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Propene oxidation over MoO_3 film deposited on an Au | YSZ | Ag system

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Abstract

Propene oxidation was carried out with an electrochemical reactor, MoO_3/Au | YSZ | Ag (YSZ: 8 mol.-% yttria-doped ZrO_2), at 475°C under oxygen pumping, and the catalytic activity of the thin MoO_3 film related to its crystal morphologies was discussed. The thin MoO_3 film was deposited on an Au anode by means of vacuum deposition or sputtering method at room temperature or 300°C. Each method showed a characteristic texture as well as crystal morphology of the MoO_3 film, resulting in variations in the catalytic activity. Sputtering at 300°C gave porous films composed of leaf-like crystals with preferential orientation of (010) plane parallel to the pore channel and perpendicular to the Au surface, resulting in the highest activity for acrylaldehyde production. A relatively high step density was observed on the oriented (010) plane of the leaf-like crystal. The high activity of this MoO_3 film is probably due to the high density of active sites for the partial oxidation of propene and also to their highly porous structure, which is favorable to the surface migration of oxygen to the reduced active sites.

1. Introduction

Molybdate catalysts show a high selectivity in alkene oxidation [1]; lattice oxide ions are key reaction participants at temperatures $>350°C$, while gaseous oxygen reoxidizes the catalyst [1–4]. The oxide ions resulting from chemisorption and dissociation of the gaseous oxygen on the catalyst surface diffuse through the bulk of the catalyst to the active site at which adsorption and oxidation of the alkene occurs. Studies on MoO_3–Bi_2O_3 catalyst have revealed a multifunctional active site, wherein α-H abstraction followed by allylic intermediate formation occurs by oxide ions bridging Bi and Mo atoms, and oxygen insertion into allylic intermediate originates from the bridging centers between Mo atoms [4,5]. It has further been suggested that, for O_2 chemisorption, reduction, and dissociation, the two lone pairs of electron associated with Bi–O–Bi species are responsible [5]. Thus, Bi has an essential role as the second component in the MoO_3–Bi_2O_3 catalyst for the oxygen supply in alkene oxidation.

A cell system using YSZ as solid electrolyte, e.g., $P(O_2)$, M | YSZ | M′, $P(O_2)'$ (M and M′; electrodes) can serve as an ‘oxygen pump’ [6] in which the oxygen flux transferred across the YSZ can be controlled by the electric potential externally applied between the two electrodes. By using an Mo–Bi oxide/Au | YSZ | Ag electrochemical membrane reactor, we found that MoO_3 alone showed the highest activity among the catalysts used and its activity reached 600 times as high as that obtained with MoO_3 as the fixed bed catalyst in the mixed gas flow reaction [7]. These observations suggest that oxygen species bound to

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molybdenum metal possess a definite role for both α-H abstraction from propene and oxygen insertion to the allylic intermediate. On the other hand, oxygen can permeate through the Bi_2O_3 film, suggesting bismuth species is effective for O_2 incorporation into the catalyst and also transportation of oxide ions through the catalyst bulk. Thus, MoO_3 alone can work as the effective catalyst for alkene oxidation under the sufficient oxygen supply, but oxygen cannot permeate through the bulk of MoO_3.

In this work, we report the results of propene oxidation over the coupled system of MoO_3 on the 'oxygen pump,' e.g., MoO_3/Au | YSZ | Ag, in which MoO_3 has various morphologies depending on the preparation method, i.e., vacuum deposition or reactive sputtering. Moreover, the mechanism of propene oxidation over the highly active MoO_3 film has been discussed related to surface morphology and fine structure of the MoO_3 crystals.

