ELSEVIER

Catalysis Today 71 (2001) 77–82

CATALYSIS TODAY

www.elsevier.com/locate/cattod

# Oxidation and ammoxidation of propane over Mo–V–Sb mixed oxide catalysts

Tetsuya Shishido*, Tsuyoshi Konishi, Ikuya Matsuura, Ye Wang,
Ken Takaki, Katsuomi Takehira

*Department of Chemistry and Chemical Engineering, Graduate School of Engineering, Hiroshima University,
Kagamiyama 1-4-1, Higashi-hiroshima, Hiroshima 739-8527, Japan*

## Abstract

Catalytic oxidation and ammoxidation of propane to acrolein and acrylonitrile, respectively, were carried out over Mo–V–Sb mixed oxide catalysts. V–Sb mixed oxide showed the activity for the oxidative dehydrogenation of propane to propene, and the selectivity to propene remarkably increased with increasing the concentration of cation vacancy in $VSbO_4$ phase. It is likely that the oxidative dehydrogenation of propane on the $VSbO_4$ phase is initiated via H-abstraction by acid–base concerted mechanism. The selectivity to acrolein and acrylonitrile increased by the addition of molybdenum species to V–Sb mixed oxide catalyst. Among a series of Mo–V–Sb oxide catalysts, $Mo_1V_1Sb_{10}O_x$ exhibited the highest selectivity to acrolein and acrylonitrile at 430 and 480°C, respectively. The highly dispersed molybdenum suboxide was formed together with the both phases of $VSbO_4$ and $\alpha$-$Sb_2O_4$ in the $Mo_1V_1Sb_{10}O_x$. The high catalytic activity of $Mo_1V_1Sb_{10}O_x$ can be explained by the bifunctional mechanism of the highly dispersed molybdenum suboxide and the $VSbO_4$ phases as follows: the oxidative dehydrogenation of propane proceeds on the $VSbO_4$ phase followed by the oxidation of propene into acrolein or the ammoxidation into acrylonitrile on the molybdenum suboxide phase. When large size of $MoO_3$ crystallites were formed, cracking reaction, i.e., C–C bond cleavage, occurred leading to non-selective total oxidation, resulting in decreasing the selectivities to acrolein and acrylonitrile. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Mo–V–Sb mixed oxide catalyst; Propane; Selective oxidation; Acrolein; Ammoxidation; Acrylonitrile

## 1. Introduction

Since liquefied petroleum gas (LPG) is abundant and contains mainly propane and butanes, the selective conversions of propane and butanes to valuable chemicals have received much attention. The selective oxidation and ammoxidation of propane and butanes to the oxygenated compounds (such as unsaturated aldehydes and acids) and nitryls are one of the most important processes in the chemical industry [1–4]. However, the selective oxidation of the light alkanes is usually accompanied by many difficulties resulting from the higher reactivity of the oxygenated products than alkanes under the reaction conditions. Because of the inertness of alkanes, reaction conditions are normally more severe than in the case of alkene oxidation, so that the subsequent oxidation of the partially oxidized products and nitryls is unavoidable, resulting in low selectivity to the desired products. Among butanes, *n*-butane can be selectively oxidized to maleic anhydride by using crystalline V–P–O catalyst [5]. This is an exceptional case of selective alkane oxidation that has been commercialized in the gas-phase process.

---

* Corresponding author. Tel.: +81-824-24-7747;
fax: +81-824-22-7191.
*E-mail address:* stetsuya@hiroshima-u.ac.jp (T. Shishido).

0920-5861/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(01)00438-2

Recently, many patents have been disclosed for the partial oxidation of propane, among which the ammoxidation to acrylonitrile is the most prominent [6,7,27–30]. Several catalytic systems based on mixed oxide have been tested [6–10,27–30], but only a few showed good catalytic performance. It has been claimed that V–Sb mixed oxide is active for ammoxidation of propane to acrylonitrile by many researchers [9,11–15]. It is likely that vanadium-based compounds have an important role in alkane activation. Also, it is well known that molybdenum-based mixed oxides are one of the key components for alkene oxidation to oxygenated compound [16].

Here we studied the oxidation and ammoxidation of propane over the V–Sb and Mo–V–Sb mixed oxide catalysts and discussed the catalytic role of $VSbO_4$ phase and the promotion effect of molybdenum species on the V–Sb mixed oxide.

