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Effect of calcination temperatures on physicochemical properties of vanadium–antimony mixed oxide catalysts

R. Irmawati*, M. Asri Razali, Y.H. Taufiq-Yap, Z. Zainal

Department of Chemistry, Faculty of Science and Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

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Abstract

A vanadium–antimony mixed oxide catalyst has been prepared via slurry method. The precursors obtained were calcined in different calcination temperatures, i.e. 673, 773 and 873 K and compared its effect on the physicochemical properties of the oxide. These catalysts were characterised by X-ray diffraction (XRD), FTIR spectroscopy, BET surface area measurements and scanning electron microscopy (SEM). Calcination at high temperature was found to promote the formation of $\approx VSbO_4$ and α-Sb_2O_4 phase, while the formation of Sb_6O_{13} phase was inhibited. The nature of the oxidizing species in the VSbO catalysts were studied by temperature programmed desorption (TPD) of oxygen and temperature programmed reduction (TPR) of hydrogen. Results revealed that two types of kinetically different oxygen states exist in the catalysts and calcination at high temperature, i.e. 873 K produced a more reducible sample.

Keywords: Vanadium–antimony oxide; Propane oxidation; TPD; TPR; Oxidant

1. Introduction

Acrylonitrile (ACN) is an important raw material for the manufacture of synthetic fibre, plastics and rubber. Its world market grew from 1.9 million tonnes in 1994 to 2.2 million tonnes in 2001 with an estimated value of US$ 620 million a year. Until today, the intermediate is industrially produced based on the ammoxidation of propene using oxygen and ammonia in the gas phase feed. However, in recent year, there were developments indicated the possibility of one-stage synthesis of ACN from propane without undergone propene intermediate. The choice to make use of saturated hydrocarbon as a new feedstock is due to the abundance of the hydrocarbon, hence the cheap price makes the catalytic process a desirable.

The catalyst reportedly to be efficient in the direct transformation of propane to ACN is based on vanadium–antimony mixed oxide [1]. This is due to the ability of the binary vanadium and antimony oxide to form $\approx VSbO_4$ phase with the same structure and characteristic as the well known $FeSbO_4$ phase, which is active for propene ammoxidation, where antimony is the active element [2]. In the mixed vanadium–antimony, two phases are said to be the most active and selective for acrylonitrile formation i.e. $\approx VSbO_4$ and α-Sb_2O_4 phase. Their function is linked to their ability to selectivity transform intermediate propene [3]. Based on the functionality of V species in $\approx VSbO_4$ phase and Sb species in α-Sb_2O_4 phase in the ammoxidation of propane, it is viable to produce the catalysts with the highest amount of these phases.

In the present study, works have been embarked onto synthesising the mixed oxide of vanadium antimonate by opting a slurry method. In this method a hydrated antimony pentoxide suspension was interacted with vanadium compounds and followed subsequently by drying and calcining. The claimed advantage of the method is the possibility to obtain catalysts with high mechanical strength, which makes it possible to utilize them in fluidised bed catalysis. Furthermore, the process flow sheet is simplified significantly, since some of its stage, such as precipitation of antimony hydroxide and vanadium hydroxides by a base from solution, filtration and washing of the obtained precipitates are eliminated, thereby minimised the quantities of wastes.

The samples were prepared in the Sb:V atomic ratio of 3.0. This is particularly important in forming a Sb-rich vanadium–antimony oxide samples. Previous study has

* Corresponding author. Tel.: +603 8946 6786; fax: +603 8943 2508.
E-mail address: irmawati@fsas.upm.edu.my (R. Irmawati).

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mentioned the function of Sb:V ratio of 3.0 in determining the required phase compositions [4].

The objective of the research reported here was to investigate the influence of calcination temperatures towards the physicochemical properties of the vanadium–antimony mixed oxide catalyst. Investigation on the oxidising nature of the calcined samples was also carried out. The characterization technique employed were X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), BET surface area measurements, temperature programmed desorption of oxygen (TPD) and temperature programmed reduction of hydrogen (TPR).