2. Experimental

An electrochemical reactor was constructed from an 8 mol.-% yttria-stabilized zirconia (YSZ) disk 32 mm in diameter and 1 mm in thickness. Au film (1 μm thick) was deposited as the anode metal on a face of the YSZ disk by vacuum evaporation. The MoO_3 catalyst (4 μm thick) was then deposited on the Au anode by vacuum evaporation of MoO_3 (99.9%) powder under $1 \cdot 10^{-6}$ Torr or reactive sputtering of Mo metal target (99.9%; 102 mm in diameter) under $1.3 \cdot 10^{-2}$ Torr of O_2/Ar (1/1) atmosphere. The Au | YSZ substrate was put at room temperature or 300°C. Power for the sputtering was 300–350 W and the sputtering rate was estimated as 0.8–1 μm/h by a quartz oscillator. Finally Ag (1.5 μm thick) was deposited as the cathode metal on another face of the YSZ disk. All the samples were annealed under air atmosphere at 500°C and used in the propene oxidation. The reaction temperature was fixed at 475°C for acquiring sufficient transfer of oxide ions through the YSZ disk [6] regardless of the suitable temperature for the molybdate catalyst. Surface morphology, crystal structure and layered structure of MoO_3/Au | YSZ | Ag were studied by XRD, SEM and TEM.

The reactor configuration is shown in Fig. 1. The two electrodes were connected at the center with inert gold wire (1 mm ϕ) to an electrical circuit for controlling the oxygen transfer flux [6] from the Ag cathode through the YSZ to the Au anode, and then into the catalyst film. The disk composed of MoO_3/Au | YSZ | Ag was sandwiched in between two alumina tubes and sealed by low-melting glass. A quartz tube fitted with a flat quartz circle at the top was located closely to the catalyst in order to keep enough contact time of propene over the catalyst surface. The reactor thus obtained was placed in the electrical furnace to control the temperature of the electrochemical cell system.

A gaseous mixture of propene (5%), nitrogen (5%), and helium (90%) was passed (1.4 l/h) over the catalyst film at 475°C for testing the activity of the catalyst. Oxygen gas (0.6 l/h) was passed into the cathode room. The applied potential for pumping oxygen was fixed at 1.0 V. The products in the effluent gas were analyzed by gas chromatography using a thermal conductivity detector and nitrogen as an internal standard.

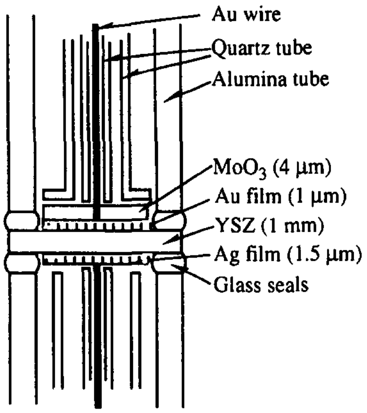


Fig. 1. Reactor configuration.

3. Results and discussion

3.1. Propene oxidation

When Mo–Bi oxide was coupled with the oxygen pump i.e, Au | YSZ | Ag, and used as an electrochemical membrane reactor [7], the coupled system showed a higher activity for propene oxidation compared to a usual fixed bed reactor in the mixed gas flow reaction. Distinct behaviors of both single metal oxides, i.e., MoO_3 and Bi_2O_3, over the oxygen pump were observed. MoO_3 alone showed the highest activity among the catalyst used and its activity was 600 times as high as that obtained with MoO_3 as the fixed bed catalyst. It is likely that molybdenum species alone are active enough for propene oxidation under oxygen pumping conditions; oxygen species bound to molybdenum metal possess a definite role for both α-H abstraction from propene to the allylic intermediate and oxygen insertion into the allylic intermediate. Oxygen can permeate through the Bi_2O_3 film when coupled with the oxygen pump, suggesting bismuth species is effective for oxygen incorporation into the catalyst and oxide ion transportation through the catalyst bulk. Thus, it was clarified that only MoO_3 is the effective catalyst for propene oxidation under sufficient oxygen supply [7].

