

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 $(\text{Re}_2\text{O}_6)^{3-}$ and $(\text{SbO})^+$ 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 ($\text{i-C}_4\text{H}_{10}$) to methacrylonitrile (MAN) at 673 K, where NH_3 not only stabilizes the catalyst but also promotes the C–H bond scission of $\text{i-C}_4\text{H}_{10}$.

$\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$, SbRe_2O_6 and $\text{Sb}_4\text{Re}_2\text{O}_{13}$ were synthesized in the similar way to that reported previously.^{6–12} The specific surface areas of the three samples were approximately $1 \text{ m}^2 \text{ g}^{-1}$. For comparison, Sb_2O_3 -supported Re_2O_7 catalyst ($\text{Re}_2\text{O}_7/\text{Sb}_2\text{O}_3$; 10 wt% Re) was prepared by an impregnation method using an aqueous solution of NH_4ReO_4 .⁹ A coprecipitated SbRe_2O_x catalyst ($\text{copr.SbRe}_2\text{O}_x$) 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% $\text{i-C}_4\text{H}_{10}$, 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 $\text{i-C}_4\text{H}_{10}$ ammoxidation on the various Re–Sb–O catalysts and bulk ReO_x and SbO_x at 673 K. $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Sb}_4\text{Re}_2\text{O}_{13}$ and Sb oxides such as Sb_2O_3 and Sb_2O_4 showed no activity. Bulk Re_2O_7 was active solely for $\text{i-C}_4\text{H}_{10}$ 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 . $\text{Re}_2\text{O}_7/\text{Sb}_2\text{O}_3$ or mechanically mixed $\text{Re}_2\text{O}_7\text{-Sb}_2\text{O}_3$ samples showed almost no activity for the $\text{i-C}_4\text{H}_{10}$ ammoxidation either. $\text{Copr.SbRe}_2\text{O}_x$ produced $\text{i-C}_4\text{H}_8$ (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 $\text{i-C}_4\text{H}_{10}$ to MAN. The selectivities to MAN and to the sum of MAN + $\text{i-C}_4\text{H}_8$ 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 + $\text{i-C}_4\text{H}_8$, as shown in parentheses in Table 1.

The active SbRe_2O_6 compound consists of connected, alternate octahedral $(\text{Re}_2\text{O}_6)^{3-}$ and $(\text{SbO})^+$ 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 $\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Sb}_4\text{Re}_2\text{O}_{13}$ 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 $\text{Re } 4f_{7/2}$ and $\text{Re } 4f_{5/2}$, respectively (compared to $\text{C } 1s = 284.6 \text{ eV}$) 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/ $\mu\text{mol g-cat}^{-1} \text{ h}^{-1}$	Selectivity (%)				
			MAN + $\text{i-C}_4\text{H}_8$	MAN	$\text{i-C}_4\text{H}_8$	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
$\text{SbOReO}_4 \cdot 2\text{H}_2\text{O}$	0	0	—	—	—	—	—
$\text{Sb}_4\text{Re}_2\text{O}_{13}$	0	0	—	—	—	—	—
$\text{mix.Re}_2\text{O}_7\text{-Sb}_2\text{O}_3$	0.5	89.3	trace	0	trace	0	~ 100
$\text{copr.SbRe}_2\text{O}_x$	0.4	71.4	20.6	0	20.6	0	79.4
$\text{Re}_2\text{O}_7/\text{Sb}_2\text{O}_3$	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} .

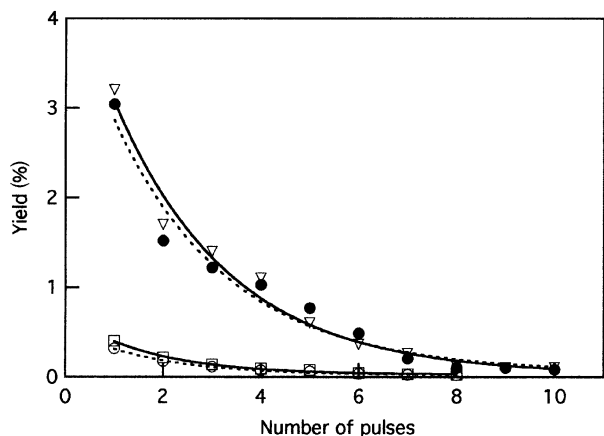


Fig. 1 Yields of MAN (▽, □) and i-C₄H₈ (●, ○) as a function of the number of pulses of i-C₄H₁₀ alone (□, ○) and an i-C₄H₁₀-O₂ mixture (▽, ●) on an NH₃-preadsorbed SbRe₂O₆ catalyst at 673 K.

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-C₄H₁₀ (773 K) and i-C₄H₈ (673 K) to methacrolein (MAL) that the activities of the three crystalline Re-Sb-O compounds are ascribed to a cooperation between Re₂O₇ and Sb₄Re₂O₁₃, 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-C₄H₈ where the three Re-Sb-O compounds are more or less active at 673 K.¹³

It is to be noted that SbRe₂O₆ was inactive for i-C₄H₁₀ selective oxidation as well as for the total oxidation at 673 K in the absence of NH₃, whereas it exhibited a good performance for i-C₄H₁₀ ammoxidation at 673 K (Table 1). These results may indicate a promoting effect of NH₃ on the C-H activation in i-C₄H₁₀. To examine the role of NH₃, a series of pulse experiments were conducted on SbRe₂O₆ at 673 K in Fig. 1. No products were produced by pulsing i-C₄H₁₀ alone or an i-C₄H₁₀-O₂ mixture on to the SbRe₂O₆ catalyst, which indicates that no C-H bond breaking in i-C₄H₁₀ molecules occurs on the catalyst. However, when the catalyst was pretreated with an NH₃ pulse (the catalyst surface was saturated with NH_x), i-C₄H₁₀ was converted to MAN and i-C₄H₈. The promotion effect of NH₃ pretreatment on the formation of MAN and i-C₄H₈ was more remarkable with the i-C₄H₁₀-O₂ pulse reaction as shown in Fig. 1. The formation of MAN and i-C₄H₈ decreased with the number of the i-C₄H₁₀-O₂ pulses. The pulse experiments show that adsorbed NH_x species are incorporated to the ammoxidation of i-C₄H₁₀ to form MAN. These results demonstrate that NH₃ not only behaves as a reactant but also

plays a crucial role in enhancing and/or generating the activity of SbRe₂O₆ for the dehydrogenation (C-H bond breaking) of i-C₄H₁₀ to i-C₄H₈. Upon pulsing NH₃ on SbRe₂O₆, N₂ and H₂O were produced indicating the reaction of NH₃ with the lattice oxygen atoms of SbRe₂O₆ to form oxygen vacancies that may also be responsible for the C-H bond breaking. To our knowledge, SbRe₂O₆ is the first case where NH₃ changes an inactive catalyst to an active one for light alkane activation, although promoting effects of NH₃ have been documented.^{14,15} Further study is necessary for depicting a detailed mechanism of the promoting effect of NH₃ on the SbRe₂O₆ selective catalysis.

In conclusion, a new class of Re mixed-oxide SbRe₂O₆ catalyzes the selective ammoxidation of i-C₄H₁₀ to MAN. The activity of SbRe₂O₆ 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 SbRe₂O₆, but also for promoting SbRe₂O₆ activity for C-H bond breaking in i-C₄H₁₀ under the ammoxidation conditions.

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