## 2. Experimental

Mo–V–Sb mixed metal oxide catalysts were prepared by the following slurry method. $Sb_2O_3$ (Wako Pure Chemical Industries) was dispersed in oxalic acid aqueous solution, in which hot aqueous solution of $NH_4VO_3$ and $(NH_4)_3Mo_7O_{24}\cdot 4H_2O$ (Wako Pure Chemical Industries) was added. The ratio of V/Sb was changed between 0.1 and 0.5 and the ratio of Mo/Sb between 0.1 and 1.0. The mixture was heated under reflux conditions at 90°C for 24 h and water was evaporated at 90°C. The resulting mixture was dried at 100°C for 15 h, ground into a fine powder and calcined at 350°C for 4 h and then at 600°C for 6 h in air. A similar procedure was adopted in preparing V–Sb mixed metal oxide catalysts. $Sb_2O_3$, $MoO_3$ and $V_2O_5$ were purchased (Wako Pure Chemical Industries) and used without further purification. $\alpha$-$Sb_2O_4$ was prepared by calcination of $Sb_2O_3$ at 600°C for 6 h in air and the structure of $\alpha$-$Sb_2O_4$ was confirmed by XRD (JCPDS 11-694).

The catalytic reactions were carried out at an atmospheric pressure in a conventional flow reactor using U-shaped Pyrex tube (Ø10 mm) with a fixed bed catalyst. In the case of propane oxidation with oxygen gas, the catalyst (0.5 g) was diluted with 1.0 g of quartz sands and was put between two quartz wool plugs in the reactor. The thermocouple was introduced from the top of the reactor and placed in the middle of the catalyst bed. The feed gas consisted of 25 vol.% of propane, 25 vol.% $O_2$ and $N_2$ balance and total flow rate was 40 ml min$^{-1}$ (GHSV $= 4.8 \times 10^3$ ml h$^{-1}$ g-cat$^{-1}$). The ammoxidation of propane was also carried out using the catalyst (1.5 g) diluted with 1.0 g of quartz sands. The feed gas consisted of 15 vol.% of propane, 30 vol.% of $O_2$, 15 vol.% of $NH_3$ and $N_2$ balance and total flow rate was 40 cm$^3$ min$^{-1}$ (GHSV $= 1.6 \times 10^3$ ml h$^{-1}$ g-cat$^{-1}$). Prior to the reaction, the catalyst was treated at 500°C with 25 vol.% of $O_2$ in $N_2$ stream for 2 h, and then cooled down to the reaction temperature under the same atmosphere. The feedstock and products were analyzed by on-line FID and TCD gas chromatographs with FFAP, Porapak-Q and Molecular Sieve 5A.

## 3. Results and discussion

The catalytic activities of the V–Sb and Mo–V–Sb mixed oxide in the propane oxidation are shown in Table 1. $V_2O_5$, $MoO_3$ and $\alpha$-$Sb_2O_4$ were used as the reference catalysts. Since propane conversion was quite low (<0.1%) without catalyst at 430°C, gas-phase reaction is considered negligible. $V_2O_5$ showed a low selectivity to propene (6.4%) at the conversion of 8.0%. Both $MoO_3$ and $\alpha$-$Sb_2O_4$ showed no activity at 430°C. It was reported that V–Sb mixed oxides showed the activity for ammoxidation of propane, where the activity strongly depended on the composition and the selectivity to acrylonitrile increased with decreasing V/Sb ratio starting from the stoichiometric one of $VSbO_4$ [9,11–15]. In the oxidation of propane over the V–Sb mixed oxide, similar phenomena were obtained, i.e., the conversion of propane decreased, while the selectivity of acrolein increased with a decrease in the V/Sb ratio. The conversion of oxygen decreased with a decrease in the V/Sb ratio. The main product was propene except $CO_x$ on $V_1Sb_{10}O_x$ at the conversion of 7.0%. The conversions of propane and oxygen over Mo–V–Sb mixed oxides were lower than those on the $V_1Sb_{10}O_x$ catalyst. Over the $Mo_1V_1Sb_{10}O_x$ catalyst, the selectivity to acrolein was almost two times higher than that on the $V_1Sb_{10}O_x$ catalyst, suggesting that the molybdenum species promote the oxidation of propene into acrolein. Over the Mo–V–Sb mixed oxides with the