When the propene–nitrogen–helium mixture (5:5:90) was passed at a rate of 1.4 l/h over the catalyst film at 475°C, MoO_3 gave acrylaldehyde and carbon oxides from propene when oxygen was pumped through the YSZ at 1.0 V of applied potential. The maximum value of rate of acrylaldehyde production and its selectivity over each MoO_3 film are shown in Fig. 2 together with the oxygen flux tested separately. S and V in the figure mean that the MoO_3 film was deposited by the reactive sputtering method and the vacuum deposition method, respectively, and suffixes 300 and r.t. (room temperature) correspond to the temperature of the Au | YSZ substrate during the MoO_3 deposition. The sputtering at 300°C of the substrate temperature (S_{300}) gave the highest values of both rate and selectivity of acrylaldehyde production as well as oxygen flux, followed by $V_{r.t.} > V_{300} > S_{r.t.}$. Au alone as the anode gave acrylaldehyde as previously reported by us [8], but the rate was small compared to the oxygen flux, resulting in the low selectivity. The oxygen transport and the reaction were tested for 60 min, during which the oxygen flux decreased, except in the case of S_{300}, while the reaction rate increased except for the sample $S_{r.t.}$. S_{300} showed the best results among the MoO_3 films used, i.e., a constant oxygen flux, and moreover a constant selectivity as well as an increasing rate of acrylaldehyde production.

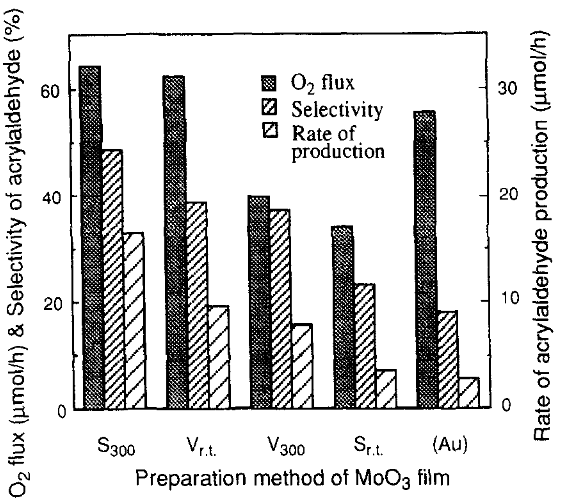


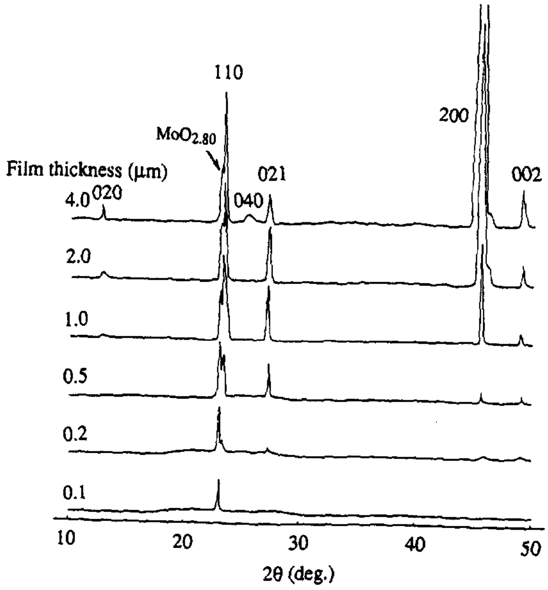
Fig. 2. Dependence of O_2 flux and acrylaldehyde production on the MoO_3 preparation method.

