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Activation of bulk MoO_3 catalysts by spray reaction method for propene photometathesis reaction

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Photometathesis of C_3H_6 proceeded on the sprayed MoO_3 catalyst under UV irradiation with wavelength <290 nm. The photoactivity on the spray catalyst was 20-fold higher than that on the commercial MoO_3. The X-ray diffraction (XRD) results showed the anisotropic growth of the crystal in the spray catalyst. The edge-rich structure was formed in the bulk molybdenum oxide by spray reaction technique.

KEY WORDS: sprayed catalysts; photometathesis; molybdenum oxide; anisotropic growth.

1. Introduction

Most of transition metal oxides have catalytic activities for various photoinduced reactions. The atomically or molecularly dispersed molybdenum oxide catalysts on the support, which have characteristic local structures, show photocatalytic activities for the oxidative dehydrogenation of alcohols [1], the oxidation of hydrocarbons [2] and the metathesis of alkenes [3]. Kazansky and coworkers [4] confirmed that the photochemically prereduced silica-molybdena catalysts showed high photoactivity for the metathesis of C_3H_6. Anpo *et al.* [5] reported that the tetrahedrally coordinated molybdenum ions on Mo/SiO_2 catalysts exhibit a higher activity for the photometathesis of C_3H_6. The photocatalysis of the molybdenum oxide was strongly affected by surface morphology. Since the bulk molybdenum oxide seemed to have no photocatalysis [6], the applications of it to photocatalysts were rarely reported.

The spray catalysts, prepared by rapid heating and quenching process, might have metastable surface states and found to have characteristic properties in various catalyses [7–9]. Thus, the sprayed bulk molybdenum oxide catalysts can be expected to exhibit characteristic behavior for photocatalysis.

In the present paper, the activation of the bulk molybdenum oxide catalyst by the spray reaction technique was investigated and applied to the propene photometathesis reaction.

2. Experimental

The spray molybdenum oxide catalysts were prepared as follows; a molybdenum aqueous solution (0.15 mol L^{-1}) was prepared from MoO_3 (Junsei Chemical Co., Ltd.) dissolved in a dilute NH_3 solution. The ultrasonically atomized solution was aspirated through a quartz tube heated at a spray reaction temperature (T_{spr}, 673–873 K). The atomized droplets were rapidly heated, dried, decomposed to the oxide and rapidly cooled at collecting site within a second. Thus, the sprayed particles were collected in a quenched state. The catalyst was designated with T_{spr} as spr873.

Catalysts were treated with O_2 for 120 min at 673 K, followed by evacuation for 15 min prior to use. The catalysts were characterized by BET surface area, UV–vis. diffuse reflectance spectra (DRS) and X-ray diffraction (XRD) measurement. Photocatalytic reaction of C_3H_6 metathesis ($P_0 = 3.3$ kPa) was performed at 275 K in a closed circulating system equipped with U-shaped quartz reactor. The pretreated catalyst (0.3 g) was UV-irradiated by using a 75 W high pressure Hg lamp through a water filter and UV cut off filter, (UV27, UV29, UV31 and UV35, cutting off the light of wavelength shorter than 270, 290, 310 and 350 nm, respectively). Molybdenyl double bond on the supported molybdenum oxide catalyst was quantitatively reduced by CO under the irradiation concomitant with the CO_2 formation [4]. Thus, the number of active sites can be estimated by the CO photooxidation reaction.

3. Results and discussion

As shown in figure 1, XRD patterns of spr673, spr773 and the commercial MoO_3 showed only α-MoO_3 phase ($2\theta = 23.4°$ (110), 25.8° (040), 27.4° (021), 33.8° (111) and 39.0° (060)), while those of spr873 were assigned to both α-MoO_3 and β-MoO_3 phase ($2\theta = 23.0°$, 24.9°, 26.5° and 34.2°). Since β-MoO_3, metastable phase, exists below 623 K [10], the molybdenum oxide, sprayed at higher than 873 K, was expected not to have metastable

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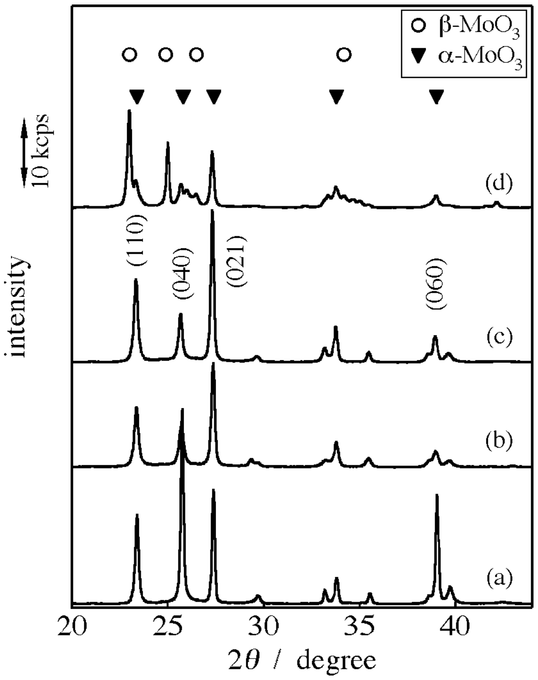


Figure 1. XRD patterns of the molybdenum oxide catalysts; (a) commercial MoO_3, (b) spr673, (c) spr773 and (d) spr873.