Table 1
Conversion and selectivity for propane oxidation[a]

| Catalyst[b] | Conversion (%) | | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | $C_3H_8$ | $O_2$ | $C_3H_6$ | ACR[c] | $C_2H_4$ | $CO_x$ |
| $V_1Sb_2O_x$ | 22.2 | 67.8 | 11.1 | 1.8 | 2.7 | 84.4 |
| $V_1Sb_5O_x$ | 16.6 | 31.2 | 22.1 | 6.1 | 0.6 | 71.3 |
| $V_1Sb_{10}O_x$ | 7.0 | 14.4 | 34.8 | 9.2 | 5.6 | 50.3 |
| $Mo_1V_1Sb_{10}O_x$ | 6.8 | 10.9 | 33.8 | 20.8 | 17.9 | 27.5 |
| $Mo_5V_1Sb_{10}O_x$ | 4.8 | 8.5 | 36.7 | 8.8 | 13.9 | 40.6 |
| $Mo_{10}V_1Sb_{10}O_x$ | 5.2 | 8.2 | 36.3 | 8.3 | 14.5 | 40.9 |
| $V_2O_5$ | 8.0 | 29.6 | 6.4 | 0.5 | 17.9 | 74.2 |

[a] 430°C, $C_3H_8/O_2/N_2 = 10/10/20\,ml\,min^{-1}$, $3.6 \times 10^3\,ml\,h^{-1}$ g-cat$^{-1}$.
[b] Metal composition was calculated from the amount of reagents.
[c] Acrolein.

Mo/Sb ratio >0.1, the selectivity to propene slightly increased, while the selectivity to acrolein decreased remarkably. We have previously reported that the selectivity to methacrolein decreased with increasing the amount of molybdenum species in the oxidation of isobutane over the Mo–V–Sb mixed oxides with the Mo/Sb ratio >0.1 [17].

Table 2 shows the results of the ammoxidation of propane at 480°C over the V–Sb and Mo–V–Sb mixed oxide catalysts. On the V–Sb mixed oxide catalysts, the sum of selectivities to propene and acrylonitrile slightly increased with decreasing V/Sb ratio. When the molybdenum species was added in the V–Sb system, the conversion of propane was not substantially affected, while the selectivity to acrylonitrile increased remarkably. This result indicates that the propene formed by the oxidative dehydrogenation was easily converted to acrylonitrile in the presence of molybdenum species. Over the $Mo_{10}V_1Sb_{10}O_x$ catalyst, the selectivity to acetonitrile was higher, while the selectivity to acrylonitrile was lower than that over the $Mo_1V_1Sb_{10}O_x$ catalyst, indicating that C–C bond cleavage occurred over the former catalyst.

In the previous paper [17], the XRD, laser Raman and XPS results clearly showed the presence of the $VSbO_4$ and α-$Sb_2O_4$ phases on both the V–Sb and Mo–V–Sb mixed oxides. Moreover, we observed the highly dispersed "suboxides", i.e., $Mo_8O_{23}$, $Mo_9O_{26}$ or $Mo_{18}O_{52}$, particles on the surface of the $Mo_1V_1Sb_{10}O_x$ catalyst and the crystalline $MoO_3$ phase on the $Mo_{10}V_1Sb_{10}O_x$ catalyst, respectively [17]. Both the activities of the oxidation and the ammoxidation of propane were quite low when vanadium species is absent, suggesting that the $VSbO_4$ phase is important for the activation of propane. Table 3 shows the unit cell parameters of the $VSbO_4$ phase calculated

Table 2
Conversion and selectivity for propane ammoxidation[a]

| Catalyst[b] | $C_3H_8$ conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|
| | | $C_3H_6$ | AN[c] | ACN[d] | $Co_x$ |
| $V_1Sb_2O_x$ | 22.6 | 34.8 | 33.2 | 15.3 | 16.7 |
| $V_1Sb_5O_x$ | 15.8 | 39.8 | 34.6 | 7.1 | 18.5 |
| $V_1Sb_{10}O_x$ | 8.5 | 33.7 | 42.4 | 5.8 | 18.1 |
| $Mo_1V_1Sb_{10}O_x$ | 7.4 | 11.5 | 61.3 | 3.7 | 21.7 |
| $Mo_{10}V_1Sb_{10}O_x$ | 9.7 | 18.5 | 42.2 | 16.8 | 22.5 |

