A crystalline $SbRe_2O_6$ catalyst active for selective ammoxidation of isobutylene and propene

Haichao Liu, Eric M. Gaigneaux*, Hideo Imoto**, Takafumi Shido and Yasuhiro Iwasawa***

Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
E-mail: iwasawa@chem.s.u-tokyo.ac.jp

Received 9 August 2000; accepted 12 October 2000

This paper reports the first performance of a crystalline $SbRe_2O_6$ catalyst, which is a new family of Re mixed oxide, for the selective ammoxidation reactions of isobutylene to methacrylonitrile and propene to acrylonitrile. The $SbRe_2O_6$ with alternate $(Re_2O_6)^{3-}$ and $(SbO)^+$ layers showed much better performance than two other known Re–Sb–O compounds $SbOReO_4{\cdot}2H_2O$ and $Sb_4Re_2O_{13}$ with tetrahedral $(ReO_4)^-$ anions and cationic $(SbO)^+$ layers. The $SbRe_2O_6$ catalyst was also much more active than a coprecipitated $SbRe_2O_x$ catalyst, a supported Re_2O_7/Sb_2O_3 catalyst, and Re oxides such as Re_2O_7, ReO_3 and ReO_2 for the selective ammoxidation. Rhenium is prerequisite to the ammoxidation catalysis of the Re–Sb mixed oxides. Sb oxides such as Sb_2O_3 and Sb_2O_4 were inactive, but Sb in the $SbRe_2O_6$ catalyst contributes positively to the methacrylonitrile and acrylonitrile syntheses. Neither change nor modification of the surface composition, crystallinity and morphology of $SbRe_2O_6$ occurred under the ammoxidation reaction conditions, where the presence of NH_3 stabilized the crystalline $SbRe_2O_6$ structure.

KEY WORDS: Re–Sb–O catalysts; crystalline $SbRe_2O_6$; selective ammoxidation; isobutylene; propene; methacrylonitrile; acrylonitrile; XRD; XPS; SEM

1. Introduction

Rhenium-based catalysts have received much attention in many industrial processes such as metathesis of alkenes and reforming of petroleum feedstocks. They also exhibited unique activities in selective hydrogenation of organic compounds, hydrodesulfurization of heavy crude oil, and dehydroaromatization of methane to hydrogen and benzene [1–7]. As for selective oxidation, however, Re finds merely a few applications to the oxidation of methanol and ethanol [8–11]. Despite such limited uses, Re can be a key element in selective catalytic oxidation processes because Re oxides possess redox properties comparable to those of V, Mo and W oxides [12] that have extensively been employed as main components in various mixed-oxide oxidation catalysts [13–17]. Recently we have studied the catalytic property of three crystalline Re–Sb mixed oxides, $SbOReO_4{\cdot}2H_2O$, $SbRe_2O_6$ and $Sb_4Re_2O_{13}$, for the selective oxidation of isobutylene and isobutane to methacrolein at 673–773 K [18–20]. They were active, but a serious problem encountered under the catalytic oxidation conditions was the partial decomposition of the catalysts involving sublimation of Re oxides. The surfaces of the Re–Sb mixed oxides were transformed to $Sb_4Re_2O_{13}$ modified with Re_2O_7, which was responsible for the selective oxidation activity [18–20]. During study to overcome this serious problem, we have found that the decomposition does not take place in the presence of ammonia. As for the Sb component of the Re–Sb mixed oxides, Sb is well known to constitute a promoter element in several mixed oxides, such as V–Sb–O, Sn–Sb–O, Mo–Sb–O, Fe–Sb–O and U–Sb–O, for selective oxidation/ammoxidation of hydrocarbons [14–17,21]. Little has been reported about the catalytic property of Re in the selective ammoxidation of hydrocarbons to produce the corresponding unsaturated nitriles. These considerations tempted us to endeavor to develop Re–Sb mixed oxides as a new family of ammoxidation catalysts. Here we report the first performance of a crystalline $SbRe_2O_6$ catalyst for the selective ammoxidation reactions of isobutylene to methacrylonitrile (MAN) and propene to acrylonitrile (AN).

