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SYNTHESIS & CHARACTERIZATION OF MULTIMETALLIC OXIDE CATALYSTS FOR SELECTIVE OXIDATION OF PROPANE TO ACRYLIC ACID; EFFECT OF PREPARATION VARIABLE AND ACTIVATION PROCEDURE

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Abstract

Several parameters involved in preparing the multi metal oxide (*MMO*) catalysts ($Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$) for the selective oxidation of propane to acrylic acid (AA) were investigated. These included the role each element plays and the effect on the performance of the catalysts exerted by the proper metal ratio, as well as various preparation method such as the mixing of starting chemicals to form an aqueous precursor mixture, effect of additive, the proper pre-calcined and calcination atmosphere and the gas flow. It was found that that each metal element plays a critical role and while an appropriate MoVTeNb metal ratio is critical to the performance of an effective catalyst, each and every step of the preparations method for an effective MoVTeNb oxide catalyst includes the intimate mixing of all starting chemicals to form a precursor solution, drying via rotavapor for solvent removal followed by calcinations under a non-flow inert atmosphere.

The characterisation results from BET, SEM-EDX, XRD, TPR, TG and DSC show the important differences depending on the preparation method and activation procedures of MoVTeNb oxide catalyst. From the BET surface area result the MoVTeNb oxide catalyst could be in the range, 1.0 m^2g^{-1} to 11.0 m^2g^{-1} and the surface morphology study concluded that. The low-magnification SEM images reveal a coarsely granular structure typical of a mixture of well-shaped crystals for the

MoVTeNb and modify the MoVTeNb samples. The modify MoVTeNb sample (prepared from citric acid and prepared with the addition of viscosity enhancers) show an exhibit a grossly different morphology. For this reason the precursor was not transformed into its final phase mixture characteristic of all other samples.

The XRD analysis is used to identify the phase inventory of the MoVTeNb oxide catalysts. The structure of orthorhombic *M1*, *M2,* $TeMo_5O_{16}$, $V_{0.95}Mo_{0.97}O_5$ and Mo_5O_{14} phase was investigated for MoVTeNb oxide catalyst. From the literature, it is known that the successful catalyst should be a mixture of two phases namely of an orthorhombic and a hexagonal variant of the MoVTeNb system referred to as M1 and M2 phases. The orthorhombic *M1* phase is the most active and selective phase and is responsible for the major of the efficiently of the best catalyst for selective oxidation process.

Thermal analysis, was be used to identify the sequence of events transforming the precipitate into the active oxide. The temperature-programmed reduction (TPR) was used to evaluate the effect of compositional variation of MoVTeNb on the propensity towards chemical reduction. Under catalysis conditions the mixed oxide must be present in a partly reduced state to be able to activate oxygen. The TGA and DTG allow the identification of the number and types, of reactions involving evaporation of small molecules from removal of ligands and water to condensation or drying processes. From all these analyses it was proven that the preparation method and the activation procedures would affect the performance of the MoVTeNb oxide catalyst.

Abstrak tesis yang dikemukakan kepada senat Universiti Malaya sebagai memenuhi keperluan untuk ijazah Master Falsafah

PENYEDIAAN DAN PENCIRIAN MANGKIN MULTI LOGAM OKSIDA UNTUK PROSES SELCTIVE OXIDATION PROPANA KEPADA ASID AKRILIK; KESAN FAKTOR PENYEDIAAN DAN KAEDAH PENGAKTIFAN

Abstrak

Beberapa faktor pembolehubah dalam penghasilan aktif katalis ‘multi’ logam teroksida ($Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$) untuk proses ‘selective oxidation’ propana kepada asid akrilik dikenalpasti. Ini termasuk, peranan setiap unsur logam tersebut dan pemilihan nisbah logam yang sesuai, kaedah penyediaan katalis seperti percampuran bahan pemula untuk membentuk campuran larutan akuas prekursor, kesan bahan penambah, kaedah pengaktifan mangkin yang sesuai dan jenis gas yang digunakan. Didapati, setiap unsur logam yang terlibat memainkan peranan penting, manakala pemilihan nisbah logam MoVTeNb adalah kritikal dalam menghasilkan katalis yang aktif. Prosedure untuk menghasilkan aktif katalis MoVTeNb teroksida adalah termasuk, percampuran bahan kimia pemula untuk menghasilkan larutan akuas prekursor, kaedah penyingkiran pelarut melalui kaedah ‘rotavapor’ dan diikuti oleh kaedah pengaktifan katalis dengan melalukannya dengan gas ‘inert’.

