

Catalytic Activity of Mixed Metal Oxides
for Selective Oxidation of Propane to Acrolein

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Various mixed metal oxide catalysts were tested for the oxidation of propane to acrolein. An Ag-doped bismuth vanadomolybdate catalyst was found to be most effective among the catalysts tested; the selectivity to acrolein reached to more than 60% at 13% conversion of propane.

The selective oxidation of alkanes to other chemicals is becoming increasingly important both in fundamental and in industrial chemistry. However, partial oxidation of alkanes is generally very difficult compared with the unsaturated reactants such as alkenes and dienes. Nevertheless, the selective n-butane oxidation to maleic anhydride has been successfully established using V-P-O catalysts^{1,2)} and the catalytic oxidative dimerization of methane has attracted much attention of researchers.^{3,4)} On the other hand, little has been reported for the partial oxidation of propane. Some patents have insisted that the catalysts such as $Ba_{5.55}Bi_{2.3}Te_3O_{18}$ ⁵⁾ and SbO_x ⁶⁾ were effective for the oxidation of propane to acrolein. However, their catalytic performances are not yet sufficient for practical applications. We wish to report here our findings concerning the catalytic partial oxidation of propane using a molecular oxygen on the mixed metal oxides.

The mixed metal oxides were prepared according to the literatures. Ag-doped bismuth vanadomolybdate catalyst was prepared by an aqueous slurry reaction of ammonium metavanadate, ammonium heptamolybdate, bismuth nitrate and silver nitrate at pH = 10. After the evaporation of water, the obtained precursor was

Table 1. Conversion and selectivity for propane partial oxidation^{a)}

Catalyst	C_3H_8/O_2 ratio	Reaction temperature °C	Propane conversion %	Acrolein selectivity %
$V_2O_5-P_2O_5$ (P/V=1/1)	0.8	469	30	tr
" (P/V=1.5)	"	450	43	0
V-P-Mg(V/P/Mg=1/1/0.1)-O	0.7	420	60	tr
V-Mg(V/Mg=1/1)-O	"	425	70	tr
$V_2O_5-MoO_3$ (V/Mo=1/1)	0.6	440	55	10
" (V/Mo=1/2)	"	439	56	15
$Bi_2O_3MoO_3$ (γ -type)	1.0	475	36	18
$Bi_2Mo_3O_{12}$ (α -type)	0.9	484	37	24
$Bi_2O_3 \cdot 2MoO_3$ (β -type)	0.6	500	20	34
$Co_8Fe_3Bi_1Mo_{12}O_y$	"	500	10	8
$Bi_{0.77}V_{0.30}Mo_{0.7}O_4$	0.7	478	16	34
$Bi_{0.85}V_{0.55}Mo_{0.45}O_4$	0.8	488	35	31
$Bi_{0.97}V_{0.91}Mo_{0.09}O_4$	"	476	13	31
$Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$	0.8	485	28	44
$Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ /pumice	0.7	473	19	34
$Bi_{0.85}V_{0.35}P_{0.2}Mo_{0.45}O_4$	0.9	486	40	18

a) Space velocity = $1800 \text{ cm}^3/\text{g-h}$, Feed gas ; $C_3H_8+O_2 = 91\%$, $N_2 = 9\%$

dried at $110 \text{ }^\circ\text{C}$ and activated at $520 \text{ }^\circ\text{C}$ for 6 h in an air stream. Catalytic partial oxidation of propane was carried out using a conventional flow system at an atmospheric pressure. A mixture of propane, oxygen and nitrogen was fed in from the top of the reactor. The feed and products were analyzed by an on-line gas chromatograph operating with two sequential columns (Gaskuropack 54, 3 m and Molecular sieve 5A, 2 m).

Table 1 shows some typical results obtained in the partial oxidation of propane on the various mixed oxide catalysts. The number in a parenthesized passage denotes the approximate atomic ratio of catalyst. The carbon balance in every reaction run was within $100 \pm 5\%$. It is well-known that $V_2O_5-P_2O_5$ catalysts give the best results for the selective formation of maleic anhydride in the oxidation of C_4 -alkane, n-butane.⁷⁾ However, the catalysts were extremely inactive for the formation of acrolein in the oxidation of propane. The major products were carbon oxides. V-P-Mg-O and V-Mg-O catalysts were reported active for the oxidative dehydrogenation of propane.⁸⁾ Certainly, small amounts of propene were

Table 2. Conversion and selectivity for propane partial oxidation over monovalent metal ion-doped bismuth vanadomolybdates^{a)}

