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

By

MOHD ASRI RAZALI

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

December 2004

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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

By

MOHD ASRI RAZALI

December 2004

Chairman: **Irmawati Ramli, PhD**

Faculty: **Science**

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 $VSbO_4$ 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 α-Sb_2O_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

MOHD ASRI RAZALI

Disember 2004

Pengerusi: **Irmawati Ramli, PhD**

Fakulti: **Sains**

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 pengumpalan. Selain itu,

penghasilan fasa $VSbO_4$ dan α-Sb_2O_4 juga bergantung kepada suhu rawatan haba. Analisis Pembelauan Sinar X dan spekstroskopi Transformasi Infra-merah Fourier menunjukan 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 mangkin bergantung kepada jumlah fasa $VSbO_4$ dan α-Sb_2O_4. Sampel VSbO telah menunjukkan aktiviti penurunan meningkat apabila suhu rawatan haba meningkat. Berdasarkan analisis Suhu Berprogram Tindak Balas mendapati proses transformasi propana kepada asid akrilik adalah melalui pembentukan perantara propena dan akrolein.

ACKNOWLEDGEMENTS

First of all, I wish to express my deepest and warmest sense of thanks, gratitude and appreciation to my lovely wife, Juraidah A. Wahab, my parents, Hj. Razali Lazim and Hjh. Rahemah Abd Rahim, my sister and my brothers which their encouragement and support made it possible for me to finish my works.

I would like to express my sincere appreciation and gratitude to my honourable project supervisor, Dr. Irmawati Ramli, and my co-supervisors Assoc. Prof. Dr. Taufiq Yap Yun Hin and Assoc. Prof. Dr. Zulkarnain Zainal for their invaluable guidance, dedicated supervision, unfailing help, advice and suggestions to fully complete the project.

I wish to express my thanks to all the laboratory assistants in Chemistry Department especially Mr. Zulhisham and Mrs. Roslina; Mr. Rafi, Ms. Azilah and Mrs. Faridah from Institute of Bioscience for their favourable help. Also, I would like to thank to all COMBICAT-UPM members include lecturers, staffs and students for their favourable help.

Finally, financial support from the Ministry of Science, Technology and Environment of Malaysia (MOSTE) under the IRPA Grant 09-02-04-0286-EA001 is gratefully acknowledged.

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:

Abdul Halim Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Hj. Mohd Basyaruddin Hj. Abdul Rahman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohamed Ibrahim Mohamed Tahir, D. Phil
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohd Ambar Yarmo, PhD
Associate Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Independent Examiner)

This thesis submitted to Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirements for the degree of Master of Science. The members of the Supervisory Committee are as follows:

Irmawati Ramli, PhD
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Taufiq Yap Yun Hin, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Zulkarnain Zainal, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

_____

AINI IDERIS, PhD
Professor/ Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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:

TABLE OF CONTENTS