Study on the selectivity of propane photo-oxidation reaction on SBA-15 supported Mo oxide catalyst

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A B S T R A C T

SBA-15 supported Mo oxide catalysts (Mo/SBA) were prepared and the local structures of the Mo species were investigated by X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) measurements. The local structure of Mo on Mo/SBA was able to be controlled from T_d monomer to O_h oligomer by increasing the Mo loading. The selectivity of propane photo-oxidation reaction was dependent on the local structure of Mo species.

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1. Introduction

The selective oxidation reaction (SOR) for light alkane such as natural gas and petroleum gas, into more useful compound is important from the point of effective use of resources. Because of stableness and low reactivity of light alkane, severe reaction condition, high temperature and pressure, are required [1–3]. Improving the activity of SOR, transition metal oxide catalysts have been investigated by many researchers [4–6]. Although photo-catalytic system can be carried out in mild condition at ambient temperature and pressure, a limited number of researches were reported for the application to SOR.

Supported molybdenum oxide is reported to have the photo-catalysis, such as metathesis of olefin [7] and selective oxidation of hydrocarbon [8]. We have recently reported that highly dispersed monomer Mo oxide on mesoporous alumina showed the high selectivity to acetone (>90%) over propane photo-oxidation reaction [9]. However, the origin of the high selectivity to acetone is still unclear because investigation of the support effect was not investigated yet. Adding to this, the control of the selectivity to other products is not achieved. Gaigneaux et al. reported that when using Mo/SiO₂–Al₂O₃ catalyst to SOR, the acidic properties of Al₂O₃ lead to the over oxidation of the hydrocarbon and

increase in CO₂ selectivity [10]. It can be said that the support nature may affect the catalysis. For these reason, the effect of the local structure should be investigated by using the same support. Thus, we focused the preparation of silica supported Mo photo-catalyst to control the selectivity over propane photo-oxidation reaction. Mesoporous materials are widely used for heterogeneous catalysts to obtain highly dispersed metal species, thus one of the most famous mesoporous silica SBA-15 was applied as support.

In this study, SBA-15 supported Mo oxide (Mo/SBA) was prepared using peroxo Mo species as Mo precursor. The local structure of Mo/SBA catalysts was characterized by XRD, BET and XAFS measurements. The selectivity and reaction pathways of propane photo-oxidation reaction were investigated and explained in terms of the molybdenum local structure.

2. Experimental

2.1. Catalyst preparation

Mesoporous silica SBA-15 was synthesized according to the method of Zhao et al. [11]: 4.0 g of triblock copolymer Pluronic P123(Aldrich) was dissolved in 120 g of 2 M HCl(Wako) solution and at room temperature. 8.5 g of TEOS (tetraethyl orthosilicate, TCI, 96.0%) was added into the solution and stirred at 313 K for 24 h. After the additional aging for 24 h at 353 K, the suspension was filtered and washed with distilled water. The resulting white

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Table 1
Textural properties of SBA-15 and catalysts.

Sample	S_{BET} ($m^2\,g^{-1}$)	V^a ($cm^3\,g^{-1}$)	D^b (nm)
SBA-15	1066	1.26	8.1
3 wt% Mo/SBA	738	0.93	7.1
6 wt% Mo/SBA	723	0.91	7.1
9 wt% Mo/SBA	495	0.64	7.1

[a] Total pore volume.
[b] Pore diameter determined by BJH method.

powder was dried at room temperature for overnight and calcined at 773 K for 6 h.

SBA-15 supported molybdenum catalysts (Mo/SBA) were prepared by conventional impregnation method using peroxo Mo solution [12] as a Mo precursor. The catalyst was dried at 373 K for 1 h, followed by calcination at 673 K for 1 h. The loading amount of Mo was regulated to 3–9 wt%.

2.2. Characterization

N_2 adsorption isotherms at 77 K of the samples were measured using BELSORP-MAX (BEL Japan, INC). Samples were degassed at 473 K for 2 h before measurement. The specific surface area and pore volume were obtained by Brunauer–Emmett–Teller (BET) method and by Barrett–Joyner–Halenda (BJH) method, respectively.

Powder X-ray diffraction patterns were recorded by MiniFlex 600 (Rigaku Co.) using Cu Kα radiation.

Mo K-edge XAFS measurements were carried out in a transmission mode at IMSS-KEK PF AR-NW10A (Proposal No. 2014G575). Curve fitting (CF) analysis was conducted by the EXAFS analysis program REX2000 (Rigaku Co.).

