A Solid Electrolyte-aided Study of Alkene Oxidation on a Molybdate Catalyst having the Scheelite Structure

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Partial oxidation of alkenes by oxygen species transported electrochemically on a scheelite-type molybdate catalyst *via* yttria-stabilized zirconia at 450—475 °C has revealed that oxygen species transported through the bulk of the catalyst insert into an allylic intermediate to form the oxygenated product, while oxygen species chemisorbed on the catalyst surface from the gas phase accelerate deep oxidation.

It is well known that, in the selective catalytic oxidation of alkenes over MoO_3–Bi_2O_3, lattice oxide ions are key reaction participants, while gaseous oxygen reoxidizes the catalyst.[1] The oxide ions resulting from dissociative chemisorption 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.[2] Use of a scheelite-type oxide, $Pb_{1-3x}Bi_{2x}\phi_xMoO_4$ (ϕ = cation vacancy) enabled us to control the mobility of lattice oxide ions, which correlates well with the catalytic activity for alkene oxidation.[3,4]

A cell system using yttria-stabilized zirconia (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,'[5] in which the oxygen flux transferred across the YSZ is controlled by the electrical potential applied externally between the two electrodes. Here, we report the result of propene and but-1-ene oxidations on thin films of $Pb_{1-3x}Bi_{2x}\phi_xMoO_4$ (x = 0, 0.04) catalyst coupled with the 'oxygen pump.'

The cell reactor was constructed as previously reported.[6] The catalyst, a thin film (4 µm thick) of $PbMoO_4$ and $Pb_{0.88}Bi_{0.08}MoO_4$, was prepared on an Au anode by vacuum evaporation of each compound, followed by reoxidation to stabilize it. Characterization by X-ray diffraction ensured that the catalyst had the desired scheelite crystal structure. The oxygen flux was controlled by the electrical potential applied to the circuit. An oxygen pressure of 101.3 kPa was

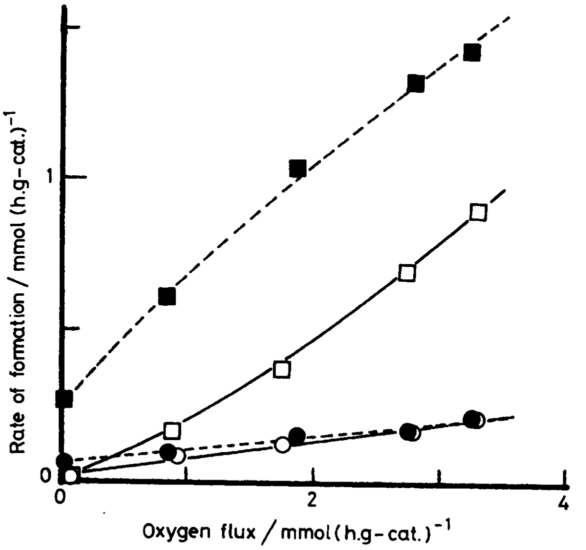

Figure 1. Oxidation of propene at 450 °C. — Propene, $PbMoO_4$, Au|YSZ|Ag,O_2; - - - -O_2, propene, $PbMoO_4$, Au|YSZ|Ag,O_2. ○ ●, Acrylaldehyde; □ ■, CO_x production.

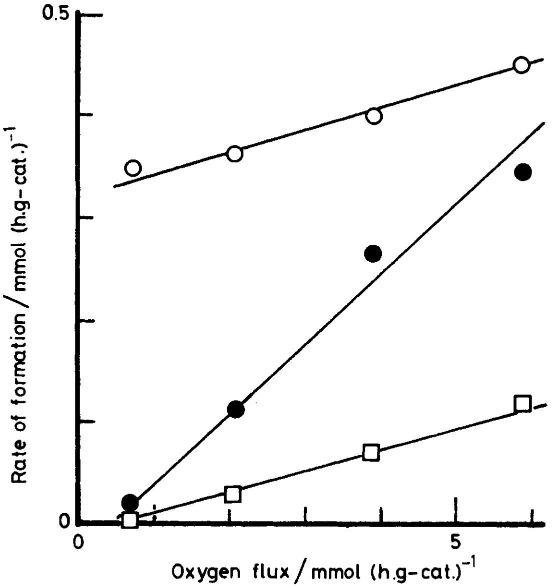

Figure 2. Oxidation of but-1-ene at 475 °C; but-1-ene, $Pb_{0.88}Bi_{0.08}MoO_4$, Au|YSZ|Ag, O_2. ○, Buta-1,3-diene; ●, methyl vinyl ketone; □, crotonaldehyde production.

