

SOLID STATE SYNTHESIS AND CHARACTERISATION OF VANADIUM ANTIMONY MIXED OXIDE CATALYSTS

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

*Department of Chemistry, Faculty of Science,
University Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia.*

Email: irmawati@science.upm.edu.my;

ABSTRACT

Vanadium antimony mixed oxide catalysts were prepared by the solid state method, and then subjected to heat treatment. Samples were analysed using XRD, FTIR, BET specific surface area (S_{BET}), scanning electron microscopy (SEM), temperature programmed desorption (TPD) and temperature programmed reduction (TPR). XRD showed a very intense and sharp peaks indicating of the high crystallinity of the particles, whereas SEM showed irregular shapes morphology which became aggregated with increase in the heating temperature. This in turn affects the S_{BET} value which became decreased as the calcination temperature was increased. FTIR spectrum of the calcined samples showed bands typical of the crystalline Sb_2O_4 and VSbO_4 were developed upon increasing calcinations temperature. In the oxygen TPD of VSbO samples, only one desorption energies of 258 kJmol^{-1} was observed. While three peak maxima were observed in the rate of anaerobic reduction of H_2 indicating that three types of kinetically different oxygen states exist in the catalyst.

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 [1]. Until today, acrylonitrile is produced by the ammoxidation of propene on catalysts made of promoted Fe-Bi-Mo-O (SOHIO process) or promoted Fe-Sb-O (NITTO process). However, in recent years, there were developments indicating 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.

For the direct of ACN formation from saturated hydrocarbon, the catalysts that are reportedly active and selective are based on mixed of vanadium and antimony (VSbO). This is due to the similar phases brought by this mixed oxide with that of FeSbO that is used commercially for the propene oxidation reaction.

In this study, the catalyst was prepared by solid state reaction between the oxide of vanadium with the oxide of antimony. The obtained precursors were then heat treated at

three different temperatures and the effect of heat treatment on physico-chemical properties of catalysts will be discussed. The characterization techniques employed were X-Ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and BET specific surface area measurement, S_{BET} . Investigation on the nature of the oxidants of the calcined samples was carried-out by conducting temperature programmed desorption of oxygen (TPD) and temperature programmed reduction of hydrogen (TPR).

EXPERIMENTAL

VSbO catalysts were prepared by a solid-state reaction between vanadium pentoxide, V_2O_5 (Merck, >99.0%) and antimony trioxide, Sb_2O_3 (Merck, >99.0%), in such amount as to obtain a Sb:V atomic ratio of 3.0. These starting materials were ground separately and then mixed together gently, but for enough time (~ 1 hour) as to obtain an intimate homogeneous mixture.

The mixtures were dried over night at 373 K in an oven. The samples were later calcined in air at 673, 773 and 873 K for 6 hours and were designated as $\text{VSbO}_{\text{SSR}673}$, $\text{VSbO}_{\text{SSR}773}$ and $\text{VSbO}_{\text{SSR}873}$, respectively.

Immediately after heat treatment, all of the samples were subjected to X-ray diffraction analyses. The analysis was carried out using a Shimadzu diffractometer model 6000 with CuK_α radiation to generate diffraction patterns from powder samples at ambient temperature. Fourier Transform Infrared spectroscopy was carried out with a Perkin Elmer FTIR 1725 X instrument using the KBr disc technique.

The specific surface area of powders was measured by the BET (Brunauer-Emmett-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 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, $25 \text{ cm}^3/\text{min}$) and holding under that stream for 1 hour before cooling to ambient temperature. The flow was then switched to helium (1 bar, $25 \text{ cm}^3/\text{min}$) and the temperature was raised at a heating rate of 5 K/min to 973 K following the conductivity of the eluted gas.

The temperature programmed reduction was obtained by heating the samples from room temperature to 473 K in a nitrogen flow (1 bar, $25 \text{ cm}^3/\text{min}$) before cooling to ambient temperature. Reaction was carried out in a mixture of 5 % hydrogen in argon at the flow of $25 \text{ cm}^3/\text{min}$ and the temperature was raised at a heating rate of 5 K/min to 1073 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).

