# Investigation of the Oxidizing Species in the V—Sb-Oxide Catalyst Prepared by the Sol-Gel Method

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The nature of the oxidizing species in V—Sb-oxide catalyst has been studied using transient kinetic techniques: temperature-programmed desorption and temperature-programmed reduction. Three strongly-bound molecular oxygen species having desorption peak maxima of 863 K, 940 K, and 1053 K were observed by temperature-programmed desorption. From both the high desorption activation energies and the total amounts of oxygen desorbed, it can be concluded that these oxygen species were originally from the lattice of V—Sb-oxide catalyst. Three peak maxima at 750 K, 786 K, and 911 K were observed in the rate of $H_2$ consumption indicating the presence of three types of kinetically different oxygen states in the catalyst.

The commercial production of acrylonitrile is currently performed by the ammoxidation of propene using Bi-molybdate- or Fe-antimonate-based catalysts. However, with the achievement of using alkane as a feedstock in the manufacturing of maleic anhydride from butane, more research has been carried out on the possibility of using propane for a single-step synthesis of acrylonitrile. The alternative choice of propane is due to its significant price compared to propene. Recently, many reports have disclosed that V—Sb-oxide-based catalyst gave the best performance for this reaction [1—5].

The purpose of this paper is to investigate the nature of the oxidants in/on V—Sb-oxide catalyst prepared by the sol-gel method. This is done by using two techniques: $O_2$ temperature-programmed desorption (TPD) and $H_2$ temperature-programmed reduction (TPR).

## EXPERIMENTAL

The gases, $O_2$, He, and 10 % $H_2$ in Ar (Malaysian Oxygen Berhad, MOX) were used directly from the cylinder. $V_2O_5$ (Fluka) and $Sb_2O_3$ (BDH).

The catalyst produced was characterized by X-ray diffraction (XRD) using the powder method carried out with a Shimadzu Diffractometer, Model XRD6000 with $CuK_\alpha$ radiation at ambient temperature. The specific surface area was measured by using nitrogen adsorption at 77 K (Micromeritics ASAP 2000).

TPD and TPR experiments were conducted using a Micromeritics 2900 TPD/TPR apparatus with a thermal conductivity detector (TCD). The reactor was heated at a rate of 20 K min$^{-1}$ up to 1173 K.

## Catalyst

The catalyst, V—Sb-oxide with $n(Sb):n(V) = 1.0$ was prepared by the sol-gel method as reported in patents [6—8]. About 90 cm$^3$ of an aqueous solution of 30 % $H_2O_2$ was added slowly to a slurry of 3.85 g of $V_2O_5$ in 300 cm$^3$ of distilled water maintained in an ice-bath for 2 h, stirring throughout. The solution was then heated up to 373 K and maintained under stirring and reflux. Initially, a sol and then a gel of vanadium monoperoxide was formed, with a parallel increase in the viscosity of the solution. Successively, 6.18 g of $Sb_2O_3$ was added to the viscous solution to provide the required $n(Sb):n(V)$ ratio of 1. A dark grey-green solution was formed and was maintained under stirring and reflux for 3 h, after which water was removed by using a hot plate. The solid recovered was dried overnight at 413 K. Then, the solid was calcined in air at 873 K for 3 h.

## RESULTS AND DISCUSSION

The X-ray diffractogram (Fig. 1) indicates the presence of well crystallized rutile $VSbO_4$ phase [5] which was characterized by peaks at $2\Theta/^\circ = 27.3$, 35.4, 38.9, 40.5, 53.7, 56.3, 63.9, and 68.3. A weak reflection of $\beta$-$Sb_2O_4$ is also observed in the catalyst. The specific surface area was found to be 56.7 m$^2$ g$^{-1}$.

