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UNIVERSITI TEKNOLOGI PETRONAS

ACTIVITY STUDY OF CU BASED CATALYTIC MATRIXES WITH ZNO AND/OR ZRO_2 FOR ENHANCEMENT OF CATALYST ACTIVE LIFETIME AND METHANOL YIELD

by

JASVINDER SINGH GILL

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ACTIVITY STUDY OF CU BASED CATALYTIC MATRIXES WITH ZNO AND/OR ZRO_2 FOR ENHANCEMENT OF CATALYST ACTIVE LIFETIME AND METHANOL YIELD

by

JASVINDER SINGH GILL

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ABSTRACT

A series of $Cu/ZnO/Al2O_3$, $Cu/ZnO/ZrO_2/Al_2O_3$ and $Cu/ZrO_2/Al_2O_3$ catalysts were prepared for methanol synthesis study in Lurgi process. Apart from Cu and Al_2O_3, these catalysts would contain ZnO and/or ZrO_2 as active Carbon monoxide (CO) hydrogenation sites. The preparation method was an alternative acid-alkali pH precipitation. The SEM-EDX data for the formulations with various atomic ratios showed high homogeneity, hence good intermixing of ingredients. TPR analysis was done on all prepared matrixes and industrial catalyst and showed the reduction temperature of 300 ^oC to 345 ^oC for all 3 types of catalysts prepared. Both Low and High Temperature peak obtained for Metal Surface Area (MSA) analysis showed that there is a general decreasing H2 adsorption trend with the increasing amount of Zirconia in the catalyst. Prepared catalyst sample A with no zirconia present showed highest low and High Temperature adsorption in comparison with commercial and prepared catalysts. This suggests that Cu-ZnO catalyst have higher activity as compared to Cu-Zirconia based catalysts. TGA analysis also reveals that prepared catalysts sample has higher thermal stability at Lurgi Operating Temperature of 250^oC compared to Industrial catalysts sample. CO conversion study reveals that sample A with no Zr present has highest conversion of up to 4%. Also determined was that Zn offers higher activity in CO hydrogenation process in catalyst samples compared to Zr when present in the same atomic %. Also monoclinic Zr phase formed in catalyst type $Cu/ZnO/ZrO_2/Al_2O_3$ gives higher MeOH Yield compared to catalyst sample where tetragonal Zr phase is formed. A consistent trend between CH4 formation during activity study and Carbon formation study by CHNS reveals the most likely route for Carbon formation was through CH4 decomposition to form Carbon on catalysts surface sample The analytical kinetic study conducted decided that coverage of O atoms should be 0.5 in the beginning of the reaction in order to maximize the initial rate of reaction..

ABSTRAK

Sekumpulan pemangkin yang mengandungi komposisi $Cu/ZnO/Al_2O_3$, $Cu/ZnO/ZrO_2/Al_2O_3$ and $Cu/ZrO_2/Al_2O_3$ telah disediakan untuk mengkaji penghasilan Methanol melalui proses Lurgi. Selain Cu dan Al_2O_3, kelas pemangkin ini juga megandungi ZnO dan/atau ZrO_2 sebagai tapak penghidrogenan Karbon monoxida (CO). Kaedah yang digunakan untuk penyediaan pemangkin adalah kaedah pemendakkan melalui penyelangan asid-alkali. Data SEM-EDX untuk semua pemangkin menunjukkan penaburan logam sama rata di permukaan pemangin. Analisis TPR untuk semua pemangkin serta pemangkin industri menunjukkan suhu penurunan dalam kategori 300 ^oC hingga 345 ^oC. Kedua-dua puncak Suhu rendah dan Tinggi yang dari analisis Luas Permukaan Logam menunjukkan penerapan H_2 yang berkurangan jika nisbah logam Zr dalam pemangkin meningkat. Pemangkin berlabel A yang tidak mengandungi Zr menunjukkan penerapan Suhu rendah dan Tinggi yang lebih tinggi berbanding pemangkin lain. Ini menunjukkan bahawa pemnagkin jenis Cu-ZnO menpunyai aktiviti yang lebih tinggi berbamding pemangkin jenis Cu-Zirkonia. Analisis TGA juga menunjukkan pemangkin yang dihasilkan mempunyai daya stabil suhu yang lebih tinggi pada suhu operasi proses Lurgi iaitu 250^oC berbanding pemangkin industri. Penyelidikan penukar-prosesan CO menunjukkan pemangkin berlabel A yang tidak mepunyai Zr mencapai penukar-prosesan paling tinggi sebanyak 4%. Ia juga telah ditentukan bahawa pemangkin yang mengandungi Zn membolehkan pencapaian aktiviti lebih tinggi bilih berbanding pemangkin yang mempunyai Zr dalam nisbah % yang sama. Juga fasa monoklinik utuk logam Zr dalam pemangkin jenis $Cu/ZnO/ZrO_2/Al_2O_3$ menghasilkan jumlah MeOH yang lebih tinggi berbanding fasa jenis tetragonal untuk logam Zr. Trend konsisten di anatara penghasilan CH_4 semasa penyelidikan aktiviti dan penyelidikan penghasilan Karbon melalui analisis CHNS menunjukkan kaedah nyahkomposisi CH_4 sebagai Jalan penghasilan karbon di permukaan pemangkin. Penyelidikan kinetic

analitikal juga menunjukkan nisbah O di permukaan pemnagkin harus 0.5 untuk mencapai aktiviti maksimum pada permulaan tindakbalas.

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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, $\mu mol_{H2}/gcat$
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
DME	-	Dimethyl ether
MF	-	Methyl Formate
CH_4	-	Methane
N_2	-	Nitrogen
N_2O	-	Nitrous Oxide
XRD	-	X-ray diffraction
s-TPR	-	Surface Temperature-programmed reduction
TPR	-	Temperature-programmed reduction
TGA	-	Thermal Gravimetric Analysis
FESEM	-	Field Emission Scanning electron microscopy
EDX	-	Energy-dispersive x-ray
CHNS	-	Carbon, Hydrogen, Nitrogen and Sulfur Analyser
STP	-	Standard temperature and pressure
WHSV	-	Weight hourly space velocity
GC	-	Gas chromatography
FID	-	Flame ionization detector
TCD	-	Thermal conductivity detector
MOX	-	Malaysia Oxygen Berhad