Hasil pencirian mangkin melalui kaedah BET, SEM-EDX, XRD, TPR, TG dan DSC menunjukkan dengan jelas bahawa kaedah penyediaan dan pengaktifan katalis memberi kesan terhadap aktif mangkin MoVTeNb teroksida. Melalui teknik pencirian BET, didapati luas permukaan mangkin MoVTeNb teroksida adalah diantara julat 1.0 m^2g^{-1} - 11.0 m^2g^{-1}. Kaedah pencirian SEM menggunakan magnifikasi yang rendah menunjukkan dengan jelas sturuktur ‘granual’ pada permukaan ‘tipikal’ campuran kristal mangkin MoVTeNb teroksida. Mangkin MoVTe teroksida yang diubahsuai

melalui kaedah penyediaan asid sitrik atau penambahan bahan additif menunjukkan struktur permukaan kristal yang berbeza daripada struktur kristal mangkin asal. Ini menunjukkan bahawa penyedian menggunakkan kaedah acid sitrik atau dengan menambahkan bahan additif kedalam resepi asal akan mengubah struktur dan fasa terakhir mangkin.

Analisis XRD digunakan untuk mengenalpasti beberapa fasa yang terdapat didalam mangkin MoVTeNb teroksida. Struktur fasa ortorombik *M1, M2*, $TeMo_5O_{16}$, $V_{0.95}Mo_{0.97}O_5$ and Mo_5O_{14} dikenalpasti. Daripada hasil kajian lepas didapati bahawa MoVTeNbOx katalis yang aktif mengandungi campuran dua fasa yang dikenali sebagai fasa ortorombik dan heksagonal iaitu fasa *M1* dan *M2*. Fasa ortorombik, *M1* dikenalpasti adalah fasa yang paling aktif dan paling sesuai untuk proses 'selective oxidation' propana.

Analisis terma pula digunakan untuk mengenalpasti kesinambungan diantara perubahan larutan mendakan yang terhasil kepada aktif oksida. 'Temperature-programmed reduction' (TPR) digunakan untuk mengkaji kesan pelbagai unsur logam yang terdapat didalam mangkin MoVTeNb teroksida dan kesannya terhadap proses penurunan bahan kimia. Dalam keadaan mangkin teroksida, setiap unsur hendaklah dalam keadaan separa penurunaan untuk mampu diaktifkan oleh oksigen. Analisis TGA dan DTG adalah untuk mengenalpasti bilangan dan jenis tindak balas yang terlibat dalam proses penyejatan molekul kecil daripada ligan iaitu proses kondensasi air atau proses pengeringan. Daripada hasil teknik pencirian mangkin yang digunakan, membuktikan bahawa proses penyediaan mangkin dan kaedah pengaktifan memberi impak yang besar dalam menghasilkan aktif mangkin MoVTeNb teroksida.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmet-Teller
BP	Boiling points (C / K/ F)
COMBICAT	Combinatorial Technologies & Catalysis Researches Center
DSC	Differential scanning calorimetry
DTG	Differential thermal gravimetric
EDX	Energy disperse X-ray
EXAFS	X-ray absorption fine-structure spectroscopy
FTIR	Fourier transforms infrared
FWHM	Full width at half maximum
HDS	Hydrodesulfurization
HEC	Hydroxyl Ethyl Cellulose
HPC	Heteropolyacid catalyst
JCPDS	Joint Committee on Powder Diffraction Standards
MMO	Multimetallic oxide catalyst
MP	Melting points (C / K/ F)
NGL	Natural gas liquids
PEG	Polyethylene glycol
P_V	Pore volume (cm^3 g^{-1})
SEM	Scanning electron microscopy
S_{BET}	B.E.T surface area (m^2 g^{-1})
SR	Standard recipe
TCD	Thermal conductivity detector
TGA	Thermogravimetric
TPR	Temperature programme reduction

TPDRO	Temperature programme desorption / reduction / oxidation
USA	Unites Stated of America
VPO	Vanadium phosphorus oxide
XPS	X-ray photon spectroscopy
XRD	X-ray powder diffraction
MoVTeNbOx (I)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst pre-calcine at **448 K** and calcine at 873 K under argon.
MoVTeNbOx (II)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst pre-calcine at **498 K**, and calcine at 873 K under argon.
MoVTeNbOx (III)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst pre-calcine at **548 K**, and calcine at 873 K under argon.
MoVTeNbOx (IV)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst pre-calcine at **598 K**, and calcine at 873 K under argon.
MoVTeNbOxNi (I)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ adding **Ni (0.05** atomic %) as a promoter.
MoVTeNbOxNi (II)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ adding **Ni (0.005** atomic %) as a promoter
MoVTeNbOxCr (I)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ adding **Cr (0.05** atomic %) as a promoter.
MoVTeNbOxCr (II)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ adding **Cr (0.005** atomic %) as a promoter.
MoVTeNbOxCo (I)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ adding **Co (0.05** atomic %) as a promoter.
MoVTeNbOxCo (II)	$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ adding **Co (0.005** atomic %) as a promoter.
A_r	Reduction pre-exponential term ($cm^3mol^{-1}s^{-1}$)
E_r	Reduction activation energy (kJ mol^{-1})
T_m	Peak maximum temperature (K)