SYNTHESIS, CHARACTERIZATION AND CATALYTIC PERFORMANCE OF Cu/ZnO/SBA-15 FOR HYDROGENATION OF CARBON DIOXIDE TO METHANOL

by

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
COST	Change one separate factor at a time
EDX	Energy dispersed X-ray
GC	Gas chromatography
GHGs	Greenhouse gases
GHSV	Gas hourly space velocity
GWP	Global warming potential
H_2-TPR	Hydrogen-temperature programmed reduction
MFC	Mass flow controller
P	Pressure
P123	triblock copolymer poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol)
RWGS	Reverse water gas shift
SBA-15	Santa Barbara Amorphous 15
SEM	Scanning electron microscopy
STY	Space time yield
T	Temperature
t	Time
TCD	Thermal conductivity detector
TCP	Tri-block copolymer
TEM	Temperature electron microscopy
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
TOS	Time on stream
wt.%	Weight percentage
XRD	X-ray diffraction

LIST OF SYMBOLS

%	Percentage
µm	Micrometre
Au	Aurum
Ce	Cerium
CH_3OH	Methanol
CH_4	Methane
cm	centi metre
CO	Carbon monoxide
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
CuO	Copper oxide
Ea	Activation energy (kJ/mol)
EO	Ethylene oxide
Fe	Ferum
g	gram
Ga	Galium
Ga_2O_3	Galium oxide
h	Hour
H	Hydrogen atom
H_2	Hydrogen
H_2O	Water
k	Rate constant
Kg	kilogram
m	meter
Mg	Magnesium
Mn	Mangan
Mpa	mega pascal
N_2	Nitrogen
N_2O	Nitrous oxide

Ni	Nickel
NiO	Nickel oxide
nm	nanometre
O	Oxygen atom
°C	Degree celcius
Pd	Palladium
PO	Propylene oxide
R	Ideal gas law constant (8.314 J/mol.K)
Si	Silicon
Ti	Titanium
TiO_2	Titanium oxide
wt.%	Weight percentage
Zn	Zinc oxide
$ZnCO_3$	Zinc carbonate
ZnO	Zinc oxide
$Zn(OH)_2$	Zinc hydroxide
ZrO_2	Zirconium oxide
θ	Diffraction angle

SINTESIS, PENCIRIAN DAN PELAKSANAAN BERMANGKIN Cu/ZnO/SBA-15 BAGI PENGHIDROGENAN KARBON DIOKSIDA KEPADA METANOL

ABSTRAK

Karbon dioksida (CO_2) adalah gas rumah hijau yang utama yang menyebabkan kepanasan sejagat. Penukaran CO_2 kepada metanol (CH_3OH) adalah salah satu alternatif kepada mahalnya perampasan CO_2 kaji bumi dan samudera. CH_3OH adalah satu bahan penting dalam industri kimia dan dikenali sebagai satu bahan bakar alternatif. Penukaran CO_2 bermangkin dan masa ruang hasil metanol (STY) adalah bagaimanapun dilaporkan sangat rendah. Oleh itu penting untuk membangunkan mangkin secara meningkatkan sifat-sifat penambahan bermangkin. Amorfus Santa Barbara 15 (SBA-15) dengan struktur heksagon yang sangat tersusun, diameter liang (~5.5 nm) dan morfologi zarah yang sekata, ketebalan dinding yang tebal (3.0 to 5.0 nm), luas kawasan permukaan, dan tinggi kestabilan haba telah berjaya disintesis sacara lazim tanpa proses penuaan hidrotermal. SBA-15 yang disintesis digunakan sebagai penyokong mangkin. Beberapa mangkin monologam dan dwilogam kuprum (Cu) atau/dan zink oxida (ZnO) disokong atas SBA-15 telah disintesis secara refluks. Sifat-sifat kimia fizik mangkin yang disediakan dikaji melalui pembelauan X-ray (XRD), penjerapan nitrogen, analisis pemetaan gravity haba (TGA), mikroskop elektron imbasan (SEM), analisis serakan tenaga X-ray (EDX), mikroskopi elektron transmisi (TEM), and hidrogen-penurunan berprogramkan suhu (H_2-TPR). Nilai optimum 5 wt.% Cu dan 15 wt.% ZnO disokong atas SBA-15 digelarkan sebagai 5Cu/15ZnO/SBA-15 dijumpai berkesan untuk memangkinkan penghidrogenan CO_2 kepada CH_3OH. Keadaan optimum proses penghidrogenan CO_2 kepada CH_3OH atas 5Cu/15ZnO/SBA-15 dijumpai pada tekanan tindak balas 4.0 MPa, suhu tindak balas 250 °C, dan halaju ruang jam jumlah gas bahan tindak balas (GHSV) 2400 h^{-1} yang memberi keputusan kepada 22.9% dan 11796.8 mmol $kgcat^{-1}$ h^{-1} masing-masing kepada penukaran CO_2 dan CH_3OH STY. Satu mekanisme laluan sintesis CH_3OH dan tindak balas anjakan balikan gas air (RWGS) atas Cu/ZnO/SBA-15 dicadangkan, berdasarkan keputusan ujikaji yang diperolehi dalam pembelajaran ini. Pengiraan tenaga pengaktifan sintesis CH_3OH dan pembentukan karbon monoksida (CO) adalah masing-masing 35.29 kJ/mol dan 68.02 kJ/mol, Penukaran CO_2 dan CH_3OH STY adalah stabil sepanjang 24 jam arus tindak balas dan didapati tiada nyahaktifan yang ketara. Aktiviti bermangkin tertinggi diperoleh melalui mangkin 5Cu/15ZnO/SBA-15 boleh dihubungkan kepada tingginya serakan Cu dan ZnO keatas permukaan SBA-15, menghasilkan jumlah tapak aktif yang lebih banyak, yang diperlukan untuk sintesis metanol. Pengendapan ZnO penghijrahan diatas permukaan Cu dijumpai untuk nyahaktif tindakbalas RWGS kepada CO; dan oleh itu meningkatkan kememilihan CH_3OH.