2. Experimental

2.1. Catalyst preparation

$SbRe_2O_6$, $SbOReO_4{\cdot}2H_2O$ and $Sb_4Re_2O_{13}$ were synthesized in the similar manner to that reported previously [9,10,18–20,22,23]. The specific surface areas of the three samples were approximately 1 $m^2\,g^{-1}$. For comparison, a Sb_2O_3-supported Re_2O_7 catalyst (denoted as Re_2O_7/Sb_2O_3) (Re loading 10 wt%) was prepared by an impregnation method using an aqueous solution of NH_4ReO_4 [19]. A coprecipitated $SbRe_2O_x$ catalyst (denoted as copr.$SbRe_2O_x$) was also prepared by a coprecipitation method using an ethanol solution of $ReCl_3$ and $SbCl_3$, followed by washing with water to eliminate the residual Cl from the catalyst.

---

[*] Present address: Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium.

[**] Present address: Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, Yoto, Utsunomiya 321-8585, Japan.

[***] To whom correspondence should be addressed.

Table 1
Isobutylene ammoxidation on different catalysts at 673 K.[a]

	Conversion (%)	Rate (mmol h^{-1} g_{cat}^{-1})	Selectivity (%)		
			MAN[b]	CH_3CN	CO_2
$SbRe_2O_6$	5.2 (12.4)[c]	3.71 (4.42)[c]	83.6 (82.6)[c]	6.1 (6.9)[c]	9.8 (10.0)[c]
$SbOReO_4 \cdot 2H_2O$	0.9	0.64	66.8	3.9	29.1
$Sb_4Re_2O_{13}$	1.9	1.36	70.7	4.6	24.2
copr.$SbRe_2O_x$	1.4	1.00	69.8	11.1	19.1
Re_2O_7/Sb_2O_3	1.2	0.86	76.8	6.8	16.4
Re_2O_7	1.6	1.14	47.9	13.2	38.9
ReO_3	1.4	1.00	51.9	17.1	31.0
ReO_2	3.1	2.21	50.6	17.8	31.6
Sb_2O_3	0	0	–	–	–
Sb_2O_4	0	0	–	–	–

[a] i-$C_4H_8/NH_3/O_2/He = 10/15/20/55$ (mol%), GHSV = 20 000 h^{-1}.
[b] MAN = methacrylonitrile.
[c] The data listed in parentheses were obtained at a GHSV of 10 000 h^{-1}.

2.2. Catalytic performance

Catalytic ammoxidation reactions were carried out in a fixed-bed flow reactor at atmospheric pressure. The reaction feed consisted of 10% i-C_4H_8 or C_3H_6, 15% NH_3 and 20% O_2 balanced with He (mol%). The catalytic performance was taken generally with 0.15 g of catalyst diluted with 1 g of quartz sand to prevent temperature gradients and hot spots in the reactor. Prior to each run, the catalyst was pretreated in a He flow (40 ml min^{-1}) at 673 K for 1 h. Then the reaction feed was introduced into the reactor at a gas hourly space velocity (GHSV) of 20 000 h^{-1} using digital mass-flow controllers. The reactants and products were analyzed using two on-line gas chromatographs equipped with three columns of Unibeads C for O_2, CO and CO_2, Gaskuropack 54 for methacrylonitrile (MAN), acrylonitrile (AN) and acetonitrile, and VZ-10 for i-C_4H_8, C_3H_6, and other hydrocarbons. It is to be noted that BET surface areas of the three Re–Sb–O compounds remained almost unchanged after the ammoxidation reactions.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were measured in air on a Rigaku Miniflex goniometer using Cu Kα radiation ($\lambda = 1.5418$ Å) at 30 kV and 15 mA. The 2θ angles were scanned from 5° to 60° at a rate of 2° min^{-1}.

