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NOTE

Ammoxidation of Propane over Catalysts Comprising Mixed Oxides of Mo and V

Acrylonitrile (ACN) is an important intermediate for the preparation of fibers, synthetic resins, synthetic rubbers, etc. Presently, ACN is produced by ammoxidation of propene in fluidized-bed reactors using mixed metal oxide catalysts. The lower price of propane relative to propene has since long provided an incentive for the development of a process for the direct conversion of propane to ACN.

Several catalysts for the production of ACN from propane have been proposed. For instance, V–Sb mixed oxides, prepared by reaction between ammonium vanadate and antimony trioxide in an aqueous slurry or by a solid-state reaction between vanadium pentoxide and antimony trioxide and usually supported on alumina, have been reported to yield 35–40% ACN (1–3). Bi–Mo (4–7), P–V (8), and Fe–Sb (9) mixed oxides also have been reported for the ammoxidation of propane. However, the yield of ACN does not exceed 20%. The ammoxidation of propane by V–Sb, Bi–Mo, P–V, or Fe–Sb mixed oxide catalysts requires temperatures of 773 K or higher. At these temperatures combustion of propane is an energetically favourable process, thereby decreasing the selectivity to ACN.

In this paper, we wish to report that Mo–V mixed metal oxides modified by the addition of Nb and Te are highly active and selective for the ammoxidation of propane at the moderate temperature. ACN yields reach more than 50% by the optimizing the reactor temperature and feed composition. The activity and selectivity for the ammoxidation of propane of this new class of catalysts are compared with those of V–Sb and Bi–Mo mixed oxides described above.

Mo–V–X–Y mixed metal oxide catalysts (X, Y = modified elements) were prepared from an aqueous slurry comprising molybdenum, vanadium, X and Y in the appropriate atomic ratios. For example, in the case of Mo–V–Nb–Te oxide catalysts (X = Nb and Y = Te), the slurry was obtained by mixing aqueous solutions of ammonium paramolybdate, ammonium metavanadate, ammonium niobium oxalate and telluric acid. The slurry was evaporated to dryness at 423 K. The dried product was calcined at 773 to 923 K in a stream of nitrogen for 2 h. Details can be found elsewhere (10, 11). The $Bi_{12}Mo_{10}O_x$ catalyst (BiMo) was prepared by mixing an aqueous solution of ammonium heptamolybdate and a solution of bismuth nitrate at room temperature. Water was evaporated, and yellow powder was calcined in a stream of air at 823 K. The $VSb_5WO_x/Al_2O_3/SiO_2$ catalyst (VSbW) was prepared by refluxing aqueous solution of ammonium metavanadate and antimony(III)oxide, tungsten metavanadate was added. After dissolving the tungsten, sols of AlO(OH) and acetic acid and SiO_2 were added. The mixture was dried and calcined in air at 923 K. Specific surface area of MoVNbTe, BiMo, and VSbW is 8, 7, and 90 m^2/g, respectively.

Ammoxidation of propane was carried out under atmospheric pressure in an ordinary flow-type fixed-bed microreactor. Typical reaction conditions were: GHSV = 500–1000 h^{-1}; catalyst amount = 0.5 cm^3; temperature = 673–693 K; feed gas molar ratio, propane/NH_3/Air = 1/1.2/10–15. The reaction effluent was introduced directly to a gas chromatography system and analyzed. Reported conversions and selectivities are based on propane.

Table 1 shows the catalytic activities of Mo–V–X–Y oxides for the ammoxidation of propane to ACN. Among the catalysts examined, $Mo_1V_{0.4}Nb_{0.1}Te_{0.2}O_x$ (MoVNbTe) is most active and selective for the reaction. $Mo_1V_{0.4}Nb_{0.1}O_x$ and $Mo_1V_{0.4}Te_{0.2}O_x$ are less active and less selective. The combination of Nb and Te seems to be necessary for high efficiency of ACN synthesis, as shown in Table 1. The X-ray diffraction pattern of MoVNbTe is unique. The effect of the catalyst composition, characterizing the physicochemical properties and crystal structure of MoVNbTe are under investigation and will be discussed elsewhere.

