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Selective Ammoxidation of Propane to Acrylonitrile over Multicomponent Metal Oxide Catalysts with Scheelite Related Structures

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Catalytic ammoxidation of propane to acrylonitrile proceeds selectively over multicomponent metal oxides containing both bismuth and molybdenum with scheelite related structures. Higher selectivity to acrylonitrile and higher space time yield are obtained at reaction temperatures higher than 500 °C and higher concentration of propane (>40%) in the feed gas.

The activation of paraffinic hydrocarbons is a new promising research area in the field of vapor phase heterogeneous catalytic reactions. Recently we have demonstrated the first successful partial oxidation of propane to acrolein with molecular oxygen using silver doped bismuth vanadomolybdate catalysts having scheelite structure.[1,2] Under the optimum conditions, 64% selectivity to acrolein at 13% conversion of propane was attained. Although the conversion of propane is not so satisfactory compared to the conventional industrial oxidation of propylene to produce acrolein, the concentration of propane in the feed gas in our reaction is 5 to 10 times higher than that of propylene. Therefore, the concentration of acrolein in the effluent gas and the space time yield reach to the almost same values with those of the industrial oxidation of propylene. It has been well known that selective catalysts to form acrolein from propylene are also effective for the ammoxidation of propylene to form acrylonitrile. The silver doped bismuth vanadomolybdate catalyst was tested for the ammoxidation of propane and it was found that the catalyst gave acrylonitrile in a good yield as was expected.[3] We wish to report here our further findings that not only the silver doped bismuth vanadomolybdate but also several kinds of multicomponent metal oxide catalysts containing both bismuth and molybdenum with scheelite related structures show excellent catalytic activity for the ammoxidation of propane to acrylonitrile.

All multicomponent metal oxide catalysts were prepared according to the literatures and used in the form of powder with 100-200 mesh after diluted 5 times by silica sand. The catalytic reaction was carried out using a conventional flow reactor equipped with a quartz tube of 18 mm inner diameter and a tubular furnace. Mixture of propane, oxygen and ammonia gas were fed in from the top of the reactor at atmospheric pressure. The reaction products were acrylonitrile, acetonitrile, C_2-hydrocarbons, propylene and carbon oxides. They were sampled after continuous run for 1 h under the reaction conditions and analyzed by gas chromatography. Results are reported on the basis of carbon balance.

Table 1 shows some typical results obtained in the ammoxidation of propane over various multicomponent metal oxide catalysts. $Bi_2Mo_3O_{12}$ is a well-known active component of the industrial catalysts for the ammoxidation of propylene. α-Phase bismuth molybdate having scheelite structure showed considerable activity to form acrylonitrile. Improved results were obtained on $Bi_3Fe_1Mo_2O_{12}$ and $Bi_3Ga_1Mo_2O_{12}$ which were first prepared by Sleight et al.[4] A series of scheelite type oxides, $Bi_{1-x/3}V_{1-x}Mo_xO_4$ were also reported by Sleight et al as the effective catalysts for the partial oxidation of propylene.[5] These oxides have cation vacancies prepared

Table 1. Conversion and product distribution for the ammoxidation of propane over various multicomponent metal oxide catalysts[a)]

