Selective ammoxidation of isobutane on a crystalline $SbRe_2O_6$ catalyst

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The catalytic ammoxidation of isobutane to methacrylonitrile at 673 K proceeds on a new class of Re mixed-oxide $SbRe_2O_6$ with alternate $(Re_2O_6)^{3-}$ and $(SbO)^+$ layers, where ammonia is prerequisite for the C–H bond scission of isobutane.

Much attention has been devoted to selective ammoxidation of light alkanes from both fundamental and industrial interests. To date, a large number of multicomponent metal-oxide catalysts containing V, Mo, *etc.* have been explored to develop efficient catalytic systems for selective ammoxidation. However, owing to the inertness of light alkanes, very few catalysts have showed good performances that are comparable to those for the corresponding alkenes.[1–4] There is thus a clear need to develop new catalytic materials for the selective ammoxidation of light alkanes. Except for the oxidation of methanol and ethanol, compared with V, Mo and W there are limited uses of Re as a key element in selective ammoxidation/oxidation, in spite of Re having similar redox properties to those of V, Mo and W oxides.[5–7] Here, we report a first Re mixed-oxide catalyst (crystalline $SbRe_2O_6$) active for the selective ammoxidation of isobutane (i-C_4H_{10}) to methacrylonitrile (MAN) at 673 K, where NH_3 not only stabilizes the catalyst but also promotes the C–H bond scission of i-C_4H_{10}.

$SbOReO_4{\cdot}2H_2O$, $SbRe_2O_6$ and $Sb_4Re_2O_{13}$ were synthesized in the similar way to that reported previously.[6–12] The specific surface areas of the three samples were approximately 1 m^2 g^{-1}. For comparison, Sb_2O_3-supported Re_2O_7 catalyst (Re_2O_7/Sb_2O_3; 10 wt% Re) was prepared by an impregnation method using an aqueous solution of NH_4ReO_4.[9] A coprecipitated $SbRe_2O_x$ catalyst (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 ions from the sample. Ammoxidation reactions were carried out in a continuous-flow, fixed-bed reactor at 673 K under the conditions of 10% i-C_4H_{10}, 15% NH_3 and 25% O_2 balanced with He and a gas-hourly-space-velocity (GHSV) of 5000 h^{-1} at atmospheric pressure. Prior to each run, the catalysts (typically 0.3 g) were pretreated at 673 K under He for 1 h. The reactants and products were analyzed by two on-line gas chromatographs with Unibeads C, Gaskuropack 54 and VZ-10 columns. The conversion of NH_3 to N_2 and NO_x was $<10\%$ under the present reaction conditions.

Table 1 presents the conversions, reaction rates and selectivities of the i-C_4H_{10} ammoxidation on the various Re–Sb–O catalysts and bulk ReO_x and SbO_x at 673 K. $SbOReO_4{\cdot}2H_2O$, $Sb_4Re_2O_{13}$ and Sb oxides such as Sb_2O_3 and Sb_2O_4 showed no activity. Bulk Re_2O_7 was active solely for i-C_4H_{10} combustion to CO_2. Bulk ReO_3 and ReO_2 produced MAN, but the selectivities were lower than 10% and the main product was CO_2. Re_2O_7/Sb_2O_3 or mechanically mixed $Re_2O_7{\cdot}Sb_2O_3$ samples showed almost no activity for the i-C_4H_{10} ammoxidation either. Copr.$SbRe_2O_x$ produced i-C_4H_8 (20.6% selectivity), but no formation of MAN was observed. Isobutane combustion was dominant also with this catalyst. Only the $SbRe_2O_6$ among these samples was active for the ammoxidation of i-C_4H_{10} to MAN. The selectivities to MAN and to the sum of MAN + i-C_4H_8 at the steady-state conversion of 4.4% were 44.9 and 84.3%, respectively. A decrease in the GHSV from 5000 to 2500 h^{-1} increased the conversion to 7.5% while keeping good selectivities to MAN and to MAN + i-C_4H_8, as shown in parentheses in Table 1.