2. Experimental

2.1. Catalysts preparation

Sb_2O_3 (Merck, >99.0%) was contacted with 30% aqueous solution of H_2O_2 (J.T. Baker, 30%) and deionised water to form a milky sol or suspension of hydrated antimony pentoxide. The mixture was refluxed for 5 h. Then, additional 30% H_2O_2 and V_2O_5 (Merck, >99.0%), were added in such amount as to obtain a Sb:V atomic ratio of 3.0.

The mixture was stirred for 15 min until the evolution of gas bubbles stopped. The resulting dark-green slurry was evaporated to near dryness and then dried overnight at 373 K. The samples were later calcined in air at 673, 773 and 873 K for 6 h and were designated as $VSbO_{SM673}$, $VSbO_{SM773}$ and $VSbO_{SM873}$, respectively.

2.2. Catalysts characterization

Immediately after heat treatment, all the samples were subjected to X-ray diffraction analyses. It was carried out using Shimadzu diffractometer model 6000 with Cu Kα radiation to generate diffraction patterns from powder samples at ambient. Fourier transform infrared (FTIR) spectroscopy was carried out with a Perkin Elmer FTIR 1725 X instrument using the KBr disc technique.

The total surface area of powders was measured by the BET (Brunauer–Emmet–Teller) method by performing nitrogen adsorption at liquid nitrogen temperature (77 K). This was done by using Thermo Finnigan Sorptomatic 1990 instrument. Scanning electron microscopy (SEM) was done using a LEO 1530 EPSEM electron microscope. The samples were coated with gold using a Sputter Coater.

The oxygen desorption analysis was obtained by heating the samples to 673 K in an oxygen flow (1 bar, 25 $cm^3\,min^{-1}$) and holding under that stream for 1 h before cooling to ambient temperature. The flow was then switched to helium (1 bar, 25 $cm^3\,min^{-1}$) and the temperature was raised at a heating rate of 5 K min^{-1} to 973 K following the conductivity of the eluted gas.

The temperature programmed reduction was obtained by pretreated the samples by heating it to 473 K in a nitrogen flow (1 bar, 25 $cm^3\,min^{-1}$) before cooling it to ambient temperature. Reaction was carried out in a mixture of 5% hydrogen in argon at the flow of 25 $cm^3\,min^{-1}$ and the temperature was raised at a heating rate of 5 K min^{-1} to 973 K. The reduction was measured by monitoring the hydrogen consumption. Both TPD and TPR experiments were conducted using a Thermo Finnigan TPDRO 1100 instrument utilising a thermal conductivity detector (TCD).

3. Results and discussion

3.1. BET surface area measurements

Table 1 list the value of BET surface area obtained of all samples calcined at 673, 773 and 873 K in air for 6 h. Results show the dependence of surface area on calcination temperature. The surface area of VSbO samples decrease with increasing calcination temperature. These surface area of samples calcined at different calcination temperature exhibit greater value than that reported in literature [1] (see Table 1).

3.2. X-ray diffraction

X-ray diffraction patterns of vanadium–antimony mixed oxide powders having calcined in air at 673, 773 and 873 K for 6 h, respectively, are shown in Fig. 1. All the three calcined samples display an intense and sharp diffraction patterns. This indicates that the solids are in crystalline phase.

Apparently, the ≈$VSbO_4$ phase (JCPDS File No. 35-1485) appeared at $2\theta = 27.4^\circ$, 35.0° and 53.5° which correspond to (1 1 0), (1 0 1), and (2 1 1) planes, respectively, is the principal phase in all the samples. With the increase of calcination temperature, the peak of crystalline ≈$VSbO_4$ phase becomes reduced a little, but the orthorhombic α-Sb_2O_4 phase (JCPDS File No. 11-0694) appeared at $2\theta = 29.0^\circ$, 37.3°, 54.6°, 56.1° and 57.2° becomes stronger.