3.2. Crystal structure and surface morphology of the film

The crystal structure and surface morphologies of the MoO_3 films obtained by the four procedures were studied. The film prepared by the vacuum deposition at room temperature was pale yellow, transparent, amorphous by XRD, and dense in the SEM image. The film treated at 500°C for 1 h in air ($V_{r.t.}$) was well crystallized as MoO_3 by XRD and many fine cracks were formed between the MoO_3 crystals. The film obtained by vacuum deposition at 300°C was pale blue and was already crystallized as MoO_3 containing partially reduced suboxide ($MoO_{2.80}$, JCPDS 12-517). After the air-treatment (V_{300}), the MoO_3 crystals grew as symmetrical plates and showed a relatively strong 200 line in XRD. The plate-like crystals grew perpendicularly to the substrate surface, resulting in the porous coverage over the Au surface. The film deposited by the reactive sputtering at room temperature was almost similar to that prepared by vacuum deposition at room temperature: pale yellow, transparent, amorphous by XRD and dense in the SEM image. After air-treatment, the film ($S_{r.t.}$) showed the lines of powder-like MoO_3 by XRD, and its surface observation in the SEM image was still dense and flat with scarce cracks compared to $V_{r.t.}$. The deposition by reactive sputtering at 300°C gave a pale grey and well crystallized MoO_3 film containing no suboxide. After air-treatment, no substantial change in the XRD pattern and the SEM image was observed in the film (S_{300}); the line 200 was still the strongest in the XRD pattern of the film, suggesting an occurrence of highly preferentially oriented crystal growth just after the deposition. Cross section of the film revealed that leaf-like MoO_3 crystals grew perpendicularly to the substrate surface, resulting in a highly porous coverage over the Au surface. From the XRD and the SEM observations, it is likely that MoO_3 crystals grew in the (100) direction perpendicular to the substrate surface and, therefore, the (100) plane was parallel to the substrate. Thus, the reactive sputtering at 300°C gave the most stable and porous MoO_3 film (S_{300}) over the Au anode, followed by $V_{300} > V_{r.t.} > S_{r.t.}$ in the order of porosity. This order well coincided with that of the activity observed in the partial oxidation of propene to acrylaldehyde.

3.3. Surface structure of the crystal

In order to explain its high activity the detailed structure of S_{300} was studied further. Change in XRD patterns of the films during the preparation by reactive sputtering at 300°C are shown in Fig. 3. When thickness of the film was small (0.1 μm), the line of the suboxide ($MoO_{2.80}$) first appeared, suggesting the formation of partially reduced species. Increase in the thickness (0.2–0.5 μm) resulted in an appearance of the lines 110 and 021 typically observed in non-oriented powder-like MoO_3. Further increase in the thickness (1 μm) was accompanied by an appearance of the line 200, which was enormously enhanced at 2–4 μm of thickness and the suboxide peak was relatively negligible. In the SEM observation of the film of 0.2 μm in average thickness, the cross section showed a thin (0.1 μm) and dense film over the substrate and small plate-like single crystallites grew on the thin film. Surface observation of the film also showed a relatively sparse formation of small crystallites. The crystallites grew to the leaf-like crystals and their number decreased with increasing film thickness. A top view of the leaf-like crystal in the SEM at high magnification is shown in Fig. 4; the S_{300} film is composed of many leaf-like MoO_3 crystals each of which grew perpendicularly to the substrate surface and had a fine structure resulting in many small subsurfaces of (100) and (001) planes on the outer surface. These (100) and (001) planes were reported to be active for the partial oxidation of olefins by Volta et al. [9].



XRD patterns during preparation of the S_{300}

Fig. 3. XRD patterns during preparation of the S_{300}.

A further clear view of fine structure of the top of the leaf-like crystal was observed by TEM after decorating the crystal by vacuum deposition of

Fig. 4. SEM image of the S_{300} crystallites.

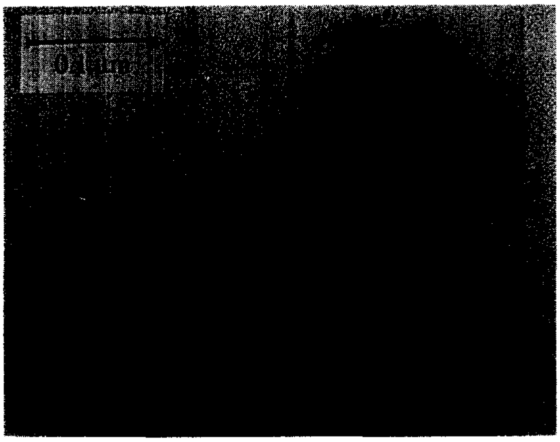


Fig. 5. TEM image of the top of the S_{300} crystallites (decorated by Au–Pd alloy particles).