SYNTHESIS, CHARACTERIZATION AND CATALYTIC PERFORMANCE OF Cu/ZnO/SBA-15 FOR HYDROGENATION OF CARBON DIOXIDE TO METHANOL

ABSTRACT

Carbon dioxide (CO_2) is the primary greenhouse gas that causes global warming. The conversion of CO_2 into methanol (CH_3OH) is an alternative to the costly geological and oceanic CO_2 sequestration. CH_3OH is an important feedstock in the chemical industries and known as an alternative fuel. The catalytic CO_2 conversion and CH_3OH space time yield (STY) is however reported to be considerably low. It is therefore of importance to develop novel catalysts with improved properties for catalytic growth. Santa Barbara Amorphous 15 (SBA-15) with highly ordered hexagonal structure, uniform pore diameter (~5.5 nm) and particle morphology, thicker wall-thickness (3.0 to 5.0 nm), high surface area (585.20 m^2/g) and high thermal stability was successfully synthesized by the conventional method without hydrothermal aging process. The synthesized SBA-15 was used as catalyst support. A number of monometallic and bimetallic catalyst of copper (Cu) or/and zinc oxide (ZnO) supported on SBA-15 were synthesized by simple reflux method. The physicochemical properties of the as-prepared catalysts were investigated by X-ray diffraction (XRD), nitrogen adsorption, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), and hydrogen-temperature programmed reduction (H_2-TPR). The best amount of 5 wt.% Cu and 15 wt.% ZnO supported on SBA-15 designated as 5Cu/15ZnO/SBA-15 was found to effectively catalyze the hydrogenation of CO_2 to CH_3OH. The best process conditions for CO_2 hydrogenation to CH_3OH over 5Cu/15ZnO/SBA-15 were found to be the reaction pressure of 4.0 MPa, the reaction temperature of 250 °C, and the reactants total gas hour space velocity (GHSV) of 2400 h^{-1} that resulted to 22.9% and 11796.8 mmol $kgcat^{-1}$ h^{-1} of CO_2 conversion and CH_3OH STY, respectively. A reaction mechanism of CH_3OH synthesis route and reverse water gas shift (RWGS) reaction on Cu/ZnO/SBA-15 was proposed, based on the experimental results obtained in this study. The calculated activation energies of CH_3OH synthesis and carbon monoxide (CO) formation were 35.29 kJ/mol and 68.02 kJ/mol, respectively. The CO_2 conversion and CH_3OH STY were stable during 24 h of reaction on stream and no obvious deactivation was observed. The higher catalytic activity obtained over the novel 5Cu/15ZnO/SBA-15 catalyst can be correlated to the high dispersion of Cu and ZnO on the SBA-15 surfaces, creating greater amount of Cu-ZnO active sites, which are necessary for CH_3OH synthesis route. The deposited ZnO migration on the Cu surfaces was found to deactivate the RWGS reaction to form CO; and therefore increasing the CH_3OH selectivity.

CHAPTER 1

INTRODUCTION

1.1 Global warming

Global warming is referring to gradual increase in the earth's atmosphere and ocean average temperature. This phenomenon has occurred over the past 100 years and currently is still being one of the major environmental problems. Scientists from the global warming research declared that the global warming has increased the earth average temperature between 0.4 to 0.8 °C and it is predicted to increase up to 1.4 to 5.8 °C over the next hundred years (Livescience, 2013). The evidences of earth warming can be seen by changes in weather and climate. More floods, droughts, intense rain, severe heat waves and other climates related events happen more frequently now. Big changes can be seen in glaciers and oceans, where the ocean are warming and becoming more acidic, ice caps are melting and sea level are rising (EPA, 2013). The most recent report of National Oceanic and Atmospheric Administration (NOAA) stated that the global average temperature in May 2013 was among the top three warmest months of May in past 130 years (NOAA, 2013).