The active $SbRe_2O_6$ compound consists of connected, alternate octahedral $(Re_2O_6)^{3-}$ and $(SbO)^+$ layers and grows as thin plate-like crystals preferably exposing the (100) plane.[12] The square basal (100) faces of $SbRe_2O_6$ crystals remained unchanged before and after the ammoxidation at 673 K as imaged by scanning electron microscopy. Further, neither change nor modification of the surface composition and crystallinity were observed by means of X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and *in-situ* micro confocal laser Raman spectroscopy. The results indicate that the crystalline $SbRe_2O_6$ works as a promising catalyst for the ammoxidation. The fresh $SbOReO_4{\cdot}2H_2O$ and $Sb_4Re_2O_{13}$ possess Re^{7+} species, but the Re species were reduced to two valent states (possibly Re^{6+} and Re^{4+}) which exhibit XPS binding energies of 42.3 and 44.7 eV, and 45.1 and 47.5 eV for Re $4f_{7/2}$ and Re $4f_{5/2}$, respectively (compared to C 1s = 284.6 eV) under the ammoxidation conditions. These binding energies are similar to those for the $SbRe_2O_6$ surface after ammoxidation at 673 K. Thus, the difference in the catalytic performances of the crystalline Re–Sb–O catalysts may not be

Table 1 Isobutane ammoxidation on different Re–Sb–O catalysts and bulk ReO_x and SbO_x at 673 K

	Conversion (%)	Reaction rate/ µmol g-cat^{-1} h^{-1}	Selectivity (%)				
			MAN + i-C_4H_8	MAN	i-C_4H_8	CH_3CN	CO_2
$SbRe_2O_6$	4.4 (7.5)[a]	785.6 (669.5)[a]	84.3 (82.6)[a]	44.9 (44.2)[a]	39.4 (38.4)[a]	4.7 (5.6)[a]	10.2 (11.4)[a]
$SbOReO_4{\cdot}2H_2O$	0	0	—	—	—	—	—
$Sb_4Re_2O_{13}$	0	0	—	—	—	—	—
mix.$Re_2O_7{\cdot}Sb_2O_3$	0.5	89.3	trace	0	trace	0	~100
copr.$SbRe_2O_x$	0.4	71.4	20.6	0	20.6	0	79.4
Re_2O_7/Sb_2O_3	0.1	17.8	0	0	0	0	100
Re_2O_7	11.6	2071.3	0	0	0	0	100
ReO_3	2.1	374.9	31.5	7.7	23.8	25.7	42.6
ReO_2	5.6	999.9	31.0	9.1	21.9	32.1	36.4
Sb_2O_3	0	0	—	—	—	—	—
Sb_2O_4	0	0	—	—	—	—	—

[a] The data listed in parentheses were obtained at a GHSV of 2500 h^{-1}.

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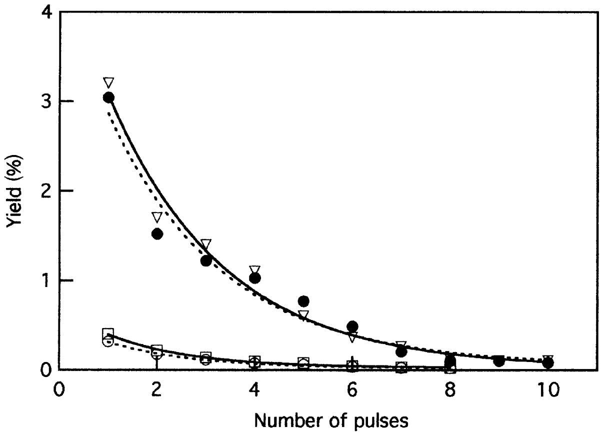

Fig. 1 Yields of MAN (∇, □) and i-C_4H_8 (●, ○) as a function of the number of pulses of i-C_4H_{10} alone (□, ○) and an i-C_4H_{10}–O_2 mixture (∇, ●) on an NH_3-preadsorbed $SbRe_2O_6$ catalyst at 673 K.

due to the difference in their surface Re oxidation states, but to the difference in their surface structures. This is entirely different from the finding in the selective oxidation of i-C_4H_{10} (773 K) and i-C_4H_8 (673 K) to methacrolein (MAL) that the activities of the three crystalline Re–Sb–O compounds are ascribed to a cooperation between Re_2O_7 and $Sb_4Re_2O_{13}$, both being formed by decomposition of the compounds under the oxidation conditions.[8–10] It is also different from the feature observed in the ammoxidation of i-C_4H_8 where the three Re–Sb–O compounds are more or less active at 673 K.[13]

