SYNTHESIS OF HIGH SURFACE AREA SUPPORTED COPPER BASED-BIMETALLIC CATALYSTS FOR HYDROGENATION OF FATTY ALCOHOLS TO FATTY AMINES

NORMAZUIN BINTI ABDUL RAHMAN

THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

UNIVERSITY OF MALAYA

KUALA LUMPUR

2011

ABSTRACT

Over the past few decades it has been observed that copper (Cu) 'supported on' or 'incorporated into' solid matrices are widely used as catalysts for various types of reactions. It was reported that the high activity of supported Cu catalyst is generated by properties of the clusters and nanoparticles including high dispersion and uniform distribution of nanoparticle Cu on the support material. All these factors exert a direct effect on the formation of active surface of Cu and their catalytic properties accordingly. In this study, Cu based catalysts supported on silica, SiO_2 were prepared by incipient wetness impregnation of SiO_2 with aqueous metal citrate salt solution. A chelated precursor was chosen because previous work has shown that catalyst prepared in the presence of some specific chelated metal-complexes resulted in catalysts with high dispersion of small metal (oxide) particles with a narrow particle size distribution. The Cu based catalysts consisting of a second metal (Zn and Ni) were also prepared and examined for their influence on surface and structural properties of the final catalysts. Characterization of the catalysts was carried out by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX), Ultraviolet Visible (UV-Vis) Spectroscopy, Fourier Transform Infrared (FTIR) and X-ray Fluorescence (XRF), Thermal Gravimetric Analysis-Mass Spectrometer (TGA-MS), Differential Scanning Calorimetric (DSC) and Temperature Programme Reduction (TPR). The catalysts were later screened for their performance in process of hydrogenation of fatty alcohol to fatty amines using high throughput reactor.

The results from the characterization indicate that second metal influences the final catalysts produced with different characteristics. The morphology and BET surface

area of SiO_2 as a support was not preserved in Cu-Zn and Cu-Ni catalysts. This is due to agglomeration that changes the basic structural units (BSU) through precipitation of active metal oxide particles, and/or through modification of the support oxide surface occurring from their contact with the impregnated liquid and also the thermal treatment during drying and calcination. The XRD analysis shows the formation of amorphous nano-structured Cu supported on SiO_2 in the calcined catalysts. The Nitrogen physisorption measurement (BET) analysis shows that higher surface area (191.84 m^2/g) was obtained in Cu-Ni catalyst and this gives the best Cu metal dispersion on support. This study shows that the choice of appropriate synthesis parameters and thermal treatment for Cu-Zn/SiO2 and Cu-Ni/SiO_2 are extremely important to obtain superior surface area of nanocrystallites active Cu metals for the target reaction. Similarly, from this study, undesirable conditions of catalysts preparation and activation parameter that gave rise to catalysts with poor structure and thermal characteristics are identified.

The two catalysts, Cu-Zn and Cu-Ni, were studied for their catalytic behaviour in hydrogenation of fatty alcohol. Upon in situ activation, the catalysts were then screened in a high-throughput Oleobed reactor, conducted at a 30 bar pressure and over a temperature range of 443-523 K. In the screening, Cu-Ni supported catalysts show significant selectivity towards hydrogenation of fatty alcohols compared with Cu-Zn.

ABSTRAK

Kajian terdahulu menunjukkan kuprum, Cu, berpenyokong atau yang digabungkan dengan matriks pepejal telah banyak digunakan sebagai mangkin untuk pelbagai jenis tindak balas. Dilaporkan bahawa aktiviti yang tinggi bagi mangkin Cu tersokong dihasilkan oleh ciri kelompok dan nanozarah termasuk penyebaran tinggi dan seragam nanozarah pada permukaan penyokong. Semua faktor ini memberikan suatu kesan langsung pada pembentukan permukaan aktif mangkin Cu dan sifat pemangkinannya. Dalam kajian ini, mangkin berasaskan Cu tersokong diatas SiO_2 telah disediakan dengan kaedah impregnasi menggunakan larutan garam logam citrat. Satu prekursor terkelat dipilih kerana kajian terdahulu menunjukkan bahawa mangkin yang disediakan dengan kompleks logam terkelat menghasilkan mangkin dengan penyebaran logam (oksida) bersaiz kecil yang tinggi dengan taburan saiz zarah yang kecil. Mangkin berasaskan Cu yang mengandungi logam kedua (Zn dan Ni) telah juga disediakan dan dikaji dari segi pengaruhnya ke atas sifat permukaan dan struktur mangkin tersebut. Mangkin seterusnya dicirikan menggunakan peralatan XRD, SEM-EDX, UV-Vis, FTIR, XRF, TGA-MS, DSC dan TPR. Mangkin tersebut seterusnya diuji keaktifan untuk tindak balas penghidrogenan lemak alkohol kepada lemak amina menggunakan reaktor bertekanan tinggi.