The temperature at which maximum propane conversion is reached by MoVNbTe, VSbW, and BiMo varies from 703 K for MoVNbTe, via 773 K for VSbW to 863 K for BiMo (Fig. 1a). For all catalysts maximum propane conversion is higher than 90%. While MoVNbTe, VSbW, and BiMo are able to convert propane when the temperature is raised high enough, the selectivity to ACN is intrinsically higher for MoVNbTe than for VSbW and BiMo (Fig. 1b). Since the specific surface area of MoVNbTe is much more smaller than that of VSbW, the surface-normalized rates of reaction of MoVNbTe is greater than that of VSbW (Figs. 1c, d). The ACN selectivity of MoVNbTe goes through a maximum of 61% at 693 K, while it increases with temperature for VSbW to 32% at 803 K. ACN selectivity of BiMo shows a complicated dependence on the reaction temperature. Combination of the activity and selectivity data reveals that the

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TABLE 1

Catalytic Activities of Mo–V–*X*–*Y* Oxides for the Ammoxidation of Propane[a]

Catalyst	Reaction temperature/K	Conversion of propane/%	Selectivity for acrylonitrile/%
$Mo_1V_{0.4}Nb_{0.1}Te_{0.2}O_x$	693	62.0	63.0
$Mo_1V_{0.4}Te_{0.2}O_x$	693	14.5	24.1
$Mo_1V_{0.4}Nb_{0.1}O_x$	693	34.2	10.5
$Mo_1V_{0.4}Nb_{0.1}Sb_{0.2}O_x$	693	12.3	18.5
$Mo_1V_{0.4}Nb_{0.1}Bi_{0.2}O_x$	693	10.6	16.5
$Mo_1V_{0.4}Mg_{0.1}Te_{0.2}O_x$	693	53.5	33.8
$Mo_1V_{0.4}Al_{0.1}Te_{0.2}O_x$	693	52.7	33.4
$Mo_1V_{0.4}Ca_{0.1}Te_{0.2}O_x$	673	47.2	29.7
$Mo_1V_{0.4}Cr_{0.1}Te_{0.2}O_x$	693	50.6	32.4
$Mo_1V_{0.4}Mn_{0.1}Te_{0.2}O_x$	673	50.2	31.7
$Mo_1V_{0.4}Fe_{0.1}Te_{0.2}O_x$	693	52.2	30.7
$Mo_1V_{0.4}Co_{0.1}Te_{0.2}O_x$	693	51.4	33.1
$Mo_1V_{0.4}Ni_{0.1}Te_{0.2}O_x$	693	51.6	30.6
$Mo_1V_{0.4}Zn_{0.1}Te_{0.2}O_x$	693	52.7	31.5
$Mo_1V_{0.4}Ba_{0.1}Te_{0.2}O_x$	673	46.3	30.2
$Mo_1V_{0.4}Ta_{0.1}Te_{0.2}O_x$	693	46.8	37.4
$Mo_1V_{0.4}W_{0.1}Te_{0.2}O_x$	673	40.8	37.7

[a] Catalyst amount: 0.5 cm^3; GHSV: 500 h^{-1}; $C_3H_8/NH_3/Air = 1/1.2/10$ (mol).

yield of ACN will be much higher for MoVNbTe than for VSbW and BiMo. This is mainly due to the much higher selectivity to ACN of MoVNbTe. The ACN yield (30%) of the VSbW catalyst is slightly lower than the 35–40% reported in the literature (1–3). This is probably related to the higher partial pressure of NH_3 used in this study. The ACN yield (10.6%) of the BiMo catalyst does not significantly differ from other studies (4, 6), although the composition of the catalyst is different.

The performance of MoVNbTe mixed oxides in the ammoxidation of propane is affected by reaction temperature and feed composition. Figure 2 shows that the propane conversion increases steadily from 56% at 673 K to 89% at 713 K. Selectivity to ACN reaches a maximum of 60% between 683 K and 693 K. Other products are mainly CO and CO_2, but small amounts of acetonitrile and hydrogen cyanide are produced too. The increase in propane conversion does not compensate the decrease in ACN selectivity completely, bringing about a broad maximum of nearly 50% ACN yield between 693 K and 713 K and a decrease in ACN yield above 713 K.

The effect of NH_3/PPA ratio is shown in Fig. 3. The selectivity from propane to ACN increases when the NH_3/propane ratio is increased from 0.6 to 1.2, regardless of temperature or catalyst composition. A further increase in NH_3/PPA ratio to 1.5 does not affect the selectivity from propane to ACN. Selectivity from NH_3 to ACN decreases steadily with increasing NH_3/PPA ratio. Although selectivity to ACN from both propane and NH_3 is of importance,