the Au–Pd alloy (Fig. 5). When alloy or metal (for example, Au–Pd, Pt–Pd or Au, etc.) was deposited on the non-metallic crystal surface by vacuum deposition in the mean thickness of 0.5–1 nm, small particles were frequently formed instead of continuous film [10]. Since the particles were preferentially deposited on the corner or edge of the surface steps, the surface steps can be observed as the line of high density particle arrangement. In Fig. 5, the particle arrangement was running in the (001) direction on the (010) plane of MoO_3. This shows many atomic steps by a small (100) plane formed on the (010) plane, suggesting the formation of high concentration of the active site on the surface of the MoO_3 crystal.

It was clarified that S_{300} was the porous film composed of many leaf-like crystals standing perpendicularly on the Au anode; the crystals have many small subsurfaces with many atomic steps resulting in the high concentration of the active site over the MoO_3 crystals in the propene oxidation. We previously reported that MoO_3 alone was highly active for the propene oxidation under sufficient oxygen supply [7] and a highly oriented crystal growth along the (010) plane gave high concentration of active surface of the (100) or (001) plane [11]. The oxidation of propene to acrylaldehyde proceeds via a reduction–oxidation of surface molybdenum oxide at the active site on the MoO_3 crystal and, therefore, oxygen must be supplied to reoxidize the reduced active site by the propene oxidation. It is easily understood that the porous structure of the MoO_3 film is advantageous for easy oxygen transportation through the cell system, MoO_3/Au | YSZ | Ag.

The most highly active S_{300} was easily reduced showing a blue color and gave a negligible amount of acrylaldehyde during propene oxidation in the co-presence of oxygen gas (propene:O_2:N_2:He = 5:5:5:85) in the anode room in the absence of oxygen supply through the YSZ. These observations strongly suggest that only the oxygen species pumped through the YSZ is effective for reoxidizing the reduced active site and this reoxidation can be done by the surface migration of the oxygen species over the MoO_3 crystal from the oxygen pump. As a matter of fact, the adsorbed oxygen species from the gaseous phase cannot significantly attribute to the regeneration of the active site due to the low ability of the MoO_3 surface for dissociatively activating molecular oxygen. The effective oxygen species from the YSZ might be in atomic state and this atomic oxygen species migrates over the surface of MoO_3 crystal since oxygen cannot permeate through the bulk of MoO_3. Thus, it is likely that both the porous structure and the high density of active site endow the S_{300} with high activity.

4. Conclusion

The electrochemical reactor, MoO_3/Au | YSZ | Ag, has been tested for propene oxidation at 475°C under oxygen pumping, where the MoO_3 film was prepared by vacuum deposition or reactive sputtering method at room temperature or 300°C. Oxygen flux transported through the cell system was as follows: $S_{300} > (Au) \approx V_{r.t.} > V_{300} > S_{r.t.}$. Rate of acrylaldehyde production was put in the following order: $S_{300} > V_{r.t.} > V_{300} > S_{r.t.} \approx (Au)$. Propene oxidation proceeds via a redox process of surface molybdenum oxides, and the reduced molybdenum species must be reoxidized by oxygen species supplied through the cell system. Selectivity in acrylaldehyde was as follows: $S_{300} > V_{r.t.} > V_{300} > S_{r.t.} \approx (Au)$. S_{300} film is composed of many leaf-like MoO_3 crystals each of which grew perpendicularly to the substrate surface and had fine structure resulting in many small subsurfaces of (100) and (001) planes on the outer surface. Moreover, many atomic steps by the small (100) plane were formed on the (010) plane, suggesting the formation of high concentration of the active site on the surface of the MoO_3 crystal. It is thus most likely that the crystal morphologies control the activity and the selectivity for propene oxidation over the MoO_3/Au | YSZ | Ag system, i.e., S_{300} showing the highest activity for the partial oxidation of propene.

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