[a] 430°C, $C_3H_8/NH_3/O_2/N_2 = 6/6/12/16\,ml\,min^{-1}$, $1.6 \times 10^3\,ml\,h^{-1}$ g-cat$^{-1}$.
[b] Metal composition was calculated from the amount of reagents.
[c] Acrylonitrile.
[d] Acetonitrile.

Table 3
Unit cell parameters for $VSbO_4$ phase in the Mo–V–Sb mixed oxide catalysts

| Catalyst[a] | $a$ (nm) | $c$ (nm) | $c/a$ | $V$ ($\times 10^{-2}$ nm$^3$) | $\Delta V$ ($\times 10^{-4}$ nm$^3$)[c] |
|---|---|---|---|---|---|
| $V_1Sb_2O_x$ | 0.4632 | 0.3050 | 0.6585 | 6.5439 | 0.74 |
| $V_1Sb_5O_x$ | 0.4631 | 0.3047 | 0.6580 | 6.5346 | 1.67 |
| $V_1Sb_{10}O_x$ | 0.4621 | 0.3041 | 0.6581 | 6.4936 | 5.77 |
| $Mo_1V_1Sb_{10}O_x$ | 0.4621 | 0.3041 | 0.6581 | 6.4936 | 5.77 |
| $V_{1.05}Sb_{0.95}O_4$[b] | 0.4609 | 0.3084 | 0.6691 | 6.5513 | – |
| $V_{0.92}Sb_{0.92}O_4$[b] | 0.4624 | 0.3037 | 0.6579 | 6.4935 | 5.78 |

[a] Metal composition was calculated from the amount of reagents.
[b] Ref. [17].
[c] $\Delta V = V_a - V_b$; $V_a$: unit cell volume of $V_{1.05}Sb_{0.95}O_4$; $V_b$: unit cell volume of $VSbO_4$ in the V–Sb mixed oxide catalyst.

from $d$-values of the diffraction peaks in the V–Sb and the Mo–V–Sb catalysts, together with those of the $V_{1.05}Sb_{0.95}O_4$ and $V_{0.92}Sb_{0.92}O_4$ reported by Birchall and Sleight [18] and Hansen et al. [19]. $V_{1.05}Sb_{0.95}O_4$ has no cation vacancy, while $V_{0.92}Sb_{0.92}O_4$ has it [18,19]. The unit cell parameters of both the V–Sb and the Mo–V–Sb mixed oxides are almost similar to those of $V_{0.92}Sb_{0.92}O_4$, indicating that the $VSbO_4$ phase in the both mixed oxides has cation vacancies.

The unit cell volume of $VSbO_4$ in the V–Sb and Mo–V–Sb mixed oxides decreased with decreasing V/Sb ratio (Table 3), resulting in increasing concentration of cation vacancy. The increase in the concentration of cation vacancy is also confirmed by XPS measurements. The binding energies of V $2p_{3/2}$ together with those of Sb $3d_{3/2}$ and Mo $3d_{5/2}$ in the V–Sb and Mo–V–Sb mixed oxides are summarized in Table 4. It was reported that the mean valence of vanadium ion increased with an increase in the concentration of cation vacancy in the mixed oxides [18,19]. The binding energy of the V $2p_{3/2}$ increased with decreasing the V/Sb ratio, indicating that the concentration of cation vacancy increased with decreasing the V/Sb ratio.