maintained at the cathode. A gaseous mixture of alkene–nitrogen–helium(5 : 5 : 90) was passed at a rate of 1.4 l h^{-1} over the catalyst film to test 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. The oxygen species was entirely consumed by the oxidation; no evolution of dioxygen was observed.

The results of propene oxidation on a $PbMoO_4$ film at 450 °C are shown in Figure 1. The rate of acrylaldehyde production increased with increasing oxygen flux despite the inactivity of $PbMoO_4$ reported by Sleight *et al.*[3] This may be due to the effect of 'oxygen pumping' previously observed on MoO_3 catalyst films.[6] When oxygen (170 ml h^{-1}) was added to the mixed-gas flow at the anode, acrylaldehyde production was not affected, while deep oxidation was accelerated. The rate of acrylaldehyde production on a $Pb_{0.88}Bi_{0.08}MoO_4$ film was 5—8 times as high as that on $PbMoO_4$. The former film afforded an oxygen flux twice as high as the latter when a potential of 1.0 V was applied at 450 °C. This clearly suggests that an increase in oxygen mobility occurs on addition of Bi to $PbMoO_4$, resulting in an increase in activity. In this case, too, no substantial change in acrylaldehyde production was observed, while deep oxidation was enhanced, when oxygen was added to the mixed-gas flow. The results obtained above clearly indicate that acryaldehyde is produced mainly by oxygen species pumped through the catalyst film and the deep oxidation is accelerated by chemisorbed oxygen species on the catalyst surface from the gas phase.

But-1-ene oxidation on $Pb_{0.88}Bi_{0.08}MoO_4$ film at 475 °C afforded oxygenated products, *e.g.*, acetaldehyde, furan, methyl vinyl ketone, or crotonaldehyde, together with buta-1,3-diene. As a control, but-1-ene oxidation was carried out over the fixed catalyst bed of pulverised $Pb_{0.88}Bi_{0.08}MoO_4$ using a mixed-gas flow system, resulting in the production of buta-1,3-diene and no oxygenated product. Thus, the formation of oxygenated products seems to be a characteristic feature of the present system. When oxygen flux was increased, production of both methyl vinyl ketone and crotonaldehyde were accelerated, while that of buta-1,3-diene was not substantilly affected (Figure 2); the rate of methyl vinyl ketone production finally reached a value as high as that for buta-1,3-diene. A similar result was obtained when β-$Bi_2Mo_2O_9$ catalyst was coupled with the 'oxygen pump.' This is the first example of a substantial production of methyl vinyl ketone from but-1-ene over the MoO_3–Bi_2O_3 system.

Both methyl vinyl ketone and crotonaldehyde can form *via* insertion of an oxygen species into the allylic intermediate which is produced by α-H abstraction of but-1-ene on the catalyst surface. These results suggest that this oxygen species should be generated by 'oxygen pumping' through the catalyst film. The addition of oxygen(70 ml h^{-1}) to the mixed-gas flow at the anode side caused an increase in the rates of both buta-1,3-diene and crotonaldehyde production. It is therefore considered that crotonaldehyde can also be produced *via* a non-allylic intermediate.

It thus seems reasonable to explain the catalytic mechanism of $Pb_{1-3x}Bi_{2x}\Phi_xMoO_4$ for propene or but-1-ene oxidation as follows. Gaseous oxygen chemisorbed on the catalyst surface dissociates to form oxide ions which diffuse through the bulk of the catalyst to the active site, where the oxygen atom inserts into the allylic intermediate to form the oxygenated product, *e.g.*, acrylaldehyde and methyl vinyl ketone, while the oxygen species chemisorbed on the surface accelerates dehydrogenation of the allylic intermediate of but-1-ene to buta-1,3-diene or deep oxidation of alkenes to carbon oxides.

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