According to Centi and Perathoner [5], they reported that the formation of the ≈$VSbO_4$ phase occurs in the 673–773 K temperature range, with α-Sb_2O_4 reflection is detected when the calcination temperature increases. Berry and Brett [6]

Table 1
BET surface area of VSbO samples calcined at various temperatures

Catalyst	Surface area (m^2/g)
$VSbO_{SM673}$	29.3
$VSbO_{SM773}$	20.7
$VSbO_{SM873}$	17.5
VSb_1 (s)	2.0[a]
VSb_1 (aq)	6.0–6.3[a]

s, solid state reaction and aq, slurry reaction.
[a] Taken from [1].

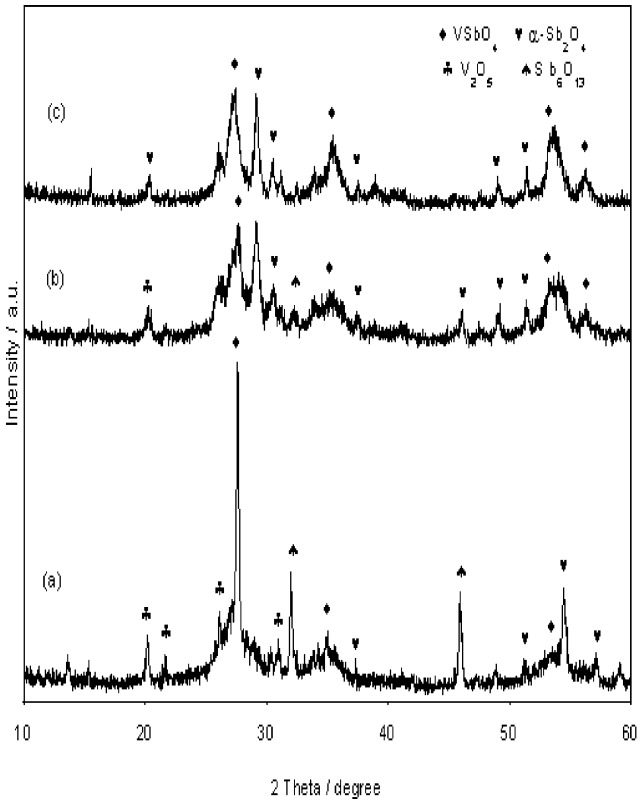


Fig. 1. XRD patterns of (a) $VSbO_{SM673}$, (b) $VSbO_{SM773}$ and (c) $VSbO_{SM873}$.

also reported that Sb_2O_3 is oxidised directly to α-Sb_2O_4 by imposing heat treatment on the sample in the temperature range 773–973 K. This observation indicates that an increase in calcination temperature promotes the formation of crystalline $\approx VSbO_4$ and α-Sb_2O_4 phase.

On the other hand, the strong diffraction patterns of Sb_6O_{13} phase at 31.9° and 46.0° observed in $VSbO_{SM673}$ catalyst are found diminished as calcination temperature increases to 773 and 873 K. This finding is in agreement with reported result by Centi and Perathoner [5], which indicated that phase are found absent for calcination temperatures above 873 K. Whereas, the reflecting of orthorhombic V_2O_5 phase (JCPDS File No. 9-0387) remaining unchanged after undergone a series of heat treatment.

3.3. Fourier transform infrared spectroscopy

Fig. 2 depicts the FTIR spectra of all the samples, while compilation of data taken from the literatures are given in Table 2. Characteristic of VSbO catalysts can be studied in the FTIR lattice-vibration in the range between 1100 and 400 cm^{-1}.

An intense band centred at 1020 cm^{-1} is a clear evident of the existence of a rutile $\approx VSbO_4$ [7]. This show the presence of crystalline $\approx VSbO_4$ phase which were detected by XRD. Reflection at 738 cm^{-1} and a shoulder at 432 cm^{-1} indicates the presence of α-Sb_2O_4 [8,6]. These bands are