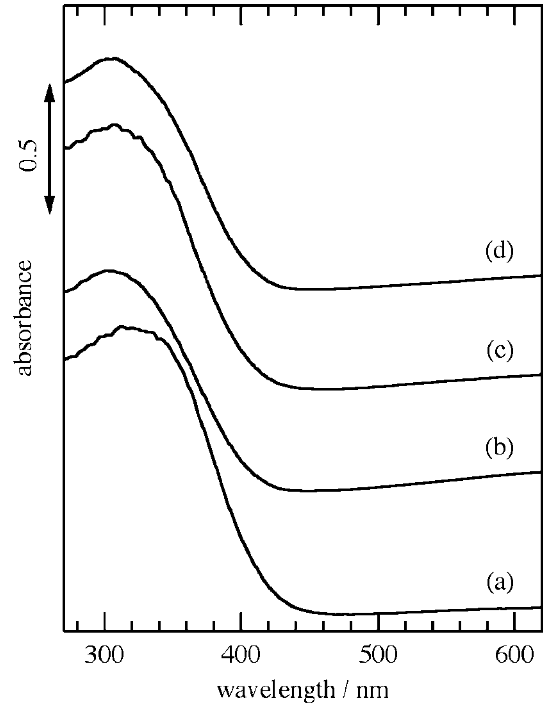
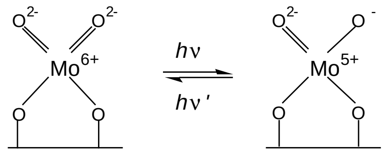


Figure 2. UV–vis DRS of the molybdenum oxide catalysts; (a) commercial MoO_3, (b) spr673, (c) spr773 and (d) spr873.

phase such as β-MoO_3. The rapid heating and quenching process of the spray reaction might produce the remarkable surface states.

There were interesting differences in the relative intensity of the XRD peaks between the spray catalysts and the commercial MoO_3. The relative intensity of (040) and (060) peaks to (110) and (021) peaks for the spray catalysts was much smaller than that for conventional α-MoO_3. With increasing T_{spr}, the anisotropy of the spray catalysts were more distinguished. These results indicate that the anisotropic growth might occur [11] during the spray reaction. This was because that the whole process of spray reaction was completed within a second, so the sprayed particle could have non-equilibrium metastable state.

Figure 2 shows the UV–vis. DRS of the spray catalysts. The UV absorption bands at about 300 nm (from 350 to 280 nm) were observed for all the samples. The excitation bands at about 260–300 nm of supported Mo/SiO_2 catalysts were observed and were assigned by Anpo *et al.* [12]. They were attributed to the following charge transfer processes on the Mo═O moieties of the tetrahedral molybdate ions (MoO_4^{2-}), involving an electron transfer from the O^{2-} to Mo^{6+} ions and reverse radiative decay from the charge transfer excited triplet state [13]. In the case of the bulk molybdenum oxides, the Mo═O bonds that occurred the charge transfer was present on the edges of MoO_6 octahedral units of molybdenum oxides. The dioxomolybdenum species were closely associated to photoinduced surface reactions.



UV irradiation to the spray catalysts in the presence of C_3H_6 led to the formation of C_2H_4, *trans*- and *cis*-2-C_4H_8. No products could be detected under the dark conditions. C_2H_4 was formed stoichiometrically accompanied with the same amount of 2-C_4H_8 on all the catalysts, that is, the metathesis reaction proceeded. It is reported that the charge transfer excited triplet state of isolated Mo species can be transformed to molybdenum-carbene species under C_3H_6 moieties [12]. This carbene species is an active center for C_3H_6 metathesis reaction. Thus, the photoexcitation mechanism of Mo on the bulk system would be same as on the supported Mo/SiO_2 system.

The effects of irradiation wavelength on the activity of C_3H_6 photometathesis were investigated using the UV cut off filter on spr773. The initial rates of C_2H_4 formation were listed in table 1. The reaction rate of C_2H_4 production under the UV27 filter was equal to that of without a filter. When the light of wavelength shorter than 290 nm was cut off, the amount of C_2H_4 formation decreased. With the UV35 filter, the activity fell down to the order of magnitude. These results indicate that the molybdenum oxide species, like the tetrahedral coordination, exist in the spray catalysts and

Table 1
The effect of irradiation wavelength on the activity of C_3H_6 photometathesis on the spr773

Filter[a]	$r_0^b/10^{-8}$ mol min^{-1} g_{cat}^{-1}
None	8.5
UV27	8.2
UV29	6.8
UV31	0.9
UV35	0.2

[a] UV cut off filter.
[b] Initial rate of C_2H_4 formation.