Scanning electron microscope (SEM) photographs were taken on a Hitachi S-4500 microscope operated at 5 kV and 10 μA.

X-ray photoelectron spectra (XPS) were recorded on a Rigaku XPS 7000 spectrometer using Mg Kα radiation (1253.6 eV) powered at 200 W. The binding energies were referred to the adventitious C 1s peak at 284.6 eV. To minimize exposure of the samples to air, after the ammoxidation reactions, the samples were rapidly cooled to room temperature under the gas flow, followed by sealing the reactor. Then, the samples were put into a N_2-filled glove box, and pressed into disks, and mounted to XPS sample holders with thin double-sided tapes. Then the sample holders were transferred to the XPS chamber within 1 min.

3. Results and discussion

Table 1 presents the conversions, reaction rates and selectivities of the i-C_4H_8 ammoxidation ($2i\text{-}C_4H_8 + 2NH_3 + 3O_2 \rightarrow 2MAN + 6H_2O$) at 673 K on the three crystalline compounds, $SbRe_2O_6$, $SbOReO_4 \cdot 2H_2O$ and $Sb_4Re_2O_{13}$. For comparison, the performances of copr.$SbRe_2O_x$, Re_2O_7/Sb_2O_3, Sb_2O_3, Sb_2O_4, Re_2O_7, ReO_3 and ReO_2, are also listed in table 1. The Re–Sb–O catalysts as well as bulk Re oxides (Re_2O_7, ReO_3 and ReO_2) were more or less active, and the selectivities to MAN were 47.9–83.6%, whereas the bulk Sb oxides (Sb_2O_3 and Sb_2O_4) showed no activity under the identical conditions. These results indicate that rhenium is prerequisite to the ammoxidation catalysis of the Re–Sb–O samples. It is to be noted that supporting Re_2O_7 on the inert Sb_2O_3 surface increased the selectivity to MAN from 47.9 to 76.8% (table 1). Further, the three crystalline Re–Sb–O compounds and copr.$SbRe_2O_x$ were also more selective than the bulk Re oxides. These results demonstrate that the presence of Sb in the Re–Sb–O samples made positive contribution to the MAN synthesis. Among the samples examined in table 1, $SbRe_2O_6$ exhibited the best performance. The selectivity to MAN was 83.6% at the steady-state i-C_4H_8 conversion of 5.2%. The steady-state catalytic performance remained almost unchanged without deactivation over 10 h on stream. Decrease in the GHSV to 10 000 h^{-1} increased the i-C_4H_8 conversion to 12.4%, while keeping a good selectivity of 82.6% as shown in parentheses in table 1.

Figure 1 shows the variation of the conversion and selectivity of the i-C_4H_8 ammoxidation on the $SbRe_2O_6$ catalyst with reaction temperature in the range 623–773 K. The conversion increased with increasing temperature, while maintaining the good selectivity to MAN (83–84%) up to 698 K. Above 698 K, methacrolein (MAL) which is a selective oxidation product ($i\text{-}C_4H_8 + O_2 \rightarrow MAL + H_2O$) appeared in