2.3. Photo-oxidation reaction

Photo-oxidation reaction at 273 K was carried out in a closed circulating system under irradiation of 75 W high-pressure Hg lamp. The catalyst (0.05 g) was loaded in U-shaped quartz cell with a flat bottom. Initial pressure of propane, O_2 and He was 0.67, 0.67 and 6.67 kPa, respectively. To investigate the reaction pathway, photo-oxidation reaction of propylene, acetone, propionaldehyde, acetaldehyde and ethylene were also carried out. Prior to the photo-catalytic reaction, the catalyst was treated with 13.4 kPa of O_2 at 573 K for 1 h, followed by evacuation at the same temperature for 0.5 h. After the photo-oxidation reaction, the catalyst was heated at 573 K to collect the products adsorbed on the catalyst. The reaction products were separated and analyzed by GC-8A (Shimadzu Co.) with TCD.

3. Results and discussion

3.1. Local structure of Mo catalysts

3.1.1. N_2 adsorption measurement

N_2 adsorption–desoprtion isotherms for SBA-15 and 3 and 6 wt% Mo/SBA are shown in Fig. 1 and BET specific surface areas, pore volumes, and pore diameters are summarized in Table 1. According to Fig. 1, every sample exhibited the type-IV isotherms and hysteresis loop typical of the SBA-15 materials [11]. It can be said that 3 wt% and 6 wt% Mo/SBA still maintained its mesoporosity and high enough BET surface area, although the BET surface areas of Mo/SBA were decreased compared to the original SBA-15. Moreover, only 9 wt% Mo/SBA has smaller BET surface area but still maintained the pore diameter indicating that maintained its mesoporosity, and
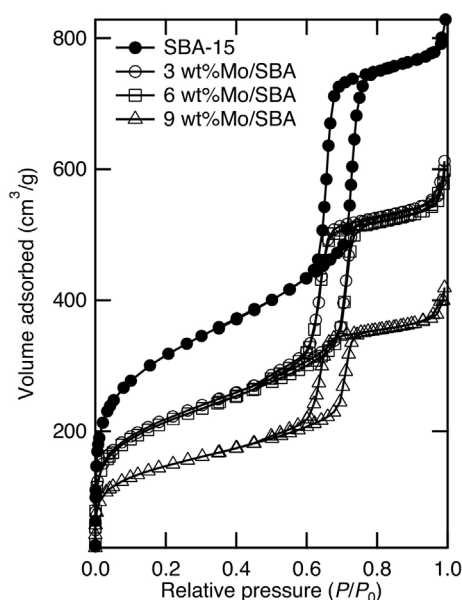

Fig. 1. N_2 adsorption–desorption isotherm of SBA-15 and catalysts.

there is no significant difference in the porosity between the 3 wt% and 6 wt% Mo/SBA.

3.1.2. XRD

XRD patterns were shown in Fig. 2. There are no diffraction peaks assignable to MoO_3 at $2\theta = 23.4$, 25.8, 27.4, and 39.0° over 3–9 wt% Mo/SBA. This result suggests that there are no crystalline MoO_3 species, so the Mo oxide species on SBA-15 seemed to be highly dispersed.

3.1.3. Mo K-edge XAFS

The Fourier transform (FT) of k^3-weighted Mo K-edge EXAFS spectra of Mo/SBA (3–9 wt%) are shown in Fig. 3. FT k-range was regulated as 35–135 nm^{-1}. FT peak at 0.16–0.20 nm was attributed to the neighboring oxygen atoms (Mo—O) and at 0.28–0.38 nm was assigned to the neighboring Mo atoms (Mo—(O)—Mo). The results of the curve-fitting analysis in k-space are summarized in Table 2. The very small peak at around 0.3 nm was observed for every Mo/SBA catalyst (3–9 wt%), and was reproduced with coordination numbers (CN) of 0.3 as Mo—(O)—Mo. From these results, it is indicated that all Mo/SBA catalysts have highly dispersed Mo species with small portion of oligomerized Mo species. Asakura
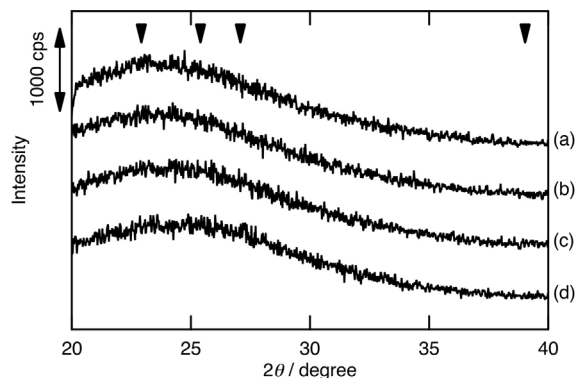

Fig. 2. XRD patterns of (a) SBA-15, (b) 3 wt% Mo/SBA, (c) 6 wt% Mo/SBA and (d) 9 wt% Mo/SBA. Triangles indicate the diffraction position of MoO_3.

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