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$Cu/ZnO/Al_2O_3$ CATALYST FOR
METHANOL SYNTHESIS

by

SAIDOLIM SAIDAKHROROV SAIDAKHROR O’G’LI

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NOVEL CARBON NANOTUBES-SUPPORTED $Cu/ZnO/Al_2O_3$ CATALYST FOR METHANOL SYNTHESIS

by

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DECLARATION OF THESIS

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DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake.

It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time, and it is dedicated for my brothers who helped me with their valuable advices and supported through all this hard times.

ABSTRACT

Methanol is the bulk feedstock for chemical industry and nowadays emerges as a suitable environment friendly fuel. Conventional methanol synthesis process from synthesis gas employs Cu/ZnO catalyst which, however, shows a steady deterioration of chemical and mechanical properties over normally triennial service period. Carbon nanotubes are increasingly recognized as promising materials for upgrading and development of novel industrial catalytic processes, either as catalysts themselves, catalyst additives or supports. Nanocatalysts are finding an increased adoption in growing range of industries. In this study the activity of in-house made alumina supported Cu/ZnO catalysts doped with CNT (Carbon Nanotubes) was explored. The data on a performance of the catalyst in fixed bed tubular reactor were obtained under industrial conditions, 250°C and 30 bar. The surface morphology of novel catalyst type was visualized by *Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray analysis, Temperature Programmed Reduction, Low Energy Ion Scattering Spectroscopy, X-Ray Photoelectron Spectroscopy, X-Ray Diffraction, EFTEM (Energy Filter Transmission Electron Microscope)* and compared with those of commercial fresh and used industrial Cu/ZnO catalysts. In-house made catalysts were treated with different concentration of Carbon Nanotubes, for study effect and activity of Carbon Nanotubes. The High Pressure Reactor Analysis system is made up of Multi tubular reactor with an on line gas chromatograph used to analyze the gaseous products from the reactor. From the studies of 1 and 2% CNT doped catalysts are showed a unique set of CO conversion rates. It was observed that the highest performance for CO hydrogenation rate come from the in-house made catalysts. The conversion rate of Industrial catalyst is much lower than 1 and 2% CNT. CO hydrogenation to methanol over the $Cu/ZnO/Al_2O_3$ catalysts doped on CNT showed that the supporter could significantly affect the activity of CO hydrogenation.

ABSTRAK

Metanol adalah bahan bekalan pukal untuk industri kimia dan ianya mucul sebgai salah satu bahan bakar yang mesra alam pada masa kini. Kebiasanya, penghasilan metanol dari logi pemprosesan diproses menggunakan gas-gas sintesis dan dibantu oleh pemangkin Cu/ZnO, namun begitu pemangkin ini sentiasa menunjukkan kemerosotan dari segi sifat-sifat kimia and mekanikal yang amat ketara dan jangka masa perkhidmatan hanya mampu bertahan selama tiga tahun. Tiub-tiub nano karbon dipercayai dapat menawarkan peningkatan dan pembaharuan bagi proses pemangkinan industri, samada sebagai bahan pemangkin, bahan tambahan ataupun sebagai penyokong pemangkin. Penggunaan pemangkin–nano oleh industri-industri yang sedang membangun semakin meluas. Dalam kajian ini, ativiti bagi alumina yang disokong oleh pemangkin Cu/ZnO dan disertakan dengan tiub-tiub nano karbon telah diterokai. Data-data terhadap prestasi pemangkin ini yang dijalankan dalam reaktor jenis *"Fixed Bed Turbular"* telah diperolehi mengikut keadaan yang diguna pakai oleh industri iaitu 250^{o}C dan 30 bar. Microskopi permukaan bagi pemangkin-pemangkin yang dihasilkan telah ditunjukkan oleh *Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray analysis, Temperature Programmed Reduction, Low Energy Ion Scattering Spectroscopy, X-Ray Photoelectron Spectroscopy, X-Ray Diffraction, EFTEM (Energy Filter Transmission Electron Microscope)*. Keputusan-keputusan yang diperoleh kemudiannya dibandingkan dengan pemangkin-pemangkin Cu/ZnO yang baru dan tehlah digunapakai oleh industri. Pemangkin yang dihasilkan pada permulaanya dirawat dengan tiub-tiub nano karbon dengan kepakatan yang pelbagai untuk melihat kesan dan aktiviti yang disumbangkan oleh tiub-tiub nano-karbon ini. Sistem Analisis Reaktor Berketekanan Tinggi yang melibatkan sebuah reaktor dilengkapi dengan *multi-turbular* dan gas komatografi secraca terus telah digunakan untuk menganilisa produk-produk gas dari reaktor.

