A Solid Electrolyte-aided Study of Propene Oxidation on an MoO_3–Bi_2O_3 Catalyst

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Partial oxidation of propene by oxygen species transported electrochemically on MoO_3–Bi_2O_3 *via* yttria-stabilized zirconia at 450 °C revealed that the oxygen atoms bound to molybdenum insert into an allylic intermediate of propene to form acrylaldehyde while bismuth species are responsible for oxygen incorporation into the catalyst.

Interest in MoO_3–Bi_2O_3 catalysts stems from the high selectivity which these materials display in alkene oxidation.[1] It is well established that in the selective catalytic oxidation of alkenes, lattice oxide ions are key reaction participants at temperatures >400 °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 occur. In the case of propene oxidation, investigations of MoO_3–Bi_2O_3

Table 1. Activity of the MoO_3–Bi_2O_3 catalyst for the YSZ-aided propene oxidation.

	YSZ-aided oxidation		Mixed gas flow oxidation	
Catalyst	Activity/ mmol g^{-1} h^{-1}	Relative value	Activity/ mmol g^{-1} h^{-1}	Relative value
MoO_3	0.9400	587	0.0016	1
α-$Bi_2Mo_3O_{12}$	0.4120	258	0.0039	2.4
β-$Bi_2Mo_2O_9$	0.8420	526	0.5340	334
γ-Bi_2MoO_6	0.3450	216	0.2710	169
Bi_2O_3	—	—	—	—

catalyst have revealed a multifunctional active site, wherein α-H abstraction followed by allylic intermediate formation occurs by oxide ions bridging bismuth and molybdenum atoms, and oxygen insertion into the allylic intermediate originates from the bridging centres between molybdenum atoms.[4,5] It has further been suggested that, for O_2 chemisorption, reduction, and dissociation, the two lone pairs of electrons associated with Bi–O–Bi species are responsible.[5] In these studies, the use of a gaseous mixture of oxygen and propene resulted in two processes occurring simultaneously, O_2 incorporation into the lattice and lattice oxygen insertion into the allylic intermediate, and therefore the separate observation of each phenomenon was difficult.

Yttria-stabilized zirconia (YSZ) is a well known solid electrolyte that can transport oxide ions through its lattice anion vacancies. 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 is controlled by the electrical potential externally applied between the two electrodes. We therefore expected that using a coupled system of MoO_3–Bi_2O_3 on the 'oxygen pump' would enable us to observe the insertion of lattice oxide ions into the allylic intermediate separately from the O_2 incorporation into the lattice.

An electrochemical reactor was constructed from an 8 mol% yttria-stabilized zirconia disc 32 mm in diameter and 1 mm in thickness. Thin compact films of Ag (2 μm thick) and Au (0.5 μm thick) were prepared as the cathode and the anode, respectively, on each face of the disc by vacuum evaporation.[7] Au was chosen as the anode on which a thin compact film of the catalyst (4 μm thick) was prepared without causing a solid phase reaction between the anode and the catalyst. As catalyst films, three phases of bismuth molybdate (α, $Bi_2Mo_3O_{12}$; β, $Bi_2Mo_2O_9$; γ, Bi_2MoO_6),[3] MoO_3, and Bi_2O_3 were prepared on the Au anode by vacuum evaporation of each compound, followed by reoxidation to stabilize it. Characterization by *X*-ray diffraction ensured that the catalyst was the desired pure single phase. The two electrodes were connected with gold wire to an electrical circuit for controlling the oxygen transfer flux from the Ag cathode to the Au anode across the YSZ, then finally into the catalyst film. An oxygen pressure of 101.3 kPa was maintained on the cathode of the cell. A gaseous mixture of propene, nitrogen, and helium was passed over the catalyst film for testing the activity of oxygen species generated on the catalyst surface. The products in the effluent gas were determined by gas chromatography using a thermal-conductivity detector and nitrogen as an internal standard. In separate experiments, reactions using the mixed gas flow system over a fixed catalyst bed were carried out as a control, where each compound of catalyst material was pulverized to a fine powder and diluted by quartz powder.