Keputusan daripada pencirian menunjukkan bahawa logam kedua mempengaruhi mangkin yang dihasilkan dengan memberikan ciri-ciri yang berbeza antara mangkin-mangkin tersebut. Didapati bahawa morfologi dan luas permukaan SiO_2 sebagai penyokong tidak dapat di kekalkan dalam mangkin Cu-Zn dan Cu-Ni. Ini disebabkan oleh proses penggumpalan (aglomerasi) yang telah mengubah unit struktur asas

(BSU) melalui pemendapan zarah logam oksida yang aktif dan/ atau melalui perubahan pada permukaan oksida penyokong. Kedua-dua kesan ini berlaku akibat daripada sentuhan sesama cecair prekursor logam dan penyokong semasa impregnasi dan juga kesan suhu yang dikenakan semasa pengeringan dan pengkalsinan. Hasil analisis menggunakan XRD menunjukkan pembentukan Cu yang bersifat amorfus serta berstruktur nano pada permukaan penyokong SiO_2 terhasil selepas pengkalsinan. Keputusan analisis menggunakan BET menunjukkan penghasilan luas permukaan (191.84 m^2/g) yang lebih besar bagi mangkin Ni dan penyebaran yang baik bagi Cu pada permukaan penyokong. Oleh itu, kajian ini menunjukkan bahawa pemilihan parameter penyediaan dan aplikasi terma yang sesuai untuk mangkin Cu-Zn/ SiO_2 dan Cu-Ni/ SiO_2 adalah amat penting bagi memperolehi Cu nano-habluran yang aktif dengan luas pemukaan tinggi.

Mangkin Cu-Zn dan Cu-Ni telah dikaji ciri pemangkinannya dalam penghidrogenan lemak alkohol. Setelah pengaktifan secara in situ, mangkin-mangkin tersebut kemudian disaring di dalam reaktor bertekanan tinggi oleobed, pada tekanan 30 bar dan suhu pada julat 443-523K. Hasil penyaringan, menunjukkan mangkin Cu-Ni memberi selektiviti yang lebih tinggi berbanding mangkin Cu-Zn dalam penghidrogenan lemak alkohol.

Acknowledgements

I would like to acknowledge gratefully my principle supervisor, Prof. Dr. Sharifah Bee. Abd. Hamid for her excellent guidance, invaluable suggestions and help rendered throughout this research work. I have benefited from her high standard of accomplishment and her open-minded approach to new ideas. This has inspire me to strive for a higher standard of excellence in the near future. Her dedication to the research and hard work were always a good example for my own research.

I warmly thank to my co-supervisor Prof. Dr. Rosiyah Yahya for the useful discussion and idea towards my work. Her understanding, encouraging and personal guidance have provided a good basis for the present thesis.

I would also like to express my heartfelt gratitude to the members of COMBICAT. Their kind support and guidance have been of great value in this study.

Last but not least, I would like to express my deepest gratitude to my mother, Haniffa Bee Md Salleh, my father, Abdul Rahman Yasin, my husband, Khairul Zamri Derani, my siblings and also to my lovely kids, Iman Naufal and Miza Insyirah for sacrificing a lot, for giving me mental and physical support to further my studies.

Normazuin Abdul Rahman

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

P&G	Procter and Gamble
KLK	Kuala Lumpur Kepong
IFP	L'Institut Francais du Petrole
COMBICAT	Combinatorial Technology and Catalysis Research Centre
C18	Hydrocarbon with 18 carbon chain
CPO	Crude Palm Oil
RBD	Refined, Bleached, Deodorized
PKO	Palm Kernel Oil
LHSV	Liquid Hourly Space Velocity
Cu	Copper
Ni	Nickel
Zn	Zinc
Cu^{2+}	Cupric ion
CuO	Copper (II) oxide
XRD	X-ray Diffraction
BET	Brunauer-Emmet-Teller
BJH	Barrett, Joyner and Halenda
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray
TEM-EDX	Transmission Electron Microscope-EDX
UV-Vis	Ultraviolet Visible
FTIR	Fourier Transform Infrared
TGA-MS	Thermal Gravimetric Analysis-Mass Spectrometer

DSC	Differential Scanning Calorimetry
TPR	Temperature Programmed Reduction
wt%	Weight percent
cm	Centimeter
mm	Millimeter
μm	Micrometer
nm	Nanometer
kW	Kilowatt
kV	Kilovolt
mA	Miliampere
Å	Angstrom
K	Kelvin
Λ	Wavelength of radiation
Θ	Bragg angle
p/p_o	Relative pressure
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
BSU	Basic Structural Unit
LMCT	Ligand Metal Charge Transfer
M1	Sample ID for silica supported Cu-Zn (3:1 ratio): with 25 wt % metal loading on support
M2	Sample ID for silica supported Cu-Ni (3:1 ratio): with 25 wt % metal loading on support