RESULTS AND DISCUSSION

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

| Catalysts | Surface area/ $\text{m}^2 \text{g}^{-1}$ |
|------------------------|--|
| VSbO _{SSR673} | 6.7 |
| VSbO _{SSR773} | 6.1 |
| VSbO _{SSR873} | 4.9 |

Table 1 lists the S_{BET} value obtained for all samples calcined which were heat treated at 673, 773 and 873 K in air for 6 hours. Results show the dependence of surface area on calcination temperature. The surface area of VSbO samples were found decreased with an increase in calcination temperature.

The difference in S_{BET} value in all samples can be explained by the sintering effect which is the process of heating and compacting powdered material at temperature below melting point. This process caused the particles weld together into a single rigid shape.

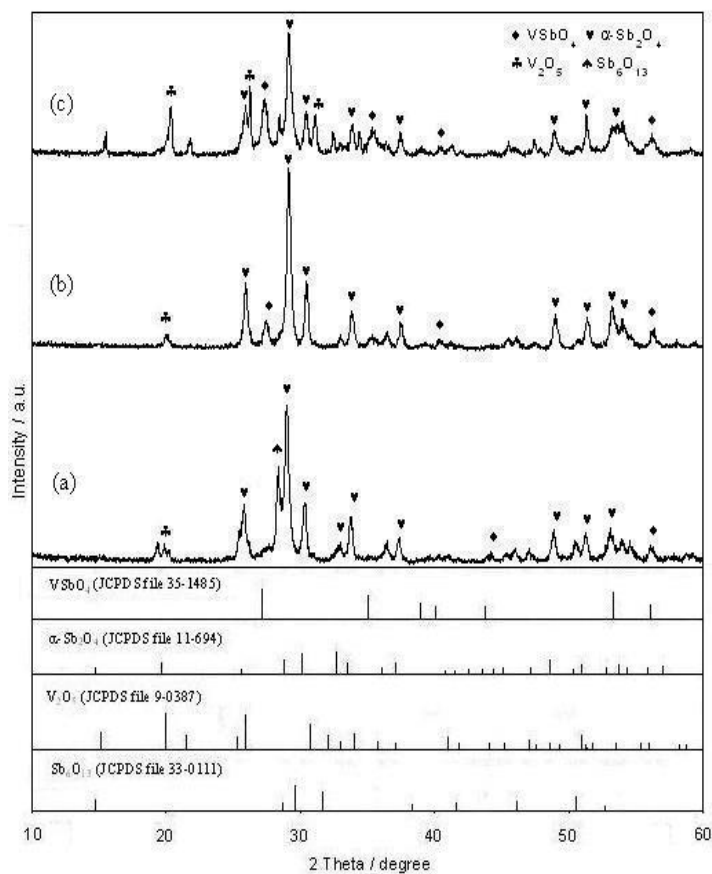


Figure 1: XRD patterns of (a) VSbO_{SSR673} (b) VSbO_{SSR773} (c) VSbO_{SSR873}

XRD patterns of VSbO catalysts are shown in Figure 1. The diffraction peaks are highly intense and sharp, an indication that the oxides are in highly crystalline form. At lower calcination temperature (i.e. VSbO_{SSR673}), the presence of α -Sb₂O₄ phase (JCPDS file 11-694) dominates the diffraction pattern, with the main peaks are observed at $2\theta = 25.8, 29.0, 30.4, 33.8, 37.4, 48.9, 51.2, 53.1$ and 54.6° . The reflections of VSbO₄ and V₂O₅ phases were shown to have lower intensities at low calcination temperature.

As temperature was increased, the reflection of Sb₆O₁₃ phase appeared at $2\theta = 28.7^\circ$ was found diminished. This finding is in agreement with reported results by Centi *et al.* [2], whom indicated that the phase was found absent for calcination temperature above 873 K. Increasing calcination temperature also causes the reflection of VSbO₄ phase (JCPDS file 35-1485) becomes more prominent with main peaks appeared at $2\theta = 27.4, 35.0, 40.2$ and 56.6° . These peaks correspond to (110), (101), (203) and (220) planes, respectively. According to Centi *et al* [2], they reported that the formation of the \approx VSbO₄ phase occurs in the 673 – 773 K temperature range. This observation indicates that an increase in calcination temperature promotes the formation of crystalline VSbO₄ phase.