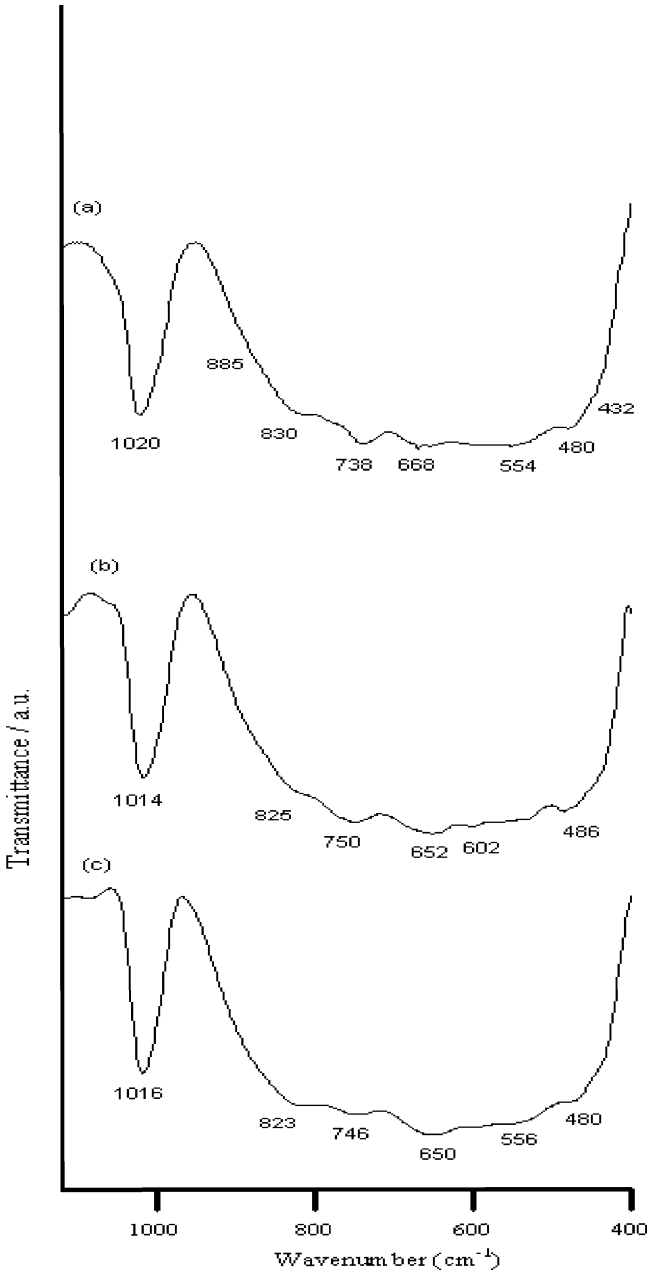


Fig. 2. FTIR spectra of (a) $VSbO_{SM673}$, (b) $VSbO_{SM773}$ and (c) $VSbO_{SM873}$.

found to be appeared in the FTIR spectra in the sample with Sb:V $\geq$2.0 [10]. Our results in XRD analysis showed the appearance of reflections for α-Sb_2O_4 as calcination temperature is increased.

The presence of crystallite of V_2O_5 are observed at 840 cm^{-1}. The existence of this band is expected due to the reported work by Centi and Perathoner [5]. They mentioned that the Sb:V ratio about 3.0 won't diminished the appearance of V^{5+} oxide crystallite, even though its relative intensity may decrease as Sb:V ratio is increased from 0.8 to 2.0 and 3.0. A weak reflection for Sb_6O_{13} is found at 890 cm^{-1} [10]. As calcination temperature increases, its

Table 2
FTIR lattice vibration of the catalysts prepared and the interpretations

Experimental band positions (cm^{-1})			Assignment		
$VSbO_{SM673}$	$VSbO_{SM773}$	$VSbO_{SM873}$	Type of vibration	Position (cm^{-1})	Reference
1020	1014	1016	ν_{Ome2}[a] in $\approx VSbO_4$	1010–1020	[7]
885			Sb_6O_{13}	890	[10]
830	825	823	V_2O_5	820–840	[5]
738	750	746	ν_{Sb-O} in Sb_2O_4[b]	685–745	[8]
668	652	650	ν_{Ome3} in $\approx VSbO_4$, rutile	630–670	[9]
	602		ν_{Sb-O} in Sb_2O_4[b]	610	[8]
554			ν_{Ome3} in $\approx VSbO_4$, rutile	500–580	[7]
480	486		ν_{Sb-O} in Sb_2O_4[b]	450–480	[6]
432			ν_{Sb-O} in Sb_2O_4[b]	430	[6]

Ome, oxygen-metal.
[a] Twofold co-ordinated oxygen (with cation vacancy).
[b] Distorted octahedral or tetrahedral Sb.

relative intensity become very weak, as has been seen in the XRD pattern.