The oxygen desorption spectrum shown in Fig. 2
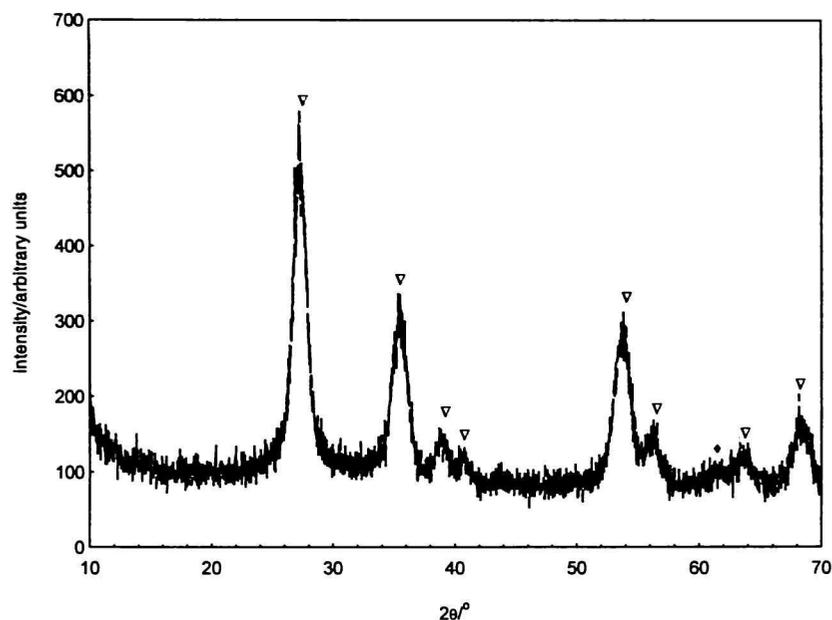
**Fig. 1.** XRD pattern of V—Sb-oxide catalyst. ∇ VSbO$_4$, ♦ $\beta$-Sb$_2$O$_4$.
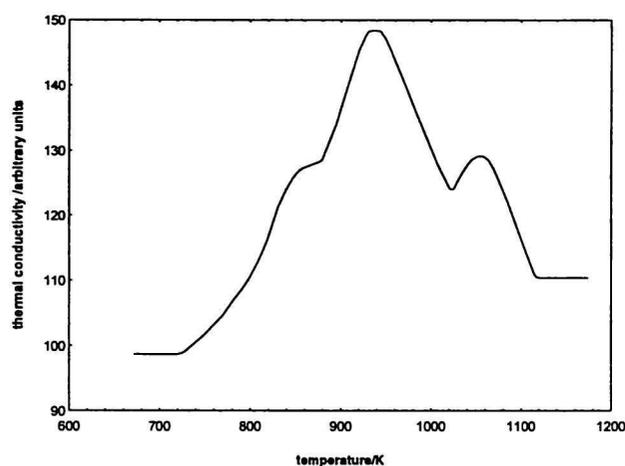


**Fig. 2.** Oxygen temperature-programmed desorption spectrum from freshly oxidized V—Sb-oxide catalyst.

was obtained by pretreating the catalyst by heating it to 673 K in an oxygen flow (10$^5$ Pa, 25 cm$^3$ min$^{-1}$), holding it under that stream at 673 K for 1 h, before cooling it to ambient temperature. Then the flow was switched to helium and the temperature was raised to 1173 K (20 K min$^{-1}$). The concentration of the oxygen was measured by following the conductivity of the oxygen.

The onset of O$_2$ evolution occurs at $\approx$ 723 K with two distinct peak maxima at 940 K and 1053 K and a shoulder at 863 K. Therefore at least three distinct different types of oxygen species exist on/in the V—Sb-oxide catalyst. The peaks at 863 K, 940 K, and 1053 K correspond to desorption activation energies of 238 kJ mol$^{-1}$, 259 kJ mol$^{-1}$, and 291 kJ mol$^{-1}$, respectively (Table 1). These values are too high for the

desorbing species to have been chemisorbed by molecular oxygen. It is probable therefore that the oxygen desorbing at this temperature results from lattice oxygen combining at the surface. The desorption activation energies were obtained by solution of the Redhead equation [9]

$$\frac{E_d}{RT_m^2} = \left(\frac{A}{\beta}\right) \exp\left(\frac{-E_d}{RT_m}\right) \qquad (1)$$

where $E_d$ is the desorption activation energy (kJ mol$^{-1}$), $A$ is the desorption A-factor (10$^{13}$ s$^{-1}$, assumed), $R$ is the gas constant (J K$^{-1}$ mol$^{-1}$), $\beta$ is the heating rate (K s$^{-1}$), and $T_m$ (K) is the temperature of the peak maximum.