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

| Experimental band positions (cm ⁻¹) | | | Assignment | | |
|--|------------------------|------------------------|---|----------------------------|--------|
| VSbO _{SSR673} | VSbO _{SSR773} | VSbO _{SSR873} | Type of vibration | Position, cm ⁻¹ | Ref |
| 1022 | 1022 | 1022 | $\nu \square V^{5+}=O$ in V ₂ O ₅ | 1020-1035 | 52 |
| 822 | 822 | 824 | $\nu(V^{5+}-O-V^{5+})$ | 820-840 | 31 |
| 738 | 744 | 740 | ν_{Sb-O} in Sb ₂ O ₄ ^b | 730-750 | 51, 52 |
| 690 | 684 | | ν_{Sb-O} in Sb ₂ O ₄ ^b | 680-690 | 51, 52 |
| 580 | 585 | 588 | ν_{Ome3} in \square VSbO ₄ , rutile | 500-580 | 36 |
| 554 | 536 | | | | |
| 472 | 464 | 478 | ν_{Sb-O} in Sb ₂ O ₄ ^b | 450-480 | 51, 52 |

^a twofold co-ordinated oxygen (with cation vacancy).

^b distorted octahedral or tetrahedral Sb.

O_{me} Oxygen-metal

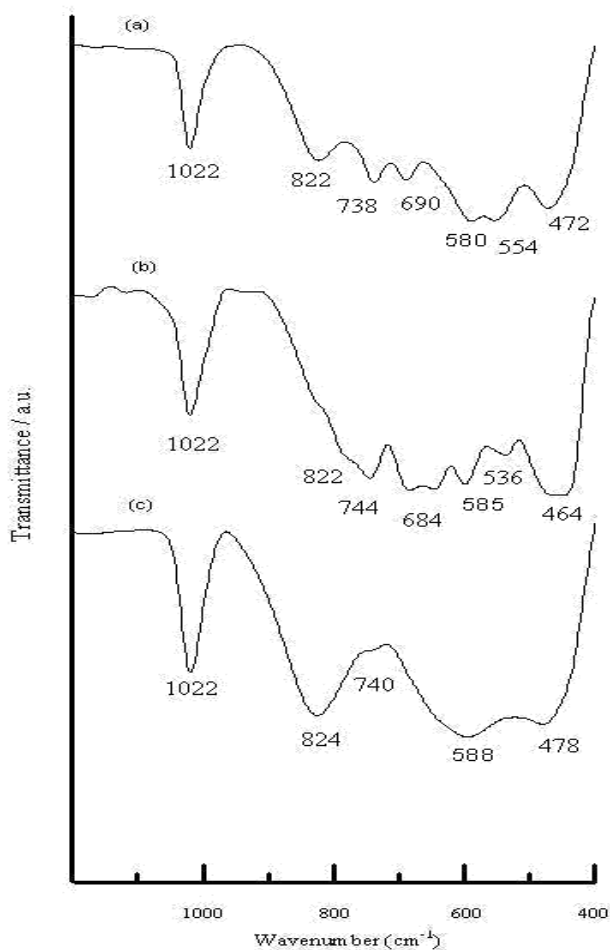


Figure 2: FTIR spectra of (a) VSbO_{SSR673} (b) VSbO_{SSR773} (c) VSbO_{SSR873}

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

FTIR spectra for all catalysts prepared show the presence of band occurring at 1022 cm^{-1} which is due to the symmetric stretching vibrations of the $\text{V}^{5+}=\text{O}$ bond in vanadyl group [3]. It is in agreement with the XRD diffractogram results that indicated when calcination temperature increases led to a further increase in the relative intensity of the band of V^{5+} oxide crystallite. VSbO_{SSR} catalysts also showed the presence of bands around 820-840 cm^{-1} that can be assigned as V^{5+} -oxide bands. Centi *et al.* [4] indicated the reaction of antimony with vanadium to form vanadium antimonate is not complete even when calcination temperature increases to 873 K.

All catalysts prepared also exhibits the vibrations of $\alpha\text{-Sb}_2\text{O}_4$ bands. The bands occurring around 735-740, 684 and 450-480 cm^{-1} are attributed to $\nu_{\text{Sb-O}}$ vibrations in Sb_2O_4 [3, 5]. The FTIR spectra also shows bands occurring around 500-580 cm^{-1} that can

be assigned as adsorption bands of the rutile structure of VSbO_4 [1]. This show the presence of crystalline $\approx\text{VSbO}_4$ phase which were detected by XRD.