Monovalent metal(M ^I) ^{b)}	Conversion %	Product distribution (mol%)				
		CH ₂ CHCHO	CO	CO ₂	C ₂	C ₃ H ₆
Li	7.8	41.5	28.0	21.6	8.8	0
Na	6.8	38.3	29.7	23.5	8.5	0
K	7.6	16.2	18.2	11.4	10.0	44.2
Rb	9.6	4.7	11.1	9.5	8.2	66.5
Ag	13.1	63.5	15.6	11.8	9.1	0
Tl	5.1	10.7	17.9	12.9	14.2	44.2

a) Reaction temperature; 500 °C, Space velocity; 3000 cm³/g-h, C₃H₈/O₂;0.55

b) M_{0.01}^IBi_{0.85}V_{0.54}Mo_{0.45}O₄

produced under the present reaction conditions but acrolein was not yielded at all. The vanadium oxide containing molybdenum oxide, on the other hand, clearly showed an activity to form acrolein. Catalysts containing molybdenum seem to have an ability for the formation of acrolein. Hence, the various molybdate-based catalysts which are widely used for the selective oxidations of propene and iso-butene were tested. All these catalysts showed better results for the propane oxidation. Among them, the scheelite type catalysts were found to show higher catalytic activity and selectivity to acrolein. Furthermore, a catalyst having the following composition, Bi_{0.85}V_{0.55}Mo_{0.45}O₄⁹⁾ was found to show the highest catalytic activity and selectivity to acrolein among the scheelite type catalysts tested (Table 1).

In order to improve its catalytic performance, we prepared various kinds of monovalent metal ion-doped bismuth vanadomolybdates and employed them for the propane oxidation. Results are shown in Table 2. The Li, Na, and Ag-doped catalysts exhibited the high selectivity for the production of acrolein. Ag-doped catalyst, especially, showed the highest selectivity to acrolein among the doped catalysts. This value is higher than that obtained on any other mixed oxide catalysts ever reported.¹⁰⁾ The K, Rb, and Tl-doped catalysts, however, showed low acrolein selectivity. These catalysts showed higher selectivities to propene which may be an intermediate in the partial oxidation of propane.

Figure 1 shows the changes in the conversion of propane and the selectivity to acrolein over the Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O₄ as a function of reaction temperature

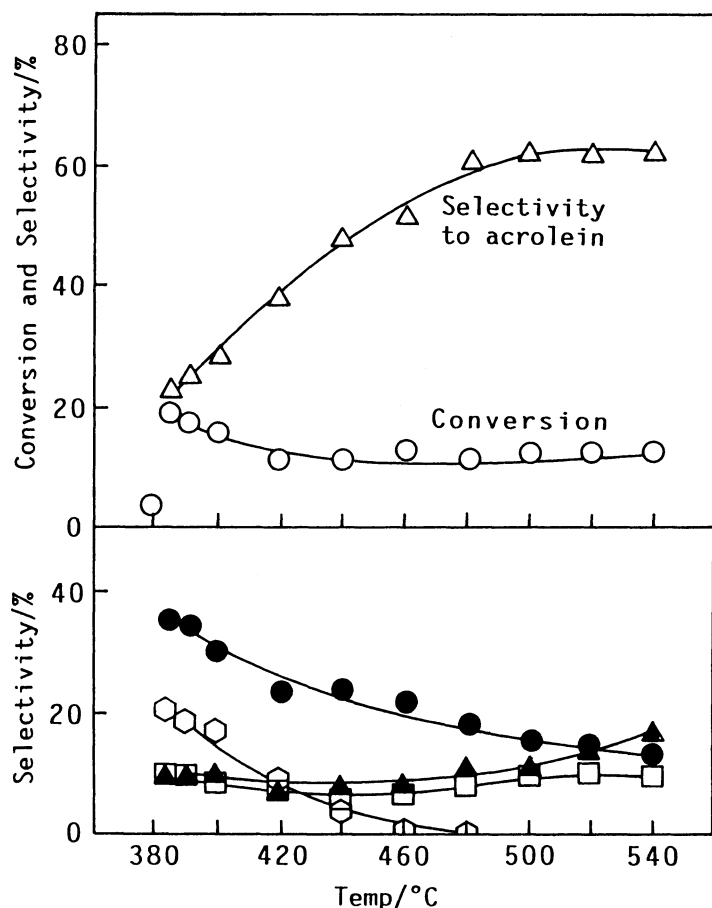


Fig. 1. The conversion of propane and the selectivity of products on $\text{Ag}_{0.01}\text{Bi}_{0.85}\text{V}_{0.54}\text{Mo}_{0.45}\text{O}_4$ catalyst with the variation of reaction temperature.

(Δ) CH_2CHCHO , (\blacktriangle) CO_2 , (\square) C_2 , (\hexagon) C_3H_6 , (\bullet) CO ,
 S.V.=3000 $\text{cm}^3/\text{g-h}$, Feed gas; C_3H_8 32%, O_2 59%, N_2 9%

from 380 to 500 °C. The changes in the conversion of propane and selectivity to acrolein with the reaction temperature were quite unusual. Oxidation of propane started suddenly at about 400 °C and showed the highest conversion at this temperature. Conversion then decreased slightly with increasing the reaction temperature. On the other hand, the selectivity to acrolein increased markedly with increasing the reaction temperature. The products besides acrolein were propene (at lower temperatures), CO , CO_2 , and C_2 -hydrocarbons. The selectivity of propene and CO decreased with increasing the reaction temperature. Under the optimum condition, 64% selectivity to acrolein at 13% conversion was obtained.

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