

**SYNTHESIS OF VANADIUM ANTIMONY OXIDE CATALYSTS VIA
SLURRY, SOL-GEL AND SOLID-STATE METHODS**

By

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**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Master of Science**

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The influence of synthesis method on the formation of VSbO catalysts was examined. The syntheses applied in the present work were slurry, sol-gel and solid-state reaction method. The precursors obtained were further heated at various calcinations temperature; 673, 773 and 873 K and the dependence of the physicochemical characteristics of all the samples on the heat treatment imposed were also investigated. The synthesis conditions for the preparation of crystalline vanadium antimony oxide as mixed phases were found. Nitrogen physisorption at 77 K revealed samples prepared by slurry method gave higher Brunauer-Emmet-Teller (BET) surface area, S_{BET} values compared to samples prepared by sol-gel and solid-state reaction methods. This was due to the chemical procedures done on the sample which promotes the formation of non-uniform particles with slit shaped particles compared to uniform particles formation displayed by other two methods. This phenomenon can be observed in Scanning Electron Microscopic, SEM micrograph. Upon heat treatment, S_{BET} value decreased for all samples prepared by different method due to sintering effect. Nevertheless, the molar fractions of VSbO₄ and α -

Sb_2O_4 phases depended on the heating temperature. As has been evidenced in X-ray Diffraction (XRD) analysis and Fourier Transform Infrared (FTIR) spectroscopy, higher calcination temperatures promote the formation of these two phases. The existence of the two phases which became dominant as the heating temperatures were gradually increased, are in accordance with reduced activities. Combination of transient kinetic studies; O_2 -Temperature Programmed Desorption, H_2 -Temperature Programmed Reduction and Temperature Programmed Reaction of propane, revealed the dependence of reducibility and catalyst activity with the relative intensity of VSbO_4 rutile and $\alpha\text{-Sb}_2\text{O}_4$ phases. The VSbO samples were found to be increased in reduced activity as calcination temperature is increased. Temperature programmed reaction analysis suggested that the transformation of propane to acrylic acid are through the formation of intermediates propene and acrolein.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**SINTESIS MANGKIN VANADIUM ANTIMONI OKSIDA MENGGUNAKAN
KAEDAH PEMENDAKAN, SOL-GEL DAN TINDAK BALAS KEADAAN
PEPEJAL**

Oleh

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Kesan kaedah penyediaan terhadap penghasilan mangkin VSbO telah dikaji. Di dalam kajian ini, penyediaan mangkin telah dilakukan melalui kaedah pemendakan, sol-gel dan tindak balas keadaan pepejal. Sampel yang disediakan kemudiannya melalui proses tindakan haba pada suhu yang berbeza; 673, 773 dan 873 K dan sifat-sifat fizikol-kimikal untuk setiap sampel terhadap kesan rawatan haba telah dikaji. Kaedah-kaedah penyediaan hablur vanadium antimoni oksida telah mengenalpasti fasa-fasa campuran berbeza. Analisis jerapan fizikal nitrogen pada 77 K mendapati sampel yang disediakan melalui kaedah pemendakan memberi nilai luas permukaan Brunauer-Emmet-Teller (BET), S_{BET} yang tertinggi berbanding kaedah sol-gel dan tindak balas keadaan pepejal. Ini mungkin disebabkan kesan tindak balas kimia yang dilakukan telah menghasilkan zarah-zarah yang berbentuk lebih seragam. Fenomena ini boleh dilihat pada mikrograf Mikroskop Imbasan Elektron. Rawatan haba juga boleh menyebabkan nilai S_{BET} berkurang untuk setiap sampel yang disediakan menggunakan kaedah yang berbeza disebabkan oleh kesan pengumpulan. Selain itu,

penghasilan fasa VSbO₄ dan α -Sb₂O₄ juga bergantung kepada suhu rawatan haba. Analisis Pembelauan Sinar X dan spektroskopi Transformasi Infra-merah Fourier menunjukkan rawatan haba pada suhu yang tinggi boleh membantu dalam penghasilan kedua-dua fasa itu. Penghasilan kedua-dua fasa yang dominan apabila suhu rawatan haba meningkat juga berkait rapat dengan aktiviti penurunan. Kombinasi kajian Suhu Berprogram Pembebasan Jerapan untuk oksigen, Suhu Berprogram Penurunan untuk hidrogen dan Suhu Berprogram Tindak Balas mendapati keupayaan penurunan dan aktiviti mungkin bergantung kepada jumlah fasa VSbO₄ dan α -Sb₂O₄. Sampel VSbO telah menunjukkan aktiviti penurunan meningkat apabila suhu rawatan haba meningkat. Berdasarkan analisis Suhu Berprogram Tindak Balas mendapati proses transformasi propena kepada asid akrilik adalah melalui pembentukan perantara propena dan akrolein.

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I certify that an Examination Committee met on 20th December 2004 to conduct the final examination of Mohd Asri Razali on his Master of Science thesis entitled "Synthesis and Characterisation of Vanadium Antimony Oxide Catalysts" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommended that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

MOHD ASRI RAZALI

Date:

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