

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

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## 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<sub>2</sub> were prepared by incipient wetness impregnation of SiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> in the calcined catalysts. The Nitrogen physisorption measurement (BET) analysis shows that higher surface area (191.84 m<sup>2</sup>/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/SiO<sub>2</sub> and Cu-Ni/SiO<sub>2</sub> 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  $\text{SiO}_2$  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  $\text{SiO}_2$  sebagai penyokong tidak dapat dikekalkan 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<sub>2</sub> terhasil selepas pengkalsinan. Keputusan analisis menggunakan BET menunjukkan penghasilan luas permukaan (191.84 m<sup>2</sup>/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<sub>2</sub> dan Cu-Ni/ SiO<sub>2</sub> adalah amat penting bagi memperolehi Cu nano-habluran yang aktif dengan luas permukaan 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.

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## 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 <sup>2+</sup>	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 <sub>0</sub>	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