3.4. Scanning electron microscopy

Fig. 3 shows the SEM images of vanadium–antimony powders calcined at different calcination temperature. The images were taken at a magnification of 10,000 and displays plate-like structure with sharp edges, which suggest the solids are in crystalline phase. This result is consistent with that obtained in the XRD analysis. Comparison of the images reveals that sample calcined at high temperature, in this study 873 K posses a rather large and more compact particle. This is due to aggregation of particles takes place as calcination temperature is increased. This result is in accordance with the BET surface areas analysis, in where an increase of the calcination temperature produced a decrease in surface area.

3.5. Temperature programmed desorption (TPD) of oxygen

The oxygen desorption profiles of all the samples are presented in Fig. 4. The experiment would detect the desorption of chemisorbed oxygen species, having desorption energies more than 80 kJ mol^{-1} and of lattice oxygen. All the samples display similar TPD spectrum with peaks are observed at ~930 K and a shoulder at ~890 K. Therefore, at least two kinetically different types of oxygen species exist in the mixed oxide catalyst. The desorption activation energies can be obtained by solution of the Redhead equation (Eq. (1)) at the peak maximum temperature [11],

$$\frac{E_d}{RT_m^2} - \left(\frac{A}{\beta}\right) \exp\left(\frac{-E_d}{RT_m}\right) = 0 \quad (1)$$

where E_d is the desorption activation energy (kJ mol^{-1}), A the desorption pre-exponential term (10^{13} s^{-1}, assumed), R the gas constant (J K^{-1} mol^{-1}), β the heating rate (K s^{-1}) and T_m (K) the peak maximum temperature.

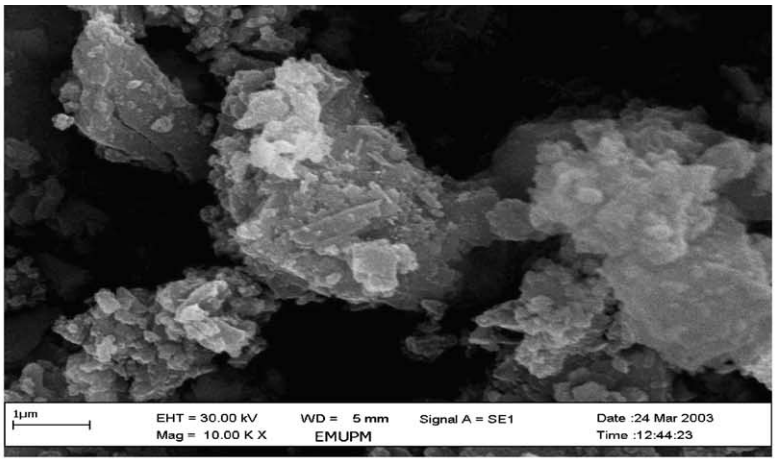
The peaks at 890 and 930 K correspond to the desorption activation energies of ~245 and 258 kJ mol^{-1}, respectively. This is a strong chemisorptive bond. Therefore, there is no weakly held oxygen species in the system.

The total amount of oxygen desorbed is 2.7×10^{20}, 4.1×10^{20} and 4.5×10^{20} atoms g^{-1} for $VSbO_{SM673}$, $VSbO_{SM773}$ and $VSbO_{SM873}$, respectively (Table 3). According to the catalysts surface area of 29.3 m^2/g for $VSbO_{SM673}$, 20.7 m^2/g for $VSbO_{SM773}$ and 17.5 m^2/g for $VSbO_{SM873}$, the total amount of oxygen species desorbed correspond