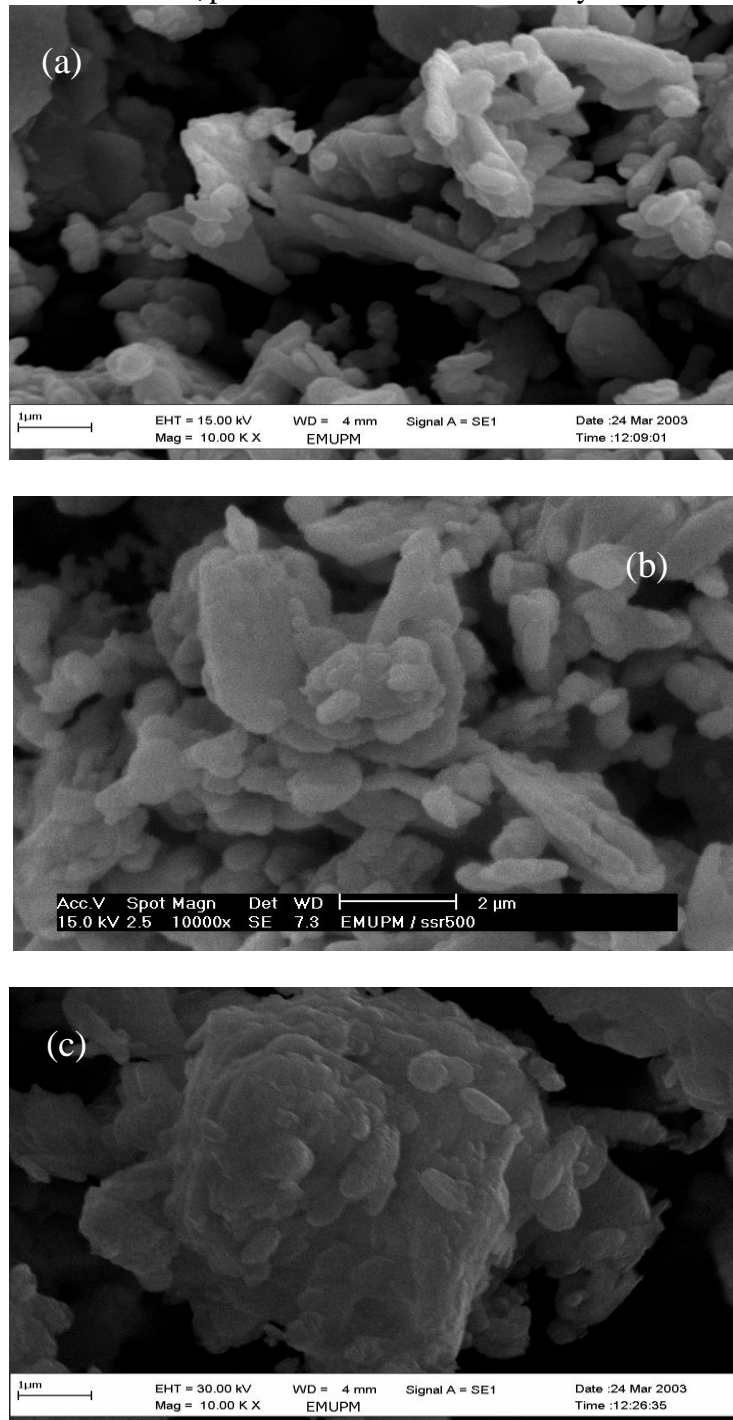


Figure 3: SEM images of (a) $\text{VSbO}_{\text{SSR673}}$ (b) $\text{VSbO}_{\text{SSR773}}$ (c) $\text{VSbO}_{\text{SSR873}}$

Figure 3 shows the SEM images of vanadium antimony catalyst calcined at different calcination temperature. For sample calcined at 673K, $\text{VSbO}_{\text{SSR673}}$ (Figure 3(a)), the images reveal the presence of rod like structure that seems intergrown with each other. When the temperature was increased to 773 and then 873 K, ($\text{VSbO}_{\text{SSR773}}$ (Figure 3(b)) and $\text{VSbO}_{\text{SSR873}}$ (Figure 3(c)), the particles were found more compact, in which smaller particles agglomerated together forming bigger ones. This result is in accordance with the BET specific surface area analysis, in which an increase of the calcination temperature produced a decrease in surface area.