In Fig. 1, the selectivities and the binding energy of the V $2p_{3/2}$ values are plotted against $\Delta V$ shown in Table 3. The $\Delta V$ value denotes a difference in unit cell volume between the $V_{1.05}Sb_{0.95}O_4$ and the $VSbO_4$ phase in the V–Sb catalysts. This value increased with increasing the concentration of cation vacancy in the $VSbO_4$ phase. In the case of the oxidation of propane, the sum of selectivities to propene and acrolein increased remarkably with increasing the concentration of cation vacancy. Also, in the case of the ammoxi-

Table 4
Binding energies, $E_b$ of different elements in Mo–V–Sb mixed oxide catalysts

| Catalyst[a] | $E_b$ (eV) | | |
|---|---|---|---|
| | Sb $3d_{3/2}$ | V $2p_{3/2}$ | Mo $3d_{5/2}$ |
| $V_1Sb_2O_x$ | 540.3 | 515.0 | – |
| $V_1Sb_5O_x$ | 539.9 | 515.9 | – |
| $V_1Sb_{10}O_x$ | 539.8 | 516.4 | – |
| $Mo_1V_1Sb_{10}O_x$ | 540.0 | 516.2 | 232.4 |
| $\alpha$-$Sb_2O_4$ | 540.2 | – | – |
| $V_2O_5$ | – | 517.7 | – |
| $MoO_3$ | – | – | 232.8 |

[a] Metal composition was calculated from the amount of reagents.

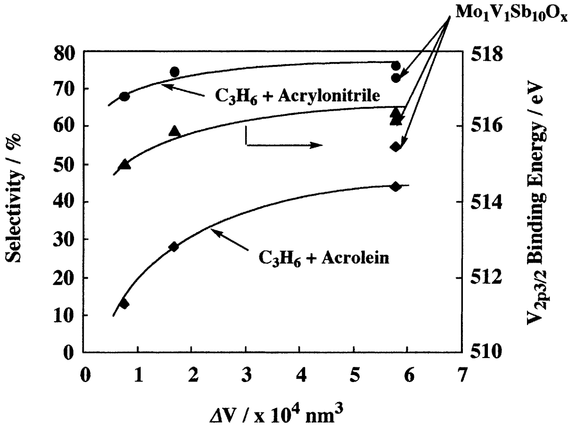

Fig. 1. Dependency of selectivities and V $2p_{3/2}$ binding energy on $\Delta V$ in the V–Sb and the Mo–V–Sb mixed oxide catalysts. $\Delta V = V_a - V_b$; $V_a$: unit cell volume of $V_{1.05}Sb_{0.95}O_4$; $V_b$: unit cell volume of $VSbO_4$ phase in the catalyst.

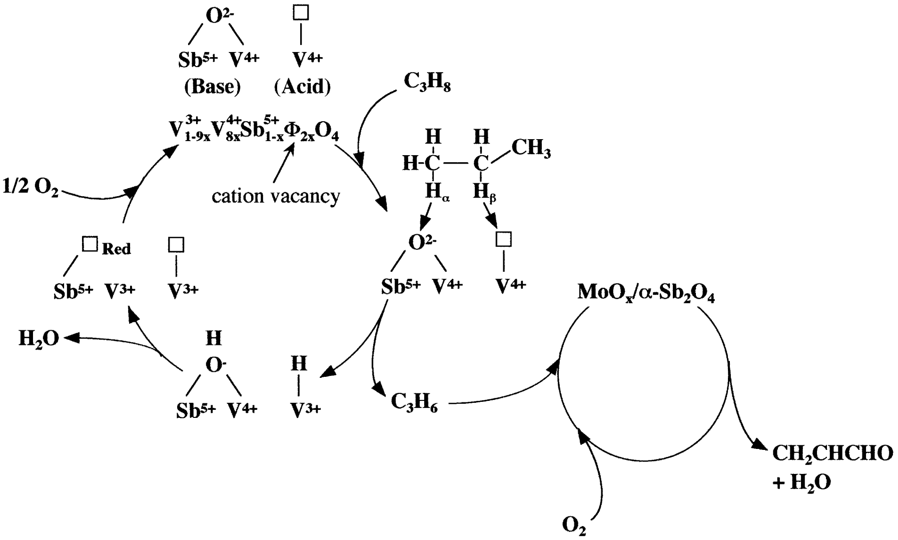

Fig. 2. Supposed reaction mechanism of the oxidation of propane over the Mo–V–Sb mixed oxide catalysts.