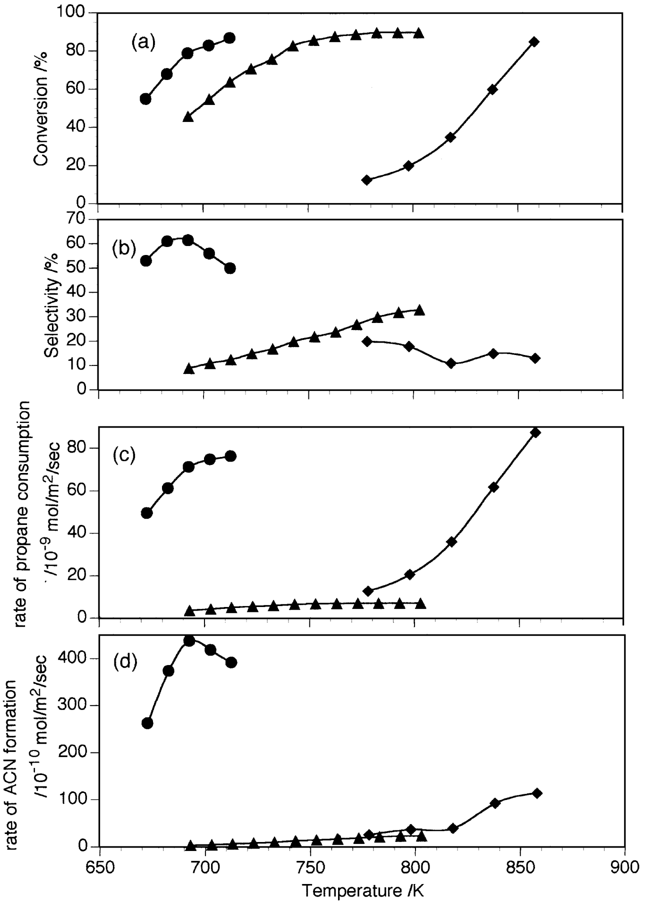

FIG. 1. (a) Conversion of propane, (b) selectivity for ACN, (c) rate of propane consumption and (d) rate of ACN formation of MoVNbTe catalyst (●), compared with VSbW (▲) and BiMo (◆) catalysts. (c) and (d) are surface-normalized rates of reaction. Catalyst amount: 0.5 cm^3, GHSV: 1000 h^{-1}, $C_3H_8/NH_3/Air = 1/1.2/15$ (mol).

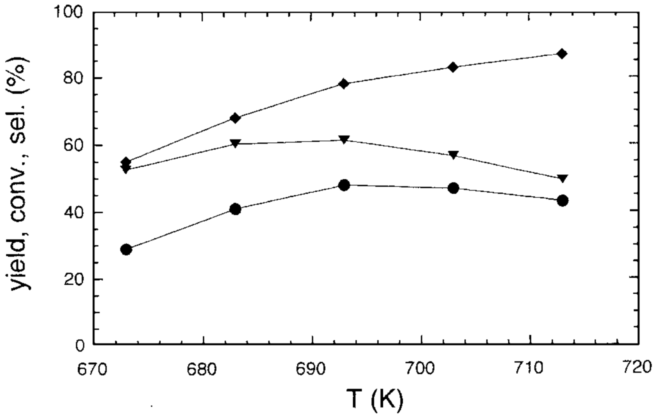

FIG. 2. Effect of reaction temperature on the yield of acrylonitrile (●), the conversion of propane (◆) and the selectivity to acrylonitrile (▼) of MoVNbTe oxide catalyst. Catalyst amount: 0.5 cm^3, GHSV: 1000 h^{-1}, $C_3H_8/NH_3/Air = 1/1.2/15$ (mol).

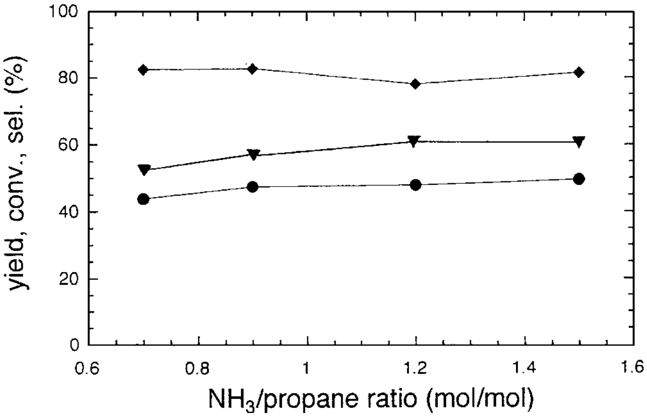

FIG. 3. Effect of NH_3/PPA ratio on the yield of acrylonitrile (●), the conversion of propane (◆) and the selectivity to acrylonitrile (▼) of MoVNbTe oxide catalyst. Catalyst amount: 0.5 cm^3, Reaction temperature: 693 K, GHSV: 1000 h^{-1}, C_3H_8/NH_3/Air = 1/x/15 (mol).

process economics dictate that the selectivity from propane to ACN should be optimized. The lifetime of MoVNbTe mixed oxides in the ammoxidation of propane seems to depend on the reaction conditions. However, the catalytic activity of MoVNbTe maintains more than 2000 h under the optimized condition.

The conclusion is that Mo–V–Nb–Te mixed metal oxide is highly active and selective for the ammoxidation of propane. The efficiency of the catalyst is higher than that of V–Sb and Bi–Mo mixed oxide catalysts. In addition to a higher ACN yield, the required reaction temperature is also lower. ACN yield reaches more than 50% by the optimizing reactor temperature and NH_3/propane feed ratio.

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