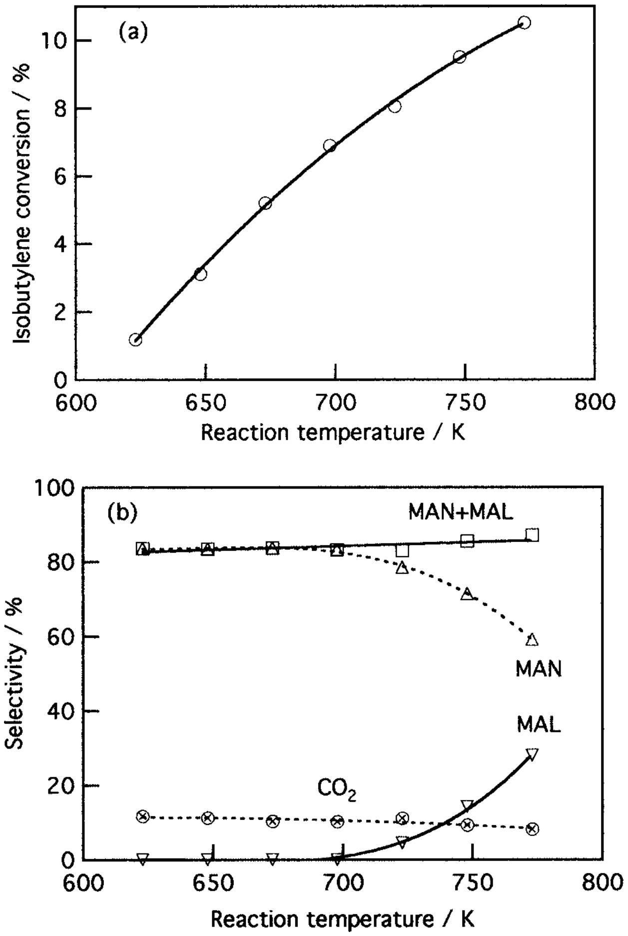

Figure 1. i-C_4H_8 conversion (a) and selectivities (b) in the catalytic ammoxidation of i-C_4H_8 on $SbRe_2O_6$ as function of reaction temperature; i-$C_4H_8/NH_3/O_2/He = 10/15/20/55$ (mol%); GHSV = 20 000 h^{-1}.

Table 2

Catalytic performance of $SbRe_2O_6$ in propene ammoxidation.[a]

	Conversion (%)	Rate (mmol h^{-1} g_{cat}^{-1})	Selectivity (%)		
			AN[b]	CH_3CN	CO_2
673 K	1.9	1.36	44.8	39.5	15.7
723 K	2.9	2.07	62.9	29.3	7.8
773 K	3.2 (8.3)[c]	2.29 (2.96)[c]	85.0 (82.1)[c]	10.4 (11.1)[c]	4.6 (6.8)[c]

[a] $C_3H_6/NH_3/O_2/He = 10/15/20/55$ (mol%), GHSV = 20 000 h^{-1}.

[b] AN = acrylonitrile.

[c] The data listed in parentheses were obtained at a GHSV of 10 000 h^{-1}.

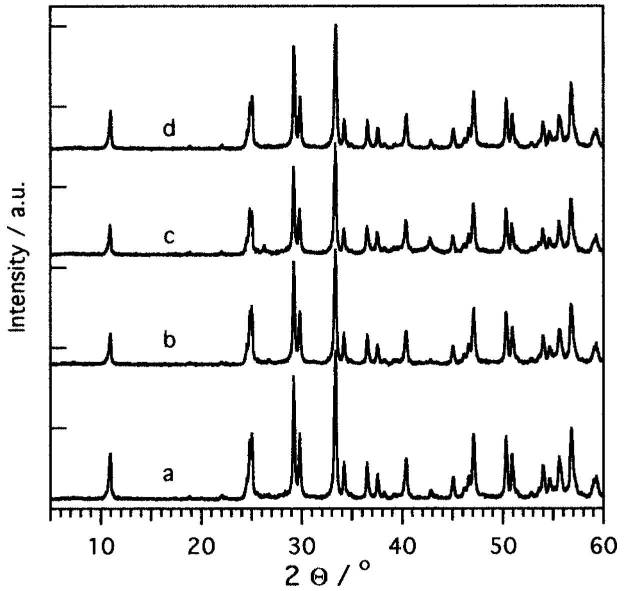

Figure 2. XRD patterns for fresh $SbRe_2O_6$ (a) and $SbRe_2O_6$ after the i-C_4H_8 ammoxidation at 673 (b) and 773 K (c) for 3 h, as well as after the C_3H_6 ammoxidation at 773 K for 3 h (d).

addition to MAN. The selectivity to MAL reached as high as 28% at 773 K. As a result, the selectivity to MAN decreased above 723 K, while the selectivity to the sum of MAL + MAN increased slightly with temperature. It is noteworthy that a degradation product CH_3CN and a combustion product CO_2 tended to decrease above 723 K.