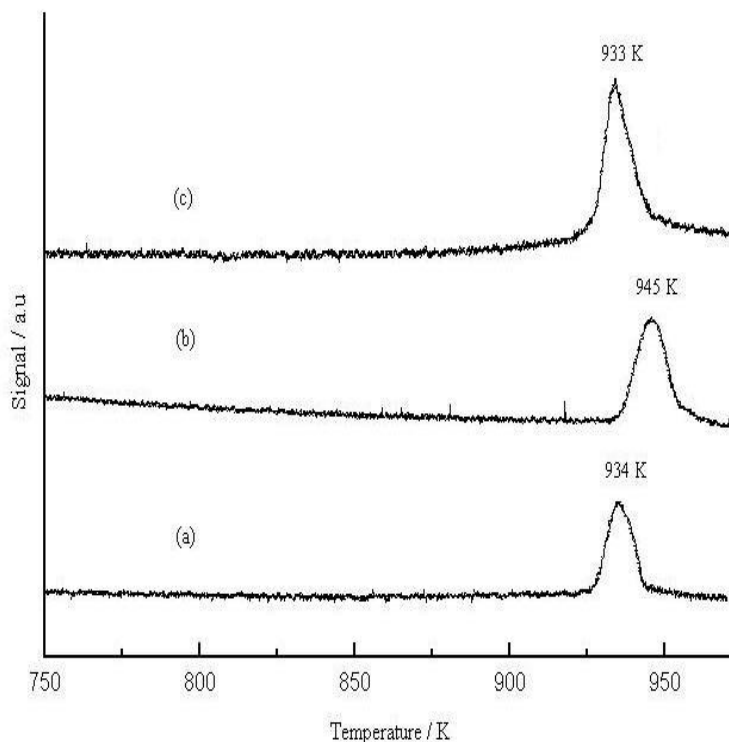


Figure 4: Temperature programmed desorption spectrum of oxygen of (a) $\text{VSbO}_{\text{SSR673}}$ (b) $\text{VSbO}_{\text{SSR773}}$ (c) $\text{VSbO}_{\text{SSR873}}$

The oxygen desorption profiles of all the samples are presented in Figure 4. The experiment would detect the desorption of chemisorbed oxygen species, having desorption energies more than 80 kJmol^{-1} and of lattice oxygen. All of the samples display similar TPD spectrum with one peak evolution is observed at temperature around 935 K. The peak is nearly symmetrical which may suggest that the desorption of oxygen from the catalyst might had went through first order kinetic. It is also showed that variation in calcination temperature do not give significant effect on the ability of the oxide to thermally desorbed the oxygen. The desorption activation energy, E_d can be obtained by solution of the Redhead equation (Eq. 1) at the peak maximum temperature [6],

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

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

The peaks correspond to the desorption activation energies of $\sim 258 \text{ kJmol}^{-1}$. This high value of desorption activation energy indicates that the oxygen species desorbing at this temperature range may originate from the lattice of the catalyst which later combining at the surface of the catalysts and evolved as oxygen molecule.

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

| Samples ^a | T_{max} (K) | Desorption activation energy, E_d (kJmol^{-1}) | Oxygen atom desorbed from the catalysts (mol g^{-1}) | Oxygen atom desorbed from the catalysts (atom g^{-1}) | Coverage ^b (atom cm^{-2}) |
|-----------------------------|----------------------|---|---|--|---|
| VSbO _{SSR673} 1 | 934 | 258 | 2.0×10^{-4} | 2.0×10^7 | 1.8×10^{15} |
| VSbO _{SSR773} 1 | 945 | 260 | 1.3×10^{-4} | 7.8×10^{19} | 1.3×10^{15} |
| VSbO _{SSR873} 1 | 933 | 258 | 1.2×10^{-4} | 7.1×10^{19} | 1.4×10^{15} |

^a Surface Area: VSbO_{SSR673} = 6.7 m^2/g , VSbO_{SSR773} = 6.1 m^2/g , VSbO_{SSR873} = 4.9 m^2/g

^b Coverage is calculated by dividing the number of oxygen atoms removed by the total surface area.

