is to describe the effects of the extent of reduction on the acidic properties of partially reduced MoO_3.

2. Experimental

0.01wt%Pt/MoO_3 was prepared by a conventional impregnation method using an aqueous solution of $[Pt(NH_3)_4]Cl_2$. A 0.1 g sample of $Pt/MoO_3$was heated to 573-773 K at a temperature ramp of 5 K/min under a H_2 flow of 60 mL/min, and was kept for a desired period, followed by the measurement of N_2 adsorption at 77 K. After the adsorption measurement, the reduced sample was heated to 773 K *in vacuo*, then oxidized to MoO_3 by introducing prescribed amounts of O_2. The average Mo valence and the mass of the reduced sample were calculated using the oxidation data. The reduced samples are denoted to Pt/MoO_x(3.9), Pt/MoO_x(1.2), etc. The value in parentheses represents the average Mo valence. The surface area was determined by the mass of the reduced sample, and by the Langmuir equation. Temperature-programmed decomposition (TPDEC) of reduced Pt/MoO_3, temperature-programmed desorption of NH_3 (NH_3-TPD), and temperature-programmed oxidation (TPO) of the catalyst used for NH_3-TPD were performed to determine the composition and the acidity of H_2-reduced Pt/MoO_3. Reaction of cyclopropane (CP) was carried out at 398 K using a glass-made apparatus with a re-circulation system. After reduction and evacuation, a gas mixture of CP and Ar (CP, 2.0×10^{-3} mol; CP/Ar, 3 molar ratio) was introduced to the reaction system.

3. Results and discussion

0.01wt%Pt/MoO_3 was reduced at 573-773 K for desired periods. Characteristics of the reduction products are summarized in Table 1. The parent Pt/MoO_3 had a surface are of 5 m^2/g. H_2 reduction enlarged the surface area markedly, and the largest surface area was obtained at an average Mo valence of near 2.0. Pt/MoO_x were found to have pores with diameters of 6-100 Å. H_2 and H_2O were evolved during TPDEC of

Table 1. Physical properties of H_2-reduced Pt/MoO_3.

Reduction conditions	Average Mo valence	Surface area (m^2/g)	H/Mo (molar ratio)	NH_3-TPD	TPO	Acidity (mmol/g)
				NH_3 (mmol/g)	N_2 (mmol/g)	
573 K, 2 h	3.9	145	0.42	0.43	0.15	0.73
623 K, 2 h	3.7	209	0.28	0.34	0.19	0.73
673 K, 2 h	3.1	265	0.19	0.31	0.23	0.78
773 K, 1 h	2.2	281	0.13	0.23	0.23	0.70
773 K, 3 h	1.6	265	0.07	0.16	0.20	0.57
773 K, 6 h	1.2	208	0.03	0.10	0.16	0.41

Pt/MoO_x, indicating the presence of hydrogen in the reduction products. From the amounts of H_2 and H_2O evolved, the molar H/Mo ratio was calculated to be 0.42 at a Mo valence of 3.9. The ratio was lowered by a decreased in the Mo valence, and Pt/MoO_x(1.2) contained little hydrogen. XRD studies showed that Pt/MoO_x contained no MoO_2 phase. Pt/MoO_x(3.9) provided diffraction lines at 2θ=37.5° and 42.7°. These lines were shifted to higher angles by a decrease in the Mo valence, and Pt/MoO_x(1.2) had diffraction lines at 2θ=38.1° and 44.3°. These diffraction lines were assigned to molybdenum oxyhydride, MoO_xH_y by Delporte et al [3]. In addition to these lines, the diffraction line corresponding to *d*(001) diffraction of the Mo metal phase was observed at 2θ=40.5° as the Mo valence was below 2.2.

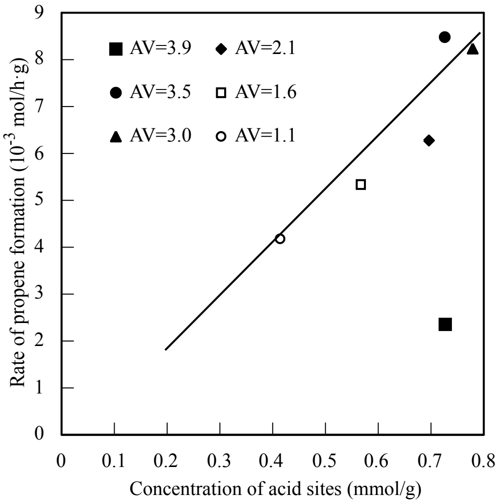

Figure 1. Relationship between the concentration of acid sites and the cyclopropane isomerization activity.

NH_3-TPD was carried out to study the acidity of Pt/MoO_x. The desorption peaks were observed at 473K and 693 K in NH_3-TPD spectrum of Pt/MoO_x(3.9). The high-temperature desorption peak was weakened by a change in the Mo valence from 3.9 to 3.1. Further reduction lowered the desorption peak at low temperature. As a consequence, the smaller amount of NH_3 was desorbed from more deeply reduced Pt/MoO_3. H_2 and H_2O were evolved without the formation of N_2 in NH_3-TPD of Pt/MoO_x, and the amounts of these compounds were large compared with those in TPDEC. These results indicate that a part of the adsorbed NH_3 was reacted with MoO_x in the course of NH_3-TPD, resulting in the formation of molybdenum oxynitride. The formation of N_2 was confirmed in TPO of Pt/MoO_x used for NH_3-TPD. As shown in Table 1, the amount of N_2 evolved was raised by a decrease in the Mo valence, and reached maximum at Mo valences of 2.0-3.0. NH_3-TPD and TPO results shows that Pt/MoO_x(3.1) was the most acidic catalyst. CP was isomerized to propene on all of Pt/MoO_x catalysts, and its isomerization activity depended on the Mo valence. As shown in Figure 1, a good relationship was observed between the isomerization activity and the acidity determined from the results of NH_3-TPD and TPO, except for Pt/MoO_x(3.9).

4. Conclusions

Porous molybdenum oxyhydride (MoO_xH_y) was obtained by H_2 reduction of Pt/MoO_3. Since a part of the adsorbed NH_3 was reacted with MoO_xH_y in NH_3-TPD, the acidity was estimated from the sum of the desorbed amounts of NH_3 in NH_3-TPD and the evolved amounts of N_2 in TPO. MoO_xH_y with a Mo valence of near 3.0 was the most acidic catalyst. MoO_xH_y catalyzed the isomerization of cyclopropane, and its activity was well related to the acidity, except for MoO_xH_y with a Mo valence of 3.9.

References

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