It is to be noted that $SbRe_2O_6$ was inactive for i-C_4H_{10} selective oxidation as well as for the total oxidation at 673 K in the absence of NH_3, whereas it exhibited a good performance for i-C_4H_{10} ammoxidation at 673 K (Table 1). These results may indicate a promoting effect of NH_3 on the C–H activation in i-C_4H_{10}. To examine the role of NH_3, a series of pulse experiments were conducted on $SbRe_2O_6$ at 673 K in Fig. 1. No products were produced by pulsing i-C_4H_{10} alone or an i-C_4H_{10}–O_2 mixture on to the $SbRe_2O_6$ catalyst, which indicates that no C–H bond breaking in i-C_4H_{10} molecules occurs on the catalyst. However, when the catalyst was pretreated with an NH_3 pulse (the catalyst surface was saturated with NH_x), i-C_4H_{10} was converted to MAN and i-C_4H_8. The promotion effect of NH_3 pretreatment on the formation of MAN and i-C_4H_8 was more remarkable with the i-C_4H_{10}–O_2 pulse reaction as shown in Fig. 1. The formation of MAN and i-C_4H_8 decreased with the number of the i-C_4H_{10}–O_2 pulses. The pulse experiments show that adsorbed NH_x species are incorporated to the ammoxidation of i-C_4H_{10} to form MAN. These results demonstrate that NH_3 not only behaves as a reactant but also plays a crucial role in enhancing and/or generating the activity of $SbRe_2O_6$ for the dehydrogenation (C–H bond breaking) of i-C_4H_{10} to i-C_4H_8. Upon pulsing NH_3 on $SbRe_2O_6$, N_2 and H_2O were produced indicating the reaction of NH_3 with the lattice oxygen atoms of $SbRe_2O_6$ to form oxygen vacancies that may also be responsible for the C–H bond breaking. To our knowledge, $SbRe_2O_6$ is the first case where NH_3 changes an inactive catalyst to an active one for light alkane activation, although promoting effects of NH_3 have been documented.[14,15] Further study is necessary for depicting a detailed mechanism of the promoting effect of NH_3 on the $SbRe_2O_6$ selective catalysis.

In conclusion, a new class of Re mixed-oxide $SbRe_2O_6$ catalyzes the selective ammoxidation of i-C_4H_{10} to MAN. The activity of $SbRe_2O_6$ may be relevant partly to its specific crystal structure. The presence of ammonia is considered to be prerequisite, not only for maintaining the stable crystal structure of $SbRe_2O_6$, but also for promoting $SbRe_2O_6$ activity for C–H bond breaking in i-C_4H_{10} under the ammoxidation conditions.

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Notes and references

1 R. K. Grasselli, *Catal. Today*, 1999, **49**, 141.
2 S. Albonetti, F. Cavani and F. Trifiro, *Catal. Rev.-Sci. Eng.*, 1996, **38**, 413.
3 C. J. Pereira, *Science*, 1999, **285**, 670.
4 T. Inoue, S. T. Oyama, H. Imoto, K. Asakura and Y. Iwasawa, *Appl. Catal., A*, 2000, **191**, 131.
5 J.-M. Jehng, H. Hu, X. Gao and I. E. Wachs, *Catal. Today*, 1996, **28**, 335.
6 W. T. A. Harrison, A. V. P. Mcmanus, A. P. Kaminsky and A. K. Cheetham, *Chem. Mater.*, 1993, **5**, 1631.
7 Y. Yuan, H. Liu, H. Imoto, T. Shido and Y. Iwasawa, *Chem. Lett.*, 2000, 674.
8 H. Liu, E. M. Gaigneaux, H. Imoto, T. Shido and Y. Iwasawa, *J. Phys. Chem. B*, 2000, **104**, 2033.
9 E. M. Gaigneaux, H. Liu, H. Imoto, T. Shido and Y. Iwasawa, *Top. Catal.*, 2000, **11–12**, 185.
10 H. Liu, E. M. Gaigneaux, H. Imoto, T. Shido and Y. Iwasawa, *Appl. Catal. A: General.*, 2000, **202**, 251.
11 H. Watanabe and H. Imoto, *Inorg. Chem.*, 1997, **36**, 4610.
12 H. Watanabe, H. Imoto and H. Tanaka, *J. Solid State Chem.*, 1998, **138**, 245.
13 H. Liu, H. Imoto, T. Shido and Y. Iwasawa, submitted for publication.
14 V. D. Sokolovskii, A. A. Davydov and O. Yu. Ovsitser, *Catal. Rev.-Sci. Eng.*, 1995, **37**, 425.
15 G. Centi and S. Perathoner, *Catal. Rev.-Sci. Eng.*, 1998, **40**, 175.