Catalyst	Temp	Conversion/%		Product distribution/%					
	°C	C_3H_8	O_2	CH_2CHCN	CH_3CN	C_2-HC	C_3H_6	CO	CO_2
$Bi_2Mo_3O_{12}$	500	9.7	45.0	50.8	11.3	14.9	3.5	11.4	8.1
$Bi_3Fe_1Mo_2O_{12}$	475	6.0	28.4	56.2	2.0	6.3	0.0	12.2	23.3
	515	13.2	47.0	50.7	0.6	9.2	0.0	12.4	27.1
$Bi_3Ga_1Mo_2O_{12}$	475	6.2	21.5	61.0	9.1	3.5	0.0	11.3	15.1
	515	12.0	33.0	65.1	3.9	11.0	0.0	6.9	12.7
$Bi_3Fe_{0.5}Ga_{0.5}Mo_2O_{12}$	475	6.3	26.0	54.1	3.8	7.6	0.0	10.1	24.4
	515	12.6	43.4	51.9	1.4	10.2	0.0	9.2	27.2
$Bi_{0.85}Nb_{0.55}Mo_{0.45}O_4$	475	7.1	24.8	59.7	7.2	10.2	0.0	11.4	11.5
	515	17.0	40.5	63.0	3.9	11.9	0.0	10.7	10.2
$Bi_{0.85}Ta_{0.55}Mo_{0.45}O_4$	475	8.0	27.2	59.7	9.7	6.9	0.0	11.0	12.7
	515	15.1	43.6	65.9	4.8	12.1	0.0	9.0	8.8
$Bi_{0.85}V_{0.55}Mo_{0.45}O_4$	475	7.6	26.4	59.3	4.6	9.0	8.0	10.7	8.4
	500	12.0	43.5	60.8	2.8	10.1	7.1	10.7	8.6
$Ag_{0.01}Bi_{0.85}V_{0.54}$-$Mo_{0.45}O_4$[b)]	475	8.0	29.5	63.2	6.2	3.0	9.6	8.0	10.0
	515	15.8	50.2	64.9	3.0	9.0	7.8	8.2	7.1
$Pb_{0.88}Bi_{0.08}MoO_4$	500	8.4	40.8	35.8	14.7	6.2	12.5	20.3	10.5
V-P-O/TiO_2(P/V=1.1)	475	11.3	40.8	11.8	11.9	5.4	3.2	51.3	16.4
$Bi_1Co_8Fe_3Mo_{12}O_y$	475	18.1	45.9	22.7	0.4	7.1	37.3	16.9	15.7
$Bi_1Mg_8Fe_3Mo_{12}O_y$	425	14.2	39.2	13.3	0.4	6.2	44.9	18.5	16.6

a) Feed composition ; C_3H_8 44, NH_3 15, O_2 41 mol%. S.V. ; 3000 cm^3/g-cat.h.

b) Ref. 3.

by the substitution of V^{5+} by Mo^{6+} and their catalytic activities are enhanced remarkably with increasing concentration of the vacancy[6] owing to the acceleration of bulk migration of oxide ion.[7,8] $Bi_{0.85}V_{0.55}Mo_{0.45}O_4$ and the related compounds, $Bi_{0.85}Nb_{0.55}Mo_{0.45}O_4$ and $Bi_{0.85}Ta_{0.55}Mo_{0.45}O_4$ were also examined for this reaction and it was found that all three oxides were quite effective for the acrylonitrile formation. Best results were obtained on the Ag-doped bismuth vanadomolybdate, $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$, as reported in the preceding communication[3] but it is clear that not only the special catalyst as $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_4$ but also a number of multicomponent metal oxide catalysts containing bismuth and molybdenum have substantial catalytic activities to form acrylonitrile in the ammoxidation of propane. Actually, a considerable number of mixed oxide catalysts have been insisted as the effective catalysts for this reaction in patents.[9] Since the reaction conditions adopted in this work and those described in the patents differ in each other, accurate comparison of the results seems to be difficult. However, the selectivity to acrylonitrile obtained in this work is rather high compared to the results insisted in the patents. On the contrary, V_2O_5-P_2O_5(P/V=1.1) supported on TiO_2 gave very poor yields of acrylonitrile. Multicomponent bismuth molybdate catalysts such as $Bi_1Co_8Fe_3Mo_{12}O_x$ and $Bi_1Mg_8Fe_3Mo_{12}O_x$ are not so effective for the reaction. At this stage, all effective catalysts tested in this investigation have structures related to the scheelite but it is not decided that the scheelite structure is essential for the selective conversion of propane to acrylonitrile.