On the most active $SbRe_2O_6$ catalyst, ammoxidation of C_3H_6 was carried out as well. As shown in table 2, the C_3H_6 ammoxidation led to the production of acrylonitrile (AN), CH_3CN and CO_2. At 673 K the steady-state C_3H_6 conversion was 1.9% and the selectivity to AN was 44.8% under a GHSV of 20 000 h^{-1}. The activity of $SbRe_2O_6$ for the C_3H_6 ammoxidation was lower than for the i-C_4H_8 ammoxidation under the equivalent conditions, which may be due to the lower adsorption probability of C_3H_6 as compared to that of i-C_4H_8 on the catalyst surface [24].

However, it is interesting to note that the formation of AN significantly depends on the reaction temperature. With increasing temperature from 673 to 773 K, as shown in table 2, the overall C_3H_6 conversion increased from 1.9 to 3.2%, and the selectivity to AN also increased to 85.0%, whereas the selectivities to by-products CH_3CN and CO_2 decreased from 39.5 and 15.7% to 10.4 and 4.6%, respectively. In both the i-C_4H_8 and C_3H_6 selective ammoxidation reactions, the total oxidation to CO_2 remarkably decreased at elevated reaction temperatures, which reveals the potential and characteristic of the crystalline $SbRe_2O_6$ as a promising catalyst for the ammoxidation reactions. At 773 K, upon decreasing the GHSV to 10 000 h^{-1}, the C_3H_6 conversion increased to 8.3%, while keeping a good selectivity of 82.1% for the AN formation (table 2). The effect of temperature on the selectivities to AN and CH_3CN is in agreement with the finding by Centi et al. in the ammoxidation of C_3H_8 and C_3H_6 on V–Sb oxides [25]. On the basis of the FT-IR data for the coadsorption of C_3H_6 and NH_3 on the catalysts, they proposed that the conversion of adsorbed C_3H_6 to CH_3CN and AN proceeded by two different pathways via acetone and allyl alcoholate intermediates, respectively. The first pathway is favored at lower temperatures, leading preferentially to the breaking of the carbon chain and the subsequent formation of CH_3CN, while the second pathway via allyl alcoholate intermediate prevails at higher temperatures, which results in the formation of AN [25].

To examine the key issue of the activity for the ammoxidation, $SbRe_2O_6$ samples were characterized by means of XRD, XPS and SEM. Figure 2 shows the XRD patterns of