dation of propane, the sum of selectivities to propene and acrylonitrile slightly increased with increasing the concentration of cation vacancy. The oxidative dehydrogenation, which is the first step in both the oxidation and the ammoxidation of propane, may be initiated via H-abstraction from propane by concerted mechanism over the present acid–base catalyst as shown in Fig. 2. The Lewis acid site (V cation) and basic site ($O^{2-}$) interacts with α- and β-hydrogen of propane, respectively. Then, both α- and β-hydrogen are simultaneously abstracted from propane to form propene. It is likely that the strength of the Lewis acid sites on the V–Sb catalysts increased with an increase in the concentration of cation vacancy, because the mean valence of vanadium ion increased as shown in Fig. 1. This may result in increasing the selectivity to propene from propane. In the case of ammoxidation, the selectivity to $CO_x$ was much lower than that in the oxidation of propane, although the reaction temperature was higher than that in the oxidation of propane. Moreover, the selectivity to propene decreased, while the selectivity to acrylonitrile increased with increasing the concentration of cation vacancy over the V–Sb mixed oxides with the V/Sb ratio $<0.2$. These results may be due to the adsorption of significant amount of ammonia on the acid sites. Since the ammonia adsorbed on the acid site (V cation) on the surface of the $VSbO_4$ phase blocked the adsorption of propane and propene, the contact time of propane and propene decreased. This short contact time of propane and propene suppressed the combustion of propane and propene to $CO_x$ and the oxidative dehydrogenation of propane to propene. Furthermore, since the concentration of ammonia on the catalyst surface was high, further transformation of propene to acrylonitrile may smoothly occur. Because of the depression of both the combustion and the oxidative dehydrogenation and the acceleration of the transformation of propene to acrylonitrile, the sum of selectivity to propene and acrylonitrile slightly increased with increasing the concentration of cation vacancy.

Over the $Mo_1V_1Sb_{10}O_x$ catalyst, both the selectivites to acrolein and acrylonitrile were much higher than that over the $V_1Sb_{10}O_x$ catalyst as shown in Tables 1 and 2. We previously reported the presence of highly dispersed molybdenum suboxide together with the $VSbO_4$ and α-$Sb_2O_4$ phases on the $Mo_1V_1Sb_{10}O_x$ catalyst [17]. As described already, the oxidative dehydrogenation of propane to propene seems to occur on the $VSbO_4$ phase and α-$Sb_2O_4$ is inactive. It is likely that the highly dispersed molybdenum suboxide behaves as the effective catalyst for the selective oxidation and ammoxidation of propane to acrolein and acrylonitrile. Delmon and co-workers

[20–23] reported that the mechanical mixture of $MoO_3$ and α-$Sb_2O_4$ showed the synergetic effects between $MoO_3$ (and/or slightly reduced $MoO_{3-x}$) and α-$Sb_2O_4$ in the oxidation of isobutene to methacrolein. This synergetic effect on the mechanical mixture cannot be explained by the formation of Mo–Sb mixed oxide. They observed the creation of new selective (1 0 0) face of the molybdenum oxide by a partial reconstruction of the non-selective (0 1 0) face by SEM and AFM [23]. They concluded that this partial reconstruction of non-selective (0 1 0) face to selective (1 0 0) face caused the synergetic effect during the catalytic reaction on mechanical mixtures of $MoO_3$ with α-$Sb_2O_4$ [20–23]. Volta et al. [24] also reported that the (0 1 0) face of molybdenum oxide mostly brings about total oxidation reactions, while the (1 0 0) face selectively performs partial oxidation of propylene to acrolein. In the present case of $Mo_1V_1Sb_{10}O_x$, it is considered that highly dispersed molybdenum suboxide formed by the interaction between excess amount of α-$Sb_2O_4$ with molybdenum species. The highly dispersed molybdenum suboxide would be oriented selective (1 0 0) face by the partial reconstruction of non-selective (0 1 0) face, and behaves as the effective catalyst for the oxidation of propene to acrolein. Therefore, the improvement of the selectivity to acrolein and acrylonitrile by the addition of molybdenum species to $VSbO_4$ and/or α-$Sb_2O_4$ can be explained by the following bifunctional mechanism (Fig. 2): propane is oxidatively dehydrogenated to propene on the $VSbO_4$ phase, followed by the oxidation of propene to acrolein and acrylonitrile on the highly dispersed molybdenum suboxide particle.