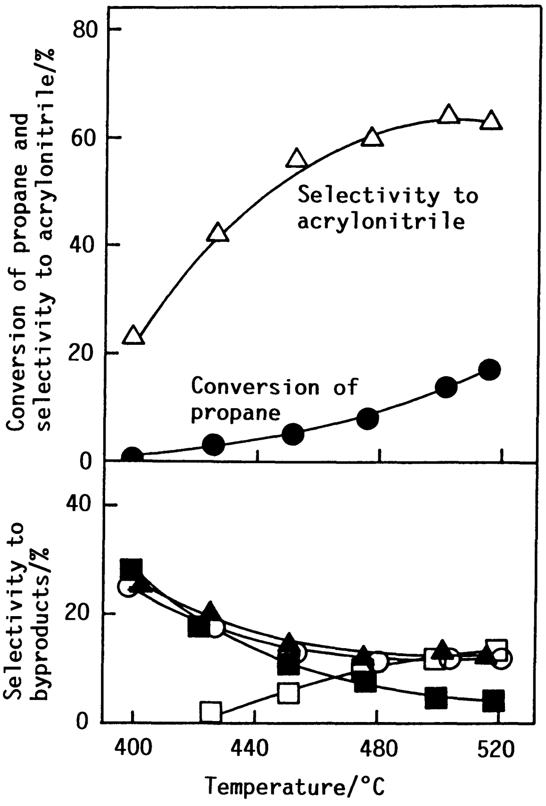

Fig. 1. Conversion of propane and selectivity to each product in the ammoxidation of propane on the $Bi_{0.85}Nb_{0.55}Mo_{0.45}O_4$ catalyst with variation of the reaction temperature. (△) CH_2CHCN, (■) CH_3CN, (□) C_2-HC, (○) CO, (▲) CO_2. S.V.; 3000 cm^3/g-h, Feed gas; C_3H_8 44%, O_2 41%, NH_3 15%.

The ammoxidation of propane was examined on the $Bi_{0.85}Nb_{0.55}Mo_{0.45}O_4$ varying the reaction temperature from 380 to 520 °C. As shown in Fig. 1, the conversion of propane increases with increasing the reaction temperature. On the other hand, observed change in the selectivity is quite different from usual catalytic oxidations. The selectivity to acrylonitrile increases markedly with increasing the reaction temperature. This phenomenon was also observed in the oxidation of propane to acrolein as reported previously.[2)] Stable selectivity higher than 60% to the main product was obtained only at higher reaction temperatures than 480 °C.

The effect of the feed gas composition on the reaction is shown in Fig. 2. The conversion of propane is little affected by C_3H_8/O_2 ratio and the selectivity to acrylonitrile rather increases with increasing C_3H_8/O_2 ratio in the feed gas. General tendencies shown in Figs. 1 and 2 were also observed in every ammoxidation over the multicomponent metal oxide catalyst tested. Thus, the highest space time yield of acrylonitrile is obtained at reaction temperatures higher than 500 °C and higher concentration of propane (>40%) in the feed gas.

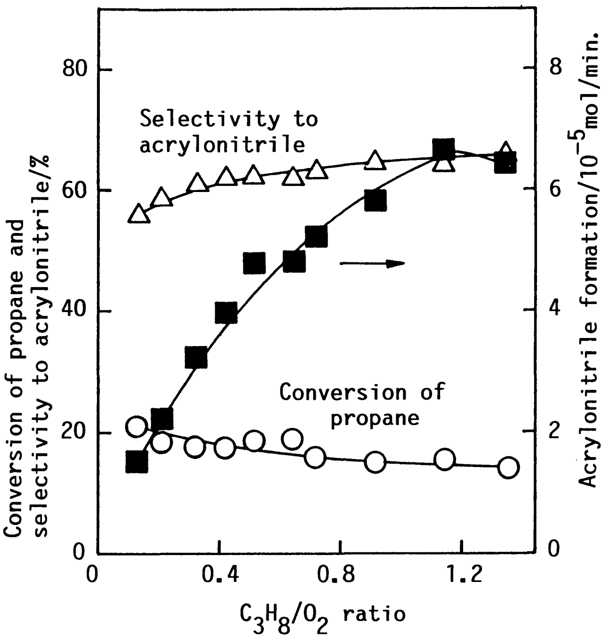

Fig. 2. Dependency of the reaction on the C_3H_8/O_2 molar ratio in the feed gas. Feed gas; (C_3H_8 + O_2) 85%, NH_3 15%. Catalyst; $Bi_{0.85}Nb_{0.55}Mo_{0.45}O_4$. Temp 515 °C, S.V.; 3000 cm^3/g-cat.h.

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