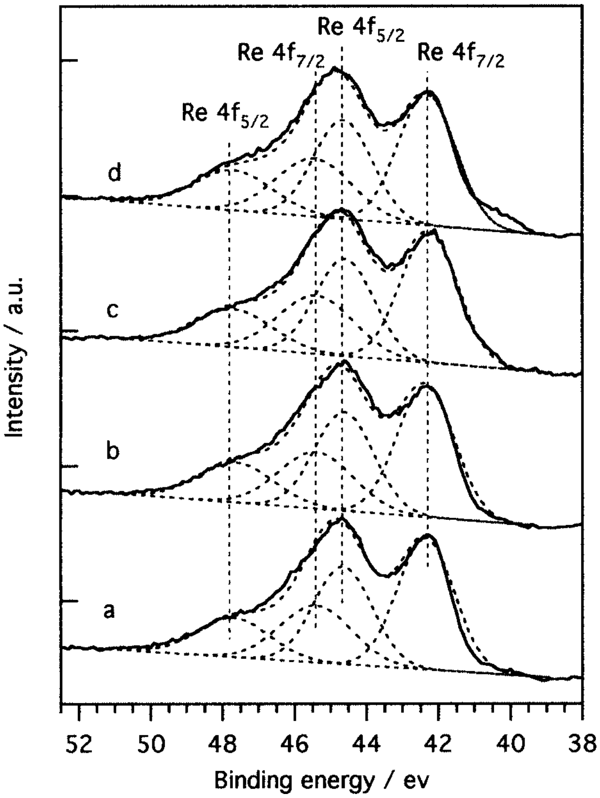

Figure 3. Re 4f XPS spectra for fresh $SbRe_2O_6$ (a) and $SbRe_2O_6$ after the i-C_4H_8 ammoxidation at 673 (b) and 773 K (c) for 3 h, as well as after the C_3H_6 ammoxidation at 773 K for 3 h (d).

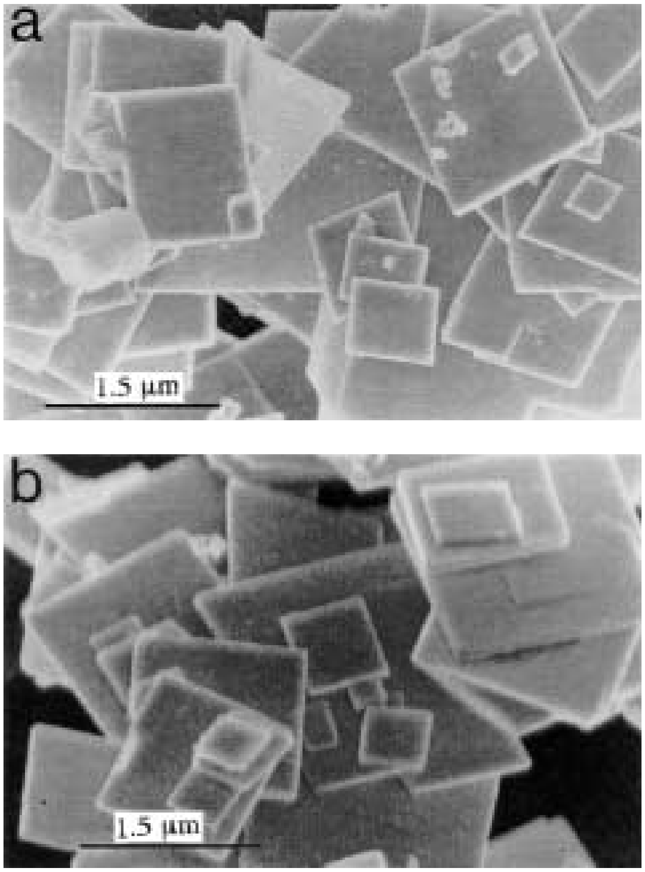

Figure 4. Scanning electron micrographs for $SbRe_2O_6$ before (a) and after (b) the i-C_4H_8 ammoxidation at 673 K for 3 h.