Corroborative evidence that these oxygen species derived from the lattice of the V—Sb-oxide catalyst is to be found by consideration of the amounts of oxygen desorbed. The total number of oxygen atoms desorbed is 2.7 × 10$^{21}$ g$^{-1}$ with a coverage of 4.8 × 10$^{15}$ cm$^{-2}$. With the assumption that the proportion of oxygen ions on the surface is roughly stoichiometric, the surface oxygen ion population is 6.9 × 10$^{14}$ cm$^{-2}$. Since the atom/ion coverage obtained is 4.8 × 10$^{15}$ cm$^{-2}$, this would correspond to about 6.8 monolayers of chemisorbed oxygen. This result confirms the conclusion that the oxygen desorbing at these temperatures is lattice oxygen. In our previous study on (VO)$_2$P$_2$O$_7$ catalyst [10], oxygen was evolved from the lattice in two desorption peaks at 993 K and 1023 K on temperature programming. This oxygen was also found to be completely selective in oxidation of butane, butene, and butadiene. Therefore lattice oxygen desorbed from V—Sb-oxide is also suggested to be highly selective in the propane ammoxidation.

**Table 1.** Amount of Oxygen Desorbed and Desorption Activation Energies Obtained by Temperature-Programmed Desorption from V—Sb-Oxide Catalyst

| Peaks | $T_m/K$ | Desorption activation energy, $E_d$ | Total amount of oxygen desorbed | Total amount of oxygen atom desorbed | Atom coverage |
|---|---|---|---|---|---|
| | | kJ mol$^{-1}$ | mol g$^{-1}$ | g$^{-1}$ | cm$^{-2}$ |
| 1 | 863 | 238 | $1.3 \times 10^{-3}$ | $7.8 \times 10^{20}$ | $1.4 \times 10^{15}$ |
| 2 | 940 | 259 | $2.6 \times 10^{-3}$ | $1.6 \times 10^{21}$ | $2.8 \times 10^{15}$ |
| 3 | 1053 | 291 | $6.9 \times 10^{-4}$ | $4.1 \times 10^{20}$ | $7.2 \times 10^{14}$ |
| Total oxygen atom desorbed | | | $4.5 \times 10^{-3}$ | $2.7 \times 10^{21}$ | $4.8 \times 10^{15}$ |

Specific surface area = 56.7 m$^2$ g$^{-1}$. Mass of catalyst = 0.32 g.

**Table 2.** Total Number of Oxygen Atoms Removed from the V—Sb-Oxide Catalyst by Reduction in H$_2$/Ar

| Peaks | $T_m/K$ | Reduction activation energy, $E_r$ | Oxygen atom removed from the catalyst | Oxygen atom removed from the catalyst | Atom coverage | Monolayer of oxygen removed* |
|---|---|---|---|---|---|---|
| | | kJ mol$^{-1}$ | mol g$^{-1}$ | g$^{-1}$ | cm$^{-2}$ | |
| 1 | 750 | 130 | $3.3 \times 10^{-3}$ | $2.0 \times 10^{21}$ | $3.5 \times 10^{15}$ | 5.0 |
| 2 | 786 | 136 | $4.3 \times 10^{-3}$ | $2.6 \times 10^{21}$ | $4.6 \times 10^{15}$ | 6.7 |
| 3 | 911 | 158 | $8.5 \times 10^{-3}$ | $5.1 \times 10^{21}$ | $9.0 \times 10^{15}$ | 12.9 |
| Total oxygen atom removed | | | $1.6 \times 10^{-2}$ | $9.8 \times 10^{21}$ | $1.7 \times 10^{16}$ | 24.6 |