When the propene–nitrogen–helium mixture (5 : 5 : 90) was passed at a rate of 1.4 l h^{-1} over the catalyst film at 450 °C, the catalyst film containing molybdenum, *e.g.* MoO_3, α-, β-, and γ-bismuth molybdates, gave acrylaldehyde and carbon oxides from propene under closed-circuit conditions when oxygen was pumped through the YSZ, and an increase in the current by oxygen pumping resulted in an increase in the rate of propene oxidation. No evolution of dioxygen was observed in these cases. On the Bi_2O_3 film, in contrast, no oxidation of propene to acrylaldehyde occurred, while dioxygen was substantially evolved together with a small amount of carbon oxides. The results obtained under the oxygen flux of 0.09 mmol h^{-1} through the YSZ are shown in Table 1, together with those obtained in the mixed gas flow reaction as the control. The latter was carried out by passing the propene–nitrogen–oxygen–helium mixture (5 : 5 : 5 : 85) at a rate of 1.47 l h^{-1} over the catalyst (1 g) bed at 475 °C. The specific activity of the catalyst is shown as the rate of acrylaldehyde formation per unit weight of the catalyst, because the catalyst surface area was too small to be estimated correctly by Brunauer–Emmett–Teller (B.E.T.) measurements. The catalyst weight of each film was calculated by using the value of the specific gravity of each phase of the MoO_3–Bi_2O_3 catalyst.[8] A relative value of the activity was calculated based on the value obtained on the MoO_3 catalyst in the mixed gas flow reaction.

The results obtained above clearly indicate that the activity of each catalyst for propene oxidation is higher in the YSZ-aided reaction than in the mixed gas flow reaction. It is noteworthy that using YSZ as the 'oxygen pump' caused a great increase in the activity of molybdenum-rich catalysts, *e.g.* MoO_3 or α-bismuth molybdate, and the former showed the highest activity among the catalysts used. The high acrylaldehyde-production activity of the MoO_3 in the YSZ-aided reaction reveals that MoO_3 alone is highly active for oxygen insertion into the allylic intermediate when sufficient oxygen was supplied as lattice oxide ions to refill the anion vacancies formed. The low activity of MoO_3 in the mixed gas flow reaction suggests a low ability for O_2 chemisorption, reduction, and dissociation. In contrast, the Bi_2O_3 film showed dioxygen evolution of 0.08 mmol h^{-1} which corresponded to *ca.* 90% of oxygen pumped through the YSZ, although no acrylaldehyde was produced, as also found for the mixed gas flow reaction on the Bi_2O_3 powder catalyst. It can therefore be considered that Bi_2O_3 can incorporate and evolve dioxygen *via* its lattice oxide ions by a reversible reduction–oxidation cycle, as shown in part by the unique ability of Bi_2O_3 oxygen electrolytes to chemisorb dioxygen dissociatively.[9]

It thus seems reasonable to explain the catalytic mechanism of MoO_3–Bi_2O_3 for propene oxidation as follows: bismuth oxide is responsible for oxygen incorporation into the catalyst and the oxygen atoms bound to molybdenum insert into the allylic intermediate to form acrylaldehyde. This conclusion is in good agreement with that obtained using *in situ* Raman spectroscopy in propene oxidation on γ-Bi_2MoO_6,[5] wherein, however, α-H abstraction of propene to give the allylic intermediate occurs by oxide ions bridging bismuth and molybdenum atoms (Bi–O–Mo). The high acrylaldehyde-production activity in the MoO_3 film when sufficient oxygen was supplied is noteworthy as this suggests that molybdenum oxide alone can catalyse both the α-H abstraction of propene and oxygen insertion to form acrylaldehyde. Attempts to establish a more complete view of the function of the MoO_3–Bi_2O_3/YSZ system on propene oxidation are underway.

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