Table 2
The number of active sites and the activity of C_3H_6 photometathesis without UV cut off filter

Catalyst	$n^a/10^{-7}$ mol g_{cat}^{-1}	$r_0^b/10^{-8}$ mol min^{-1} g_{cat}^{-1}
spr673	1.7	4.7
spr773	3.0	8.5
spr873	2.2	7.9
MoO_3[c]	0.7	0.4

[a] Number of active sites determined from CO photooxidation reaction.
[b] Initial rate of C_2H_4 formation.
[c] Purchased from Junsei Chemical Co. Ltd.

they show the photocatalytic activity toward C_3H_6 metathesis reaction.

Table 2 shows the activity for photometathesis reaction of C_3H_6 without filter on the spray catalysts prepared by different T_{spr}. Although the all catalysts had almost equal BET surface area (ca. 20 m^2 g^{-1}), the number of active sites and the initial rate of C_2H_4 formation were different (spr773 > spr873 > spr673 ≫ the commercial MoO_3). Turnover number (TON) was calculated from the amount of C_2H_4 formation during 180 min divided by the amount of photoactive sites. The TONs of catalysts were over 10, which means that the photoinduced metathesis reaction proceeded not stoichiometrically but catalytically.

As shown in figure 3(A), the commercial MoO_3 had a structure based on layered octahedral units [10]. Because they were normally large crystals, they have few edges of units, which could behave as the active sites (thick line). Although the spray catalysts prepared from the commercial MoO_3, they had the more number of active sites than their starting materials did (figure 3(B)). In general, that the higher T_{spr} could produce more number of active sites. The decrease in the number of active sites for spr873 was related to the formation of β-MoO_3 phase. Since β-MoO_3 has a structure based on

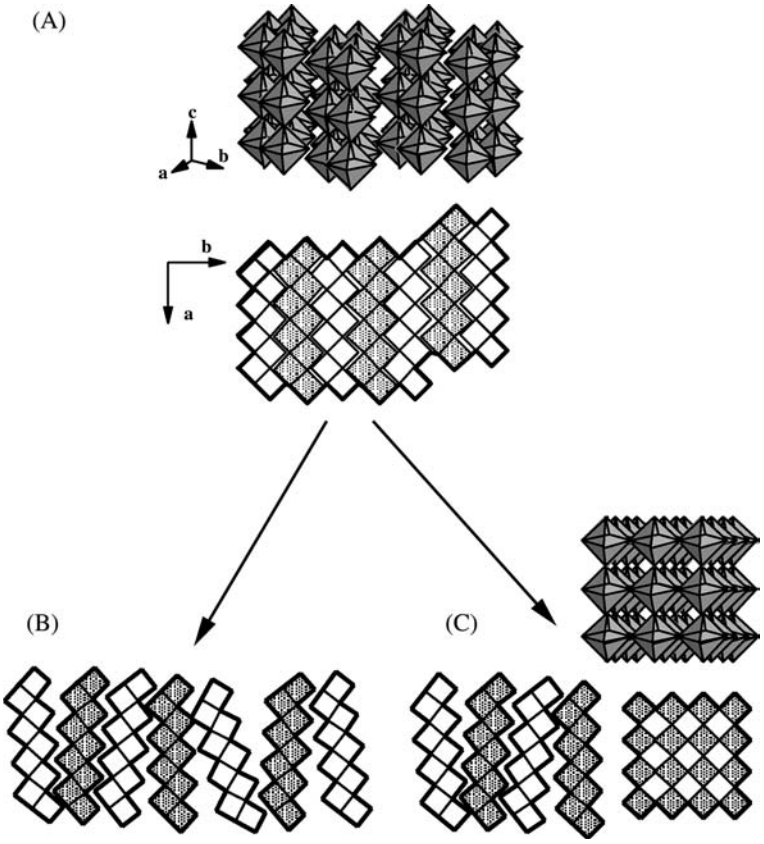


Figure 3. Structure of (A) the commercial MoO_3, (B) spr673 and spr773 having anisotropic morphology and (C) spr873 having anisotropic morphology and β-MoO_3 phases. Thick line represents the edge site of the octahedral units.

corner-shared octahedral units [10], it was difficult to have the dioxomolybdenum species on the edge of units than α-MoO_3 (figure 3(C)). The anisotropic growth of α-MoO_3 occurred in the spray catalysts, so the layer of octahedral molybdenum oxides unit perpendicular to the *b*-axis were not orderly along the *a*-axis (figure 3(B)).

Together with the XRD results, it can be concluded that the anisotropic growth of α-MoO_3 with edge-rich structure produced the molybdenyl double bonds associated with the active sites on the spray catalysts.

4. Conclusion

1. The molybdenum oxide species on spr673 and spr773 were attributed to α-MoO_3. As T_{spr} was raised to 873 K, β phase of MoO_3, which is unstable phase, appeared besides α-MoO_3.
2. Although bulk molybdenum oxide had little photocatalysis, the spray molybdenum oxide catalysts showed the higher activity for propene photometathesis reaction. Moreover, the activity increased with increasing T_{spr}.
3. Sprayed molybdenum oxide was activated by the light with wavelength of shorter than 290 nm and showed the activity for propene photometathesis reaction.

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