$SbRe_2O_6$ before and after the i-C_4H_8 ammoxidation reactions at 673 and 773 K, as well as after the C_3H_6 ammoxidation at 773 K for 3 h. It was found that the XRD patterns after the i-C_4H_8 and C_3H_6 ammoxidation were identical to that for the fresh $SbRe_2O_6$. Figure 3 shows the XPS spectra for $SbRe_2O_6$ in the Re 4f region before and after the i-C_4H_8 ammoxidation at 673 and 773 K, as well as after the C_3H_6 ammoxidation at 773 K. The fresh $SbRe_2O_6$ catalyst possessed three peaks at the XPS binding energies of 42.3, 44.8 and 47.7 eV. The peak at 42.3 eV is assigned to Re $4f_{7/2}$ for Re^{4+}, while the Re $4f_{5/2}$ level should be observed around 44.7 eV [11]. Thus we have deconvoluted the XPS spectra as shown in figure 3. The deconvoluted peak at 44.7 eV is assigned to Re^{4+} $4f_{5/2}$. In addition to the Re^{4+} XPS peaks, the peaks at 45.3 and 47.7 eV were observed, which are assigned to Re $4f_{7/2}$ and Re $4f_{5/2}$ possibly for Re^{6+} species because the Re $4f_{7/2}$ binding energy (45.3 eV) is lower by 1.2–1.6 eV than that reported for Re_2O_7 (Re^{7+}) and higher by 0.8–1.0 eV than that for ReO_3 (Re^{6+}) [26,27]. The $SbRe_2O_6$ samples after the ammoxidation of i-C_4H_8 and C_3H_6 exhibited no significant difference in the Re 4f XPS spectra as compared to the fresh sample. Sb 4d and Sb $3d_{3/2}$ bands appeared at 34.5 and 539.8 eV, respectively, which are the typical binding energies of Sb^{3+}, independent of the ammoxidation reactions. In agreement with the XRD and XPS observations, the SEM micrographs in figure 4 for $SbRe_2O_6$ before and after the i-C_4H_8 ammoxidation at 673 K show that the morphology of the regular basal faces of the $SbRe_2O_6$ crystals remained unchanged after the ammoxidation. These characterization data demonstrate that neither change nor modification of the surface composition, crystallinity, and morphology of $SbRe_2O_6$ occurs under the ammoxidation reaction conditions.

The three Re–Sb–O compounds have different crystalline structures. The $SbRe_2O_6$ compound consists of alternate octahedral $(Re_2O_6)^{3-}$ and $(SbO)^+$ layers which are connected with each other [23]. The other two crystalline compounds $SbOReO_4 \cdot 2H_2O$ and $Sb_4Re_2O_{13}$ are built up from tetrahedral $(ReO_4)^-$ anions and cationic $(SbO)^+$ layers [9,22]. In accordance with the formula of the latter two compounds, their XPS spectra showed the oxidation states of Re and Sb to be 7+ and 3+, respectively. After the i-C_4H_8 ammoxidation at 673 K, low valent Re species (Re^{6+} and Re^{4+}) were produced [28]. This shows the reduction of the two Re–Sb–O compounds under the ammoxidation conditions. Although the $SbOReO_4 \cdot 2H_2O$ and $Sb_4Re_2O_{13}$ catalysts under the ammoxidation of i-C_4H_8 at 673 K showed the similar oxidation states of active Re species to those for the $SbRe_2O_6$ catalyst, the former two catalysts were much inferior to the $SbRe_2O_6$ catalyst, as shown in table 1. Thus the difference in the catalytic performances of the three crystalline Re–Sb–O catalysts may be due not to the difference in their surface Re oxidation states, but to the difference in their surface structures. Further investigation on the detail of active species is needed to explore the ammoxidation reaction mechanism. Nevertheless, $SbRe_2O_6$ which is a new family of Re-based mixed oxide may provide a promising catalytic system for ammoxidation of hydrocarbons.

4. Conclusions

(1) The three crystalline Re–Sb–O compounds $SbRe_2O_6$, $SbOReO_4 \cdot 2H_2O$ and $Sb_4Re_2O_{13}$ were active for the selective ammoxidation of i-C_4H_8 to methacrylonitrile. $SbRe_2O_6$ was much superior to the other compounds.

(2) The performances of the copr.$SbRe_2O_x$ and Re_2O_7/Sb_2O_3 catalysts were much worse than that of the $SbRe_2O_6$ catalyst.

(3) The $SbRe_2O_6$ catalyst was also active for the selective ammoxidation of C_3H_6 to acrylonitrile. The selectivity to acrylonitrile was improved dramatically by increasing the reaction temperature.

(4) From comparison of the catalytic performances of different samples examined in this work, it is concluded that Re is prerequisite to the ammoxidation catalysis of the Re–Sb–O compounds and the presence of Sb made a positive contribution to the performance for methacrylonitrile synthesis.

(5) No structural change in the bulk and surface of $SbRe_2O_6$ was observed after the ammoxidation of i-C_4H_8 and C_3H_6.