Specific surface area = 56.7 m$^2$ g$^{-1}$. Mass of catalyst = 0.03 g. *The monolayers of oxygen removed are calculated by dividing the oxygen atom coverage by $6.9 \times 10^{14}$ cm$^{-2}$ – the stoichiometric value of monolayer oxygen coverage.
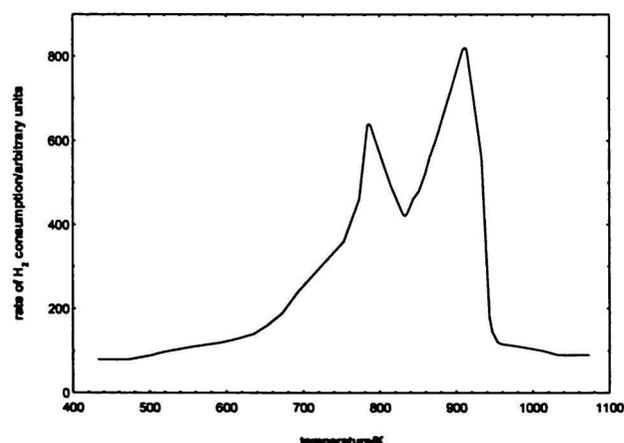


**Fig. 3.** H$_2$/Ar temperature-programmed reduction of V—Sb-oxide catalyst.

Additional information as to the nature and the oxidizing species available from the V—Sb-oxide catalyst was obtained by temperature-programmed reduction in H$_2$/Ar stream (10 % H$_2$ in argon) of a fresh sample of catalyst (0.03 g) raising the temperature from room temperature to 1173 K at 20 K min$^{-1}$ in that stream. The TPR profile in H$_2$ so obtained is shown in Fig. 3.

Two distinct peak maxima are observed at 786 K and 911 K with a shoulder at 750 K in the rate of H$_2$ consumption. This oxygen which is thermally induced to desorb from this V—Sb-oxide catalyst does so with peak maxima of 863 K, 940 K, and 1053 K. The peak maximum at 750 K which occurs in the rate

of H$_2$ consumption could result from the H$_2$ reacting with this oxygen which is thermally evolving from the lattice at this temperature.

The onset of reduction of the surface oxygen by H$_2$ is at about 488 K. A rough estimate of the amount of H$_2$ consumed (oxygen atom removed from the lattice) at two separate maxima was made by deconvoluting the hydrogen peaks. The atom amounts are $2.0 \times 10^{21}$ g$^{-1}$ for the 750 K, $2.6 \times 10^{21}$ g$^{-1}$ for the 786 K, and $5.1 \times 10^{21}$ g$^{-1}$ for the 911 K peak. These are listed in Table 2.

The amount of oxygen released from the catalyst in the first peak is approximately the same as the amount released from the catalyst by desorption (Fig. 2). This and the fact that the peak maximum temperature for the rate of hydrogen consumption is only slightly lower than the oxygen desorption peak maximum suggests that these oxygen species are the same and that the rate-limiting step in the production of H$_2$O is the migration of these oxygen species from the lattice to the surface. Values of the activation energies for the reaction

$$H_2 + O(s) \rightarrow H_2O + \square \qquad (A)$$
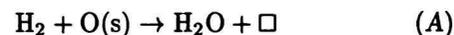
where O(s) is a surface lattice oxygen species and $\square$ is an oxygen vacancy can be obtained from a modified version of the Redhead equation

$$\frac{E_r}{RT_m^2} = \left(\frac{A_r}{\beta}\right) [H_2]_m \exp\left(\frac{-E_r}{RT_m}\right) \qquad (2)$$

where $T_m$ is the peak maximum temperature (K) in the rate of consumption of H$_2$, $E_r$ is the reduction

activation energy (kJ mol$^{-1}$), $A_r$ is the reduction pre-exponential term (cm$^3$ mol$^{-1}$ s$^{-1}$) which is given by the value of a standard collision number of $10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$, and $[H_2]_m$ is the gas phase concentration of hydrogen (mol cm$^{-3}$) at the peak maximum. The values obtained for the peaks at 750 K, 786 K, and 911 K are 130 kJ mol$^{-1}$, 136 kJ mol$^{-1}$, and 158 kJ mol$^{-1}$, respectively.

## CONCLUSION

The oxygen temperature-programmed desorption of V—Sb-oxide catalyst showed lattice oxygen to be desorbed in three states at 863 K, 940 K, and 1053 K. The $H_2$ reduction of this catalyst gave three peaks at 750 K, 786 K, and 911 K. The amount of oxygen removed from the lowest peak in the rate of $H_2$ consumption was the same as that evolved from the catalyst by TPD. The rate-determining step in the oxidation of $H_2$ to $H_2O$ appears to be the diffusion of the oxygen from the bulk of the lattice to the surface.

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