The surface of bulk molybdenum oxide ($MoO_3$) is acidic in nature [25] and increasing the amount of dispersed $MoO_3$ on a metal oxide support leads to a higher local acid concentration on the surface [26]. When large size of $MoO_3$ crystallites exist, cracking reaction such as C–C bond cleavage occurs. Furthermore, the large size of $MoO_3$ tends to be oriented to show non-selective (0 1 0) face by the epitaxial growth as reported by Volta et al. [24]. Thus, it is likely that non-selective total oxidation occurs together with cracking reaction over the $Mo_{10}V_1Sb_{10}O_x$, resulting in decreasing the selectivities to acrolein and acrylonitrile.

## References

[1] G. Centi, F. Trifiro, Chemtech 24 (1994) 18.
[2] H.H. Kung, Adv. Catal. 40 (1994) 1.
[3] G. Centi, Catal. Lett. 22 (1993) 53.
[4] S.T. Oyama, J.W. Hightower, Catalytic selective oxidation, ACS Sym. Ser. 523 (1993) 1.
[5] B.K. Hodnett, Catal. Rev. 27 (1985) 373.
[6] J.F. Brazil, L.C. Glaeser, US Patent 5 008 427 (1991).
[7] M. Hatano, A. Kayo, US Patent 5 049 692 (1991).
[8] Y. Moro-oka, W. Ueda, in: Catalysis, Vol. 11, The Royal Society of Chemistry, Cambridge, UK, 1994, p. 93.
[9] G. Centi, R.K. Grasselli, F. Trifiro, Catal. Today 13 (1992) 661.
[10] V.D. Sokolovskii, A.A. Davydov, O. Yu Ovsiter, Catal. Rev. 37 (1995) 425.
[11] R. Nilsson, T. Lindblad, A. Andersson, C. Song, S. Hansen, Stud. Surf. Sci. Catal. 82 (1994) 293.
[12] J. Nilsson, A.R. Landa-Ca'novas, S. Hanson, A. Andersson, Stud. Surf. Sci. Catal. 110 (1997) 413.
[13] G. Centi, E. Foresti, F. Guarnieri, Stud. Surf. Sci. Catal. 82 (1994) 281.
[14] G. Centi, R.K. Grasselli, E. Patane, F. Trifiro, in: New Development in Selective Oxidation, Elsevier, Amsterdam, 1990, p. 515.
[15] R.K. Grasselli, G. Centi, F. Trifiro, Appl. Catal. 57 (1990) 149.
[16] R.K. Grasselli, J.D. Burrington, Adv. Catal. 30 (1981) 133.
[17] T. Shishido, A. Inoue, T. Konishi, I. Matsuura, K. Takehira, Catal. Lett. 68 (2000) 215.
[18] T. Birchall, A.W. Sleight, Inorg. Chem. 15 (1976) 868.
[19] S. Hansen, K. Stahl, R. Nilsson, A. Andersson, J. Solid State Chem. 102 (1993) 340.
[20] E.M. Gaigneaux, M. Dieterie, P. Ruiz, G. Mestl, B. Delmon, J. Phys. Chem. B 102 (1998) 10542.
[21] E.M. Gaigneaux, P. Ruiz, E.E. Wolf, B. Delmon, Appl. Surf. Sci. 121–122 (1997) 552.
[22] E.M. Gaigneaux, P. Ruiz, E.E. Wolf, B. Delmon, Catal. Today 32 (1996) 37.
[23] E.M. Gaigneaux, P.E. Tsiakaras, D. Herla, L. Ghenne, P. Ruiz, B. Delmon, Catal. Today 33 (1997) 151.
[24] J.C. Volta, O. Bertrand, N. Floquet, J. Chem. Soc., Chem. Commun. (1985) 1283.
[25] K. Tanabe, M. Misono, Y. Ono, H. Hattori, in: New Solid Acids and Bases, Kodansha, Tokyo, 1989, p. 51.
[26] H. Jeziorowski, H. Knozinger, J. Phys. Chem. 83 (1979) 1166.
[27] A.T. Guttmann, R.K. Grasselli, J.F. Brazil, US Patent 4 746 641 (1988).
[28] J.P. Bartek, A.T. Guttmann, US Patent 4 797 381 (1989).
[29] D.D. Suresh, US Patent 4 760 159 (1988).
[30] T. Ushikubo, Y. Koyasu, H. Nakmura, JP Patent 157 241 (1997).