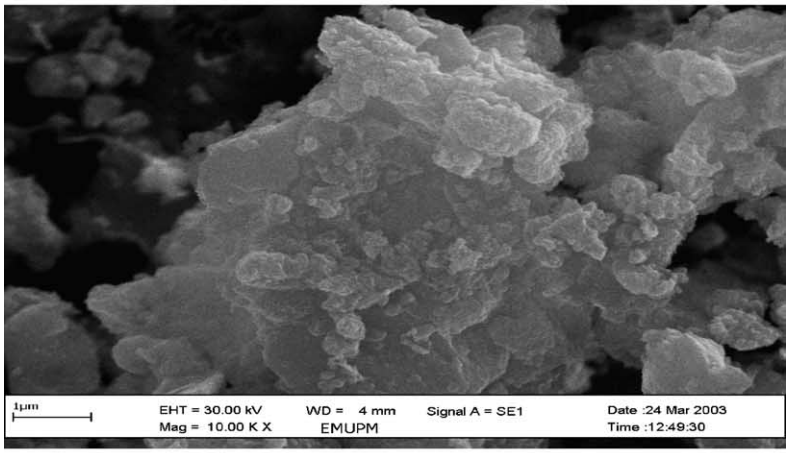
Table 3
Total number of oxygen atoms desorbed from the VSbO catalysts obtained by temperature programmed desorption of oxygen

Sample[a]	T_{max} (K)	Desorption activation energy, E_d (kJ mol^{-1})	Oxygen atom desorbed from the catalysts (mol g^{-1})		Oxygen atom desorbed from the catalysts (atoms g^{-1})		Coverage[b] (atoms cm^{-2})
$VSbO_{SM673}$							
1	892	246	2.1×10^{-4}	4.4×10^{-4}	1.3×10^{20}	2.7×10^{20}	8.9×10^{14}
2	937	259	2.3×10^{-4}		1.4×10^{20}		
$VSbO_{SM773}$							
1	868	240	3.0×10^{-4}	6.7×10^{-4}	1.8×10^{20}	4.1×10^{20}	1.9×10^{15}
2	929	257	3.7×10^{-4}		2.3×10^{20}		
$VSbO_{SM873}$							
1	886	245	4.9×10^{-4}	7.6×10^{-4}	2.9×10^{20}	4.5×10^{20}	2.6×10^{15}
2	929	257	2.7×10^{-4}		1.6×10^{20}		

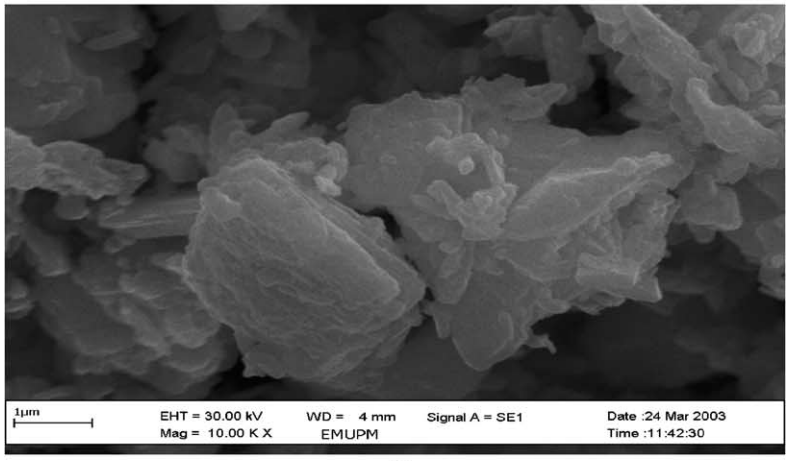
[a] Surface area: $VSbO_{SM673}$ = 29.3 m^2/g, $VSbO_{SM773}$ = 20.7 m^2/g, $VSbO_{SM873}$ = 17.5 m^2/g.
[b] Coverage is calculated by dividing the number of oxygen atoms removed by the total surface area.



(a)



(b)



(c)

Fig. 3. SEM images of (a) $VSbO_{SM673}$, (b) $VSbO_{SM773}$ and (c) $VSbO_{SM873}$.

to roughly ∼1.3, 2.8 and 3.9 monolayer of chemisorbed oxygen. These values were obtained by assuming that there are approximately 10^{15} atoms cm^{-1} on the surface of VSbO catalyst and that the proportion of oxygen ions on the surface is roughly stoichiometric. It is therefore lattice oxygen species being removed from the fresh samples.