The total amount of oxygen desorbed for VSbO_{SSR} catalysts (Table 3) are slightly decreased as the calcination temperature increases. Referring to the catalysts' specific surface area values of 6.7, 6.1 and 4.9 m^2/g for VSbO_{SSR673}, VSbO_{SSR773}, and VSbO_{SSR873}, the total amount of oxygen species desorbed correspond to roughly ~ 2.6 , 1.8 and 2.0 monolayer of chemisorbed oxygen. These values were obtained by assuming that there is approximately $10^{15} \text{ atom cm}^{-1}$ on the surface of VSbO_{SSR} 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, which is in agreement with the high E_d values obtained for all samples.

Additional information as to the nature and the amount of oxidising species available from the VSbO_{SSR} catalysts could be obtained by TPR analysis by flowing hydrogen in

argon (5% H₂ in Argon , 1 bar, 25 cm³ min⁻¹) using a fresh sample of catalysts and raising the temperature from ambient to 1073 K at 5 K min⁻¹ in that stream.

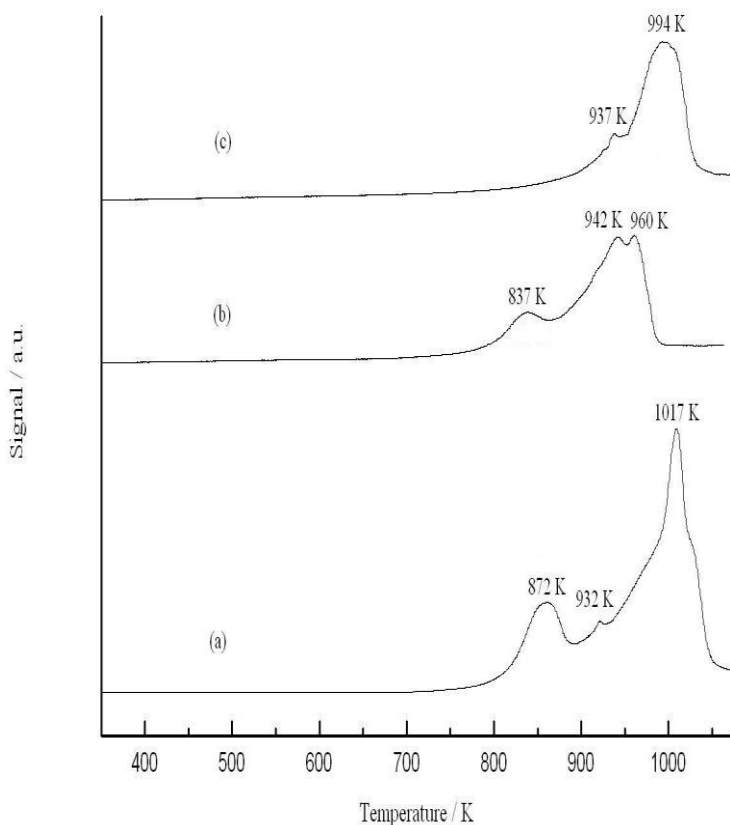
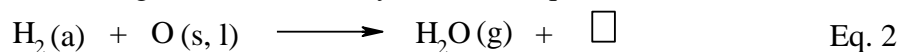


Figure 5: Temperature programmed reduction of hydrogen of (a) VSbO_{SSR673} (b) VSbO_{SSR773} (c) VSbO_{SSR873}

The reduction profiles are displayed in Figure 5 in which at least two reduction peaks are observed in each samples. This suggesting that at least there are two kinetically different oxygen species exist in the samples. The reduction reaction is probably occurred between chemisorbed H₂ with surface and lattice oxygen species, to form water leaving catalyst vacancies, □, behind according to the Rideal-Eley reaction (Eq. 2).



in where (a), (s), (g) denotes adsorbed, surface, lattice and gaseous species and □ is catalyst vacancy.

This analysis is in correlation with the gas-solid interaction mechanism which was discussed by Fadoni and Lucarelli [7]. The value of the reduction activation energies, E_r

for all the peaks are obtained from a modified version of the Redhead equation (Eq. 3) [6],

$$\frac{E_r}{RT_m^2} = \left(\frac{A_r}{\beta} \right) [H_2]_m \exp\left(\frac{-E_r}{RT_m} \right) \quad \text{Eq. 3}$$

where T_m is the peak maximum temperature, E_r is the reduction activation energy (kJmol^{-1}), A_r is the reduction pre-exponential term ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) which is given the value of a standard collision number of $10^{13} \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$ and $[H_2]_m$ is the gas phase concentration of hydrogen (molcm^{-3}) at the maximum peak.