(6) The good performance of $SbRe_2O_6$ for the ammoxidation may be relevant to the octahedral $(Re_2O_6)^{3-}$ layer structure connecting with $(SbO)^+$ chains through Re–O–Sb bonds.

Acknowledgement

This work has been supported by Core Research for Evolutional Science and Technology (CREST) of Japan Science and Technology Corporation (JST).

References

[1] J.C. Mol, Catal. Today 51 (1999) 289.
[2] J. Okal, L. Kepinski, L. Krajczky and M. Drozd, J. Catal. 188 (1999) 140.
[3] W.H. Davenport, V. Kollonitsch and C.H. Kline, Ind. Eng. Chem. 60 (1968) 10.
[4] R. Thomas, E.M. van Oers, V.H.J. de Beer, J. Medema and J.A. Moulijn, J. Catal. 67 (1982) 241.
[5] J. Räty and T.A. Pakkanen, Catal. Lett. 65 (2000) 175.
[6] L. Wang, R. Ohnishi and M. Ichikawa, J. Catal. 190 (2000) 276.
[7] R. Ohnishi, K. Issoh, L. Wang and M. Ichikawa, Stud. Surf. Sci. Catal. 130 (2000) 3603.
[8] D.S. Kim and I.E. Wachs, J. Catal. 141 (1993) 419.
[9] W.T.A. Harrison, A.V.P. Mcmanus, A.P. Kaminsky and A.K. Cheetham, Chem. Mater. 5 (1993) 1631.
[10] Y. Yuan, H. Liu, H. Imoto, T. Shido and Y. Iwasawa, Chem. Lett. (2000) 674.
[11] Y. Yuan, T. Shido and Y. Iwasawa, J. Chem. Soc. Chem. Commun. (2000) 1421.
[12] I.E. Wachs, G. Deo, A. Andreini, M.A. Vuurman and M. de Boer, J. Catal. 160 (1996) 322.
[13] Y. Moro-oka and W. Ueda, Adv. Catal. 40 (1994) 233.
[14] R.K. Grasselli, Catal. Today 49 (1999) 141.
[15] S. Albonetti, F. Cavani and F. Trifirò, Catal. Rev. Sci. Eng. 38 (1996) 413.
[16] G. Centi and F. Trifirò, Catal. Rev. Sci. Eng. 28 (1986) 165.
[17] J. Nilsson, A.R. Land-Canovas, S. Hansen and A. Andersson, J. Catal. 186 (1999) 442.
[18] H. Liu, E.M. Gaigneaux, H. Imoto, T. Shido and Y. Iwasawa, J. Phys. Chem. B 104 (2000) 2033.
[19] E.M. Gaigneaux, H. Liu, H. Imoto, T. Shido and Y. Iwasawa, Topics Catal. 11–12 (2000) 185.
[20] H. Liu, E.M. Gaigneaux, H. Imoto, T. Shido and Y. Iwasawa, Appl. Catal. A 202 (2000) 251.
[21] F.J. Berry, Adv. Catal. 30 (1981) 97.
[22] H. Watanabe and H. Imoto, Inorg. Chem. 36 (1997) 4610.
[23] H. Watanabe, H. Imoto and H. Tanaka, J. Solid State Chem. 138 (1998) 245.
[24] I.Z. Onsan and D.L. Trimm, J. Catal. 38 (1975) 257.
[25] G. Centi, F. Marchi and S. Perathoner, Appl. Catal. A 149 (1997) 225.
[26] E.S. Shpiro, V.I. Avaev, G.V. Antoshin, M.A. Ryashentseva and Kh.M. Minachev, J. Catal. 44 (1978) 402.
[27] A. Cimino, B.A. de Angelis, D. Gazzoli and M. Valigi, Z. Anorg. Allg. Chem. 460 (1980) 86.
[28] H. Liu, H. Imoto, T. Shido and Y. Iwasawa, J. Catal., submitted.