3.6. Temperature programmed reduction (TPR) of hydrogen

Fig. 5 shows the temperature programmed reduction spectrum obtained by flowing hydrogen in argon (5% H_2, 1 bar, 25 cm^3 min^{-1}) continuously over the pretreated sam-

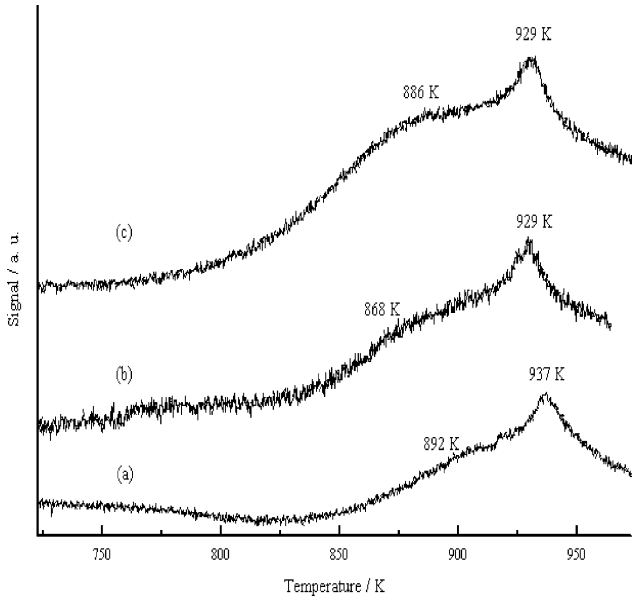


Fig. 4. Temperature programmed desorption spectrum of oxygen of (a) $VSbO_{SM673}$, (b) $VSbO_{SM773}$ and (c) $VSbO_{SM873}$.

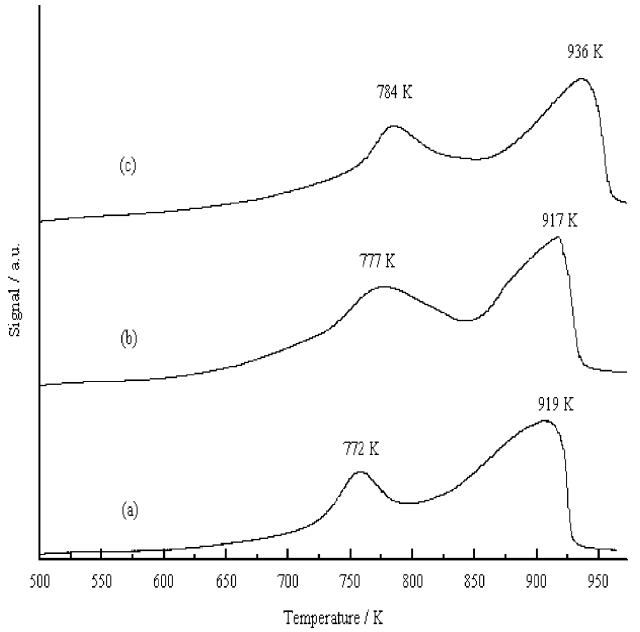


Fig. 5. Temperature programmed reduction of hydrogen of (a) $VSbO_{SM673}$, (b) $VSbO_{SM773}$ and (c) $VSbO_{SM873}$.

ples. The reaction temperature was increased linearly at $5\,K\,min^{-1}$. The onset of reduction of the surface oxygen by hydrogen is ~580 K, a temperature which is lower than that (673 K) used in the selective oxidation of propene [12].

All three samples display similar spectrum with two distinct peak maxima are observed at ~775 and 920 K. The oxygen which is thermally induced to desorbed from these catalysts does so with the peak maxima of 890 and 930 K. So, the 775 and 920 K maximum, which occurs in the rate of H_2O production, could result from the H_2 reacting with this oxygen, which is thermally evolving from the lattice at this temperature.

