Selective Oxidation of Propane to Acrolein over Ag-doped Bismuth Vanadomolybdate Catalysts

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Acrolein was formed as a major product in the partial oxidation of propane using molecular oxygen over Ag-doped bismuth vanadomolybdate catalysts having a scheelite structure.

Selective partial oxidations of alkanes are accompanied by many difficulties due to their low reactivities compared to alkenes and dienes, although the selective oxidation of n-butane to maleic anhydride has been achieved successfully using V–P–O catalysts.[1,2] Recently, catalytic oxidative dimerization of methane has attracted much attention.[3,4] Moreover, it may be possible and more attractive to oxidise propane to acrolein in the gas phase.[5,6] Here we report the discovery that Ag-doped bismuth vanadomolybdates are promising catalysts for the conversion of propane to acrolein.

The catalyst was prepared from a mixed solution of ammonium metavanadate, ammonium heptamolybdate, bismuth nitrate, and silver nitrate. The powder of ammonium metavanadate was dispersed in a basic solution (pH 10) of ammonium heptamolybdate, followed by addition of a mixed nitrate solution of bismuth nitrate and silver nitrate and subsequent evaporation of water. The paste obtained was dried at 110 °C and calcined for 6 h at 520 °C in a stream of air. Catalytic activity and selectivity for the oxidation of propane to acrolein were determined by using a conventional flow system under the following reaction conditions; reaction temperature 380—500 °C; pressure 1 atm; space velocity, 3000 $cm^3 g^{-1} h^{-1}$; feed concentration propane 32%, oxygen 59%, nitrogen balance. The reactor used in this study was made of a quartz tube (diameter 18 mm, length 35 cm). The catalyst was diluted with silica sand and a 6 mm diameter axial quartz rod was necessary to keep the axial temperature at the centre of the catalyst bed constant. A mixture of propane, oxygen, and nitrogen was fed in from the top of the reactor. The feed and product streams were analysed by a gas chromatograph using

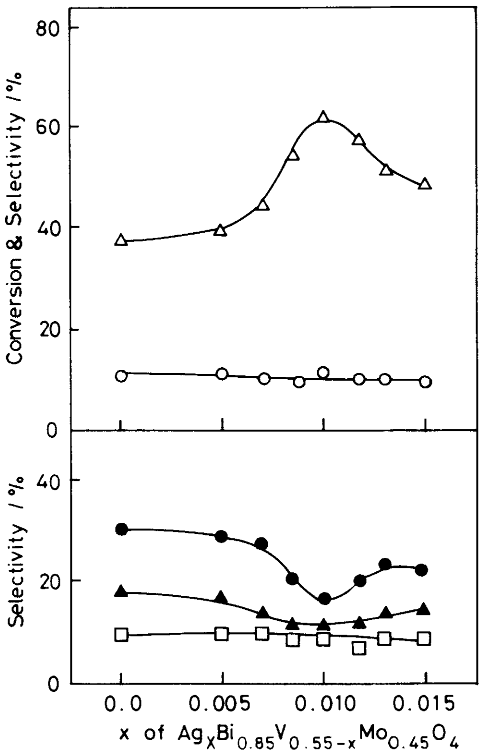

Figure 1. The conversion of propane (○) and the selectivity of products on $Ag_xBi_{0.85}V_{0.55-x}Mo_{0.45}O_4$ with variation of Ag amounts. (△) Acrolein, (▲) CO_2, (□) C_2, (●) CO, S.V. = 3000 cm^3/g^{-1} h^{-1}, C_3H_8/O_2 molar ratio = 0.55.

Gaskuropak 53 (3 m) and Molecular sieve 5A (2 m) as packing materials.

The scheelite-type metal oxide catalysts doped with the silver cation, $Ag_xBi_{1-y/3}V_{1-y}Mo_yO_4$, were found to be particularly active for the selective production of acrolein in the oxidation of propane with molecular oxygen. Ag was a uniquely effective dopant for the selectivity to acrolein. Addition of other mono-valent metal cations was ineffective for acrolein formation, mainly promoting the combustion or propene formation.

Figure 1 shows the conversion of propane and the selectivity to acrolein on the Ag-doped bismuth vanadomolybdate catalysts having different Ag contents. The selectivity to acrolein was strongly affected by the addition of small amounts of silver. The selectivity was increased gradually by the silver addition at first, then decreased by the further addition, showing a maximum at x = 0.01. After the optimisation of catalyst composition of each component, the following composite metal oxide, $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$, was obtained as the most effective catalyst. Under an integral flow condition (reaction temperature; 500 °C, C_3H_8; 32 mole% in feed, C_3H_8/O_2 molar ratio; 0.55, and space velocity, 3000 cm^3 g^{-1} h^{-1}), 64% selectivity to acrolein at 13% conversion of propane was attained.

Tricomponent metal oxides having the scheelite structure, $Bi_{1-y/3}V_{1-y}Mo_yO_4$ which are the basic compounds of the catalyst tested here, are reported by Sleight *et al.*[7] as effective catalysts for the selective partial oxidation of propene to acrolein and their catalytic behaviour under the reaction conditions was extensively investigated by Moro-oka *et al.* using an $^{18}O_2$ tracer.[8,9] This structural material, however, showed poor selectivity to acrolein (less than 40%) in the propane oxidation. Our results strongly suggest that Ag is a key active element for this reaction although as yet its precise function in this catalyst is not clear.

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