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

| Samples ^a | T_{max} (K) | Reduction activation energy, E_r (kJmol^{-1}) | Oxygen atom removed from the catalysts (mol g^{-1}) | Oxygen atom removed from the catalysts (atom g^{-1}) | Coverage ^b (atom cm^{-2}) | | |
|------------------------|----------------------|--|--|---|---|----------------------|----------------------|
| VSbO _{SSR673} | 872 | 146 | 6.6×10^{-4} | 2.9×10^3 | 3.9×10^{20} 1.3×10^{21} | 1.7×10^{21} | 2.5×10^{16} |
| | 1017 | 170 | 2.2×10^{-3} | | | | |
| VSbO _{SSR773} | 837 | 140 | 7.1×10^{-4} | 2.7×10^3 | 4.3×10^{20} 6.3×10^{20} | 1.1×10^{21} | 1.8×10^{16} |
| | 960 | 161 | 2.0×10^{-3} | | | | |
| VSbO _{SSR873} | 937 | 157 | 2.2×10^{-4} | 1.6×10^3 | 1.3×10^{20} 8.5×10^{20} | 9.8×10^{20} | 2.0×10^{16} |
| | 994 | 166 | 1.4×10^{-3} | | | | |

^a Surface Area: VSbO_{SSR673}= 6.7 m²/g, VSbO_{SSR773}= 6.1 m²/g, VSbO_{SSR873}= 4.9 m²/g

^b Coverage is calculated by dividing the number of oxygen atoms removed by the total surface area.

The reduction activation energies for all the catalysts for the peak maximum between 837 – 1017 K corresponds to 140-170 kJmol^{-1} (see Table 4). The total amounts of oxygen removed from the catalysts were slightly decreased as the calcination temperature was increased. From Table 4, total amount of oxygen atoms removed from the catalysts for VSbO_{SSR673}, VSbO_{SSR773} and VSbO_{SSR873} catalysts are 1.7×10^{21} , 1.1×10^{21} atom g^{-1} and 9.8×10^{20} atom g^{-1} , respectively.

CONCLUSIONS

Variations in calcination temperature have been demonstrated to have an effect on the catalysts physico-chemical properties. An increase in calcination temperature produced more aggregated solids with smaller specific surface area value compared to sample

calcined at lower temperature. It also promotes the formation of \approx VSbO₄ and α -Sb₂O₄ crystalline phase which is reported to be active and selective for propane ammoxidation. The oxygen desorbed was suggested to be of chemisorbed and lattice species according to high desorption and reduction energies obtained. This was further supported by the total amount of oxygen removed by desorption and reduction which showed that more than a monolayer of oxygen species were removed. This condition may suggestively disrupt the morphology of the catalysts.

ACKNOWLEDGEMENT

Financial assistance from Malaysian Ministry of Science, Technology and Innovation under the IRPA Grant 09-02-04-0286-EA001 is gratefully acknowledged.

REFERENCES

- [1] H. W. Zanthoff, W. Grunert, S. Buchholv, M. Heber, L. Stievano, F. E. Wagner, G.U. Wolf, *J. Mol. Catal. A: Chemical*, **162** (2000) p.443
- [2] G. Centi and S. Perathoner, *Stud. Surf. Sci. Catal.*, **91** (1995) p.59
- [3] Berry, F. J., Brett. M. E., *J. of Chem. Soc, Dalton Trans.* (1983) p.13.
- [4] Centi, G., Perathoner, S., Trifiro, F., *Appl. Catal. A*, **157** (1997) p.143.
- [5] G. Centi, R. K. Grasselli, E. Patane, F. Trifiro, *Stud. Surf. Sci. Catal.*, **55** (1990) p.515
- [6] Redhead, P. A, *Trans. Faraday Soc.*, **57** (1961) p. 641
- [7] Fadoni, M., Lucarelli, L. Temperature Programmed Desorption, Reduction, Oxidation and Flow Chemisorption of Heterogeneous Catalysis: Theoretical Aspects, Instrumentations and Applications (1999) 38.