A rough estimate of the amount of oxygen removed was made by deconvoluting the H_2O peaks. The total amount are 3.4×10^{21}, 3.5×10^{21} and 3.7×10^{21} atoms g^{-1} for $VSbO_{SM673}$, $VSbO_{SM773}$ and $VSbO_{SM873}$, respectively. These are listed in Table 4. The total amount of oxygen atom removed from the pretreated catalysts as H_2O is 13 times greater than the number of oxygen atom being desorbed thermally in the temperature programmed desorption of oxygen. This clearly show that the introduction of reducing agent i.e. hydrogen in the TPR gaseous stream has tremendously induced the removal of oxygen species on/in the oxide.

The reduction activation energies for the interaction of chemisorbed H_2 with surface and bulk oxygen of the pretreated catalysts to form H_2O can be obtained from a modified version of the Redhead equation:

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

where T_m is the peak maximum temperature (K) in the rate of production of H_2O, E_r the reduction activation

Table 4
Total number of oxygen atoms removed from the VSbO catalysts obtained by temperature programmed reduction in hydrogen

Sample[a]	T_{max} (K)	Reduction activation energy, E_r (kJ mol^{-1})	Oxygen atom removed from the catalysts (mol g^{-1})		Oxygen atom removed from the catalysts (atoms g^{-1})		Coverage[b] (atoms cm^{-2})
$VSbO_{SM673}$							
1	772	129	1.9×10^{-3}	5.6×10^{-3}	1.2×10^{21}	3.4×10^{21}	1.1×10^{16}
2	919	154	3.7×10^{-3}		2.2×10^{21}		
$VSbO_{SM773}$							
1	777	130	1.5×10^{-3}	5.9×10^{-3}	9.2×10^{20}	3.5×10^{21}	1.7×10^{16}
2	917	153	4.4×10^{-3}		2.6×10^{21}		
$VSbO_{SM873}$							
1	784	131	3.2×10^{-3}	6.2×10^{-3}	1.9×10^{21}	3.7×10^{21}	2.1×10^{16}
2	936	156	3.0×10^{-3}		1.8×10^{21}		

[a] Surface area: $VSbO_{SM673} = 29.3\,m^2/g$, $VSbO_{SM773} = 20.7\,m^2/g$, $VSbO_{SM873} = 17.5\,m^2/g$.
[b] Coverage is calculated by dividing the number of oxygen atoms removed by the total surface area.

energy ($kJ\,mol^{-1}$), A_r the reduction pre-exponential term ($cm^3\,mol^{-1}\,s^{-1}$) which is given 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 maximum peak [11].

The values of the reduction activation energies for the peaks at 775 and 920 K are ~130 and 154 $kJ\,mol^{-1}$, respectively. The high activation energies obtained derive from the need to remove oxygen from the lattice. The reaction could occur according to the Rideal–Eley reaction (Eq. (3)), with the H_2 molecules removing the surface oxygen upon collision. The oxygen species become available as a result of a migration from the lattice to the surface.

$$H_2\,(g) + O\,(s) \rightarrow H_2O\,(g) + \square \quad (3)$$

in which O (s) is a surface lattice oxygen, (s) the surface and □ an oxygen vacancy.

Comparisons of the oxygen coverage determined for each sample (Table 4), suggested that sample which were calcined at high temperature, in this study 873 K give a greater coverage values. This indicates of the higher availability of oxygen species on the catalyst surface, which is suggested due to the formation of ≈$VSbO_4$ and α-Sb_2O_4 phase generated by the heat treatment.

4. Conclusion

Variation in calcination temperatures has an important effect on the properties of the vanadium–antimony oxide. An increase in calcination temperature produced more aggregated solids with small surface area value compared to sample calcined at low temperature. It is also promotes the formation of ≈$VSbO_4$ and α-Sb_2O_4 crystalline phase which is reported to be active and selective for propane oxidation. Encouraging results were obtained with temperature programmed studies. In where, a higher calcined VSbO sample was found to remove more oxygen species under reactive condition. However, we cannot determine whether these oxygen species are selective or not. Therefore, a further reaction studies are required to allow us to carry out detailed investigation on the selectivity and activity of the catalysts.

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