Pemangkin yang telah disertakan dengan 1% dan 2% CNT menunjukkan set kadar penukaran CO yang unik. Kadar penukaran bagi pemangkin industri adalah kurang daripada pemangkin yang disertai dengan 1% dan 2% CNT. Penghidrogenan CO kepada methanol terhadap pemangkin $Cu/ZnO/Al_2O_3$ disertai diatas CNT telah menunjukkan bahawa penyokong dapat memberikan impak signifikan terhadap aktiviti penghidrogenan CO.

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LIST OF SYMBOLS

α-alumina	-	Alpha type Alumina
γ-alumina	-	Gamma type Alumina
θ-alumina	-	Theta type Alumina
δ-alumina	-	Delta type Alumina
Cu	-	Copper atom
Zn	-	Zinc Atom
Al	-	Alumina Atom
Zr	-	Zirconia Atom
Å	-	Angstrom unit (10^{-10} m)
θ	-	Reflection/diffraction angle, º
λ	-	Wavelength radiation (nm)
mV	-	miliVolt
keV	-	kiloelectroVolt
R	-	Ideal gas constant, 8.314 J/mol.K
T	-	Temperature, ^{o}C
P	-	Pressure, bar
MSA	-	Metal Surface area, m^2/g
N_A	-	Avogadro's number, 6.022×10^{23}
Mol H_2	-	moles of hydrogen consumed per unit mass catalyst, μmol_{H2}/gcat
c_m	-	No. of surface Cu atoms per unit area, 1.47x 10^{19} atoms/m^2
S.F	-	Stoichiometric factor, 2
W_{Cu}	-	Cu metal content, wt%
MW_{Cu}	-	Cu molecular weight.
ϕ_{av}	-	average copper particle size
ρ	-	Density, cm^3/g
D_{Cu}	-	Copper Dispersion, %

X_{CO}	-	Conversion of CO, %
$(n_x)^i$	-	Content of molecule X feed stream, mol %
$(n_x)^f$	-	Content of molecule X in the outlet stream, mol %
S_x	-	Selectivity of product X, %
g_{cat}	-	Catalyst mass, g
x- M	-	Molecule X adsorbed on metal (Zn or Zr) surface
M*	-	Free metal(Zn or Zr site)
θ_x	-	coverage of molecule X on metal (Zn or Zr) surface (x=V means vacant sites)
k_i	-	forward reaction rate constant for reaction i
K_i	-	Equilibrium reaction rate constant. $K_i=k_i/k_{-i}$
P_A	-	Pressure of gas A in the system ($P_A=P_A/P^o$). P^o is the reference pressure at STP
r_i	-	Rate of Reaction for reaction i. ($r_i=r_{+i}-r_{-i}$)

LIST OF ABBREVIATIONS

Syngas		Synthesis gas
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
H2	-	Hydrogen
MeOH	-	Methanol
CH_3OH		Methanol
DME	-	Dimethyl ether
MF	-	Methyl Formate
CH_4	-	Methane
N_2	-	Nitrogen
N_2O	-	Nitrous Oxide
XRD	-	X-ray diffraction
CNT	-	Carbon Nanotubes
TPR	-	Temperature-programmed reduction
C	-	Carbon
H		Hydrogen
FESEM	-	Field Emission Scanning electron microscopy
EDX	-	Energy-dispersive x-ray
BASF	-	Baden Aniline and Soda Factory
STP	-	Standard temperature and pressure
GC	-	Gas chromatography
FID	-	Flame ionization detector
TCD	-	Thermal conductivity detector
MOX	-	Malaysia Oxygen Berhad