The global warming has been created by greenhouse gases (GHGs) that are capable of absorbing infrared radiation, thereby trapping and holding heat in the atmosphere. Records from total GHGs emissions in 2011 show that the largest contributor is carbon dioxide (CO_2), followed by methane (CH_4), nitrous oxide (N_2O) and several other fluorine-containing halogenated substances (HFCs, PFCs, SF_6) with emissions of 83.7, 8.8, 5.3 and 2.2%, respectively as shown in Figure 1.1 (IPCC, 2007). The impact of GHGs on global warming depends on three factors: abundance of the gas in the planet, duration of its stay in the atmosphere and its global warming potential (GWP) (EPA, 2013). The GWP of a greenhouse gas is defined as the ratio of the timeintegrated radiative forcing from the direct release of 1 kg of a trace substance relative to that of 1 kg of a reference gas (IPCC, 2001). CO_2 has a major impact because of its abundance and ability to stay in the atmosphere up to thousands of years. CH_4 can stay in the atmosphere about 10 years and its GWP is 21 times than that of CO_2. Meanwhile, GWP of N_2O is 310 and its atmospheric lifetime is 114 years. In case of fluorinated gases (HFCs, PFCs, and SF_6), their high heat trapping capacity makes them potential gases contributing to global warming, although they present in very small concentrations (IPCC, 2001; EPA, 2013).

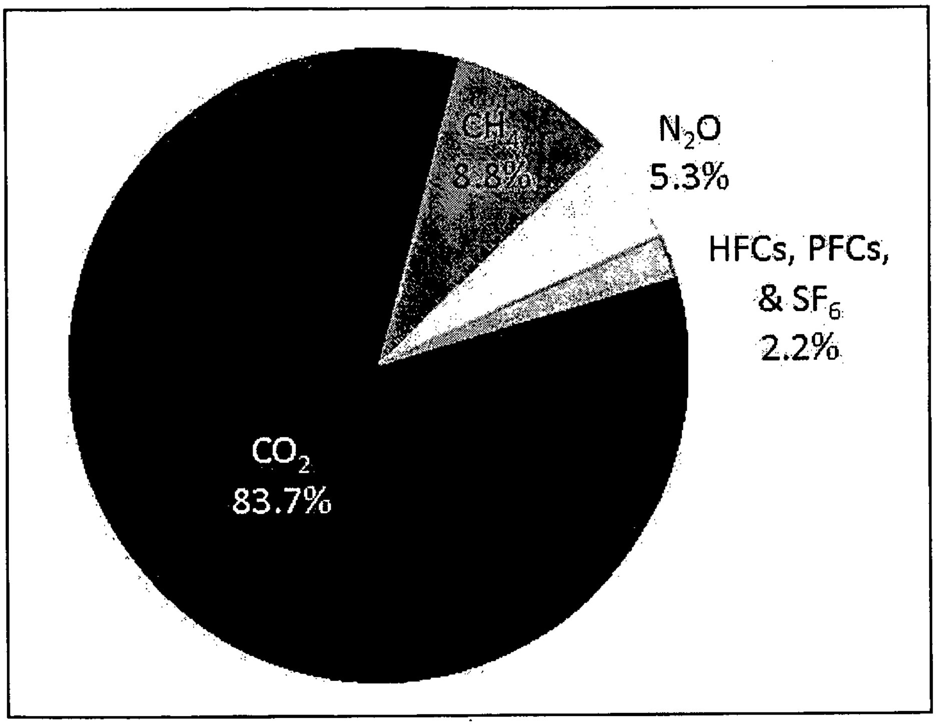

Figure 1.1: GHGs emission by gas in 2011 (IPCC, 2011).

The natural atmospheric concentrations of GHGs have changed by human activities parallel with the growth of energy consumption, transportation, man-made materials and technology (IPCC, 2007; NOAA, 2013). The largest source of CO_2, and overall greenhouse gas emissions, is fossil fuel combustion and its consumption has increased since the industrial revolution; around 270 years ago (Bill et al., 1997). CH_4

emissions are primarily resulted from domestic livestock, agricultural activities, coal mining, and decomposition of wastes in landfills. Agricultural soil management, mobile source fuel combustion and stationary fuel combustion are the major sources of N_2O emissions. Semiconductor manufacturing, primary aluminium production by-product, and electrical transmission and distribution systems are the primary contributors to fluorinated compounds emission (Song, 2006).

1.2 CO_2 in atmosphere

CO_2 is considered as an important ingredient in the carbon cycle of the earth and in the ecological system for plants and animals life, since it is used as carbon source in photosynthesis process and in food production. However, the abundance of CO_2 is more than carbon cycle demand which has led to environmental pollution. The level of CO_2 concentration in the atmosphere has been increasing significantly from decade to decade since 1955 and the most recent data of atmospheric CO_2 are 399.89 ppm for May 2013 (NOAA 2013, EPA, 2013). In addition to fossil-fuel combustion, several other sources emit significant quantities of CO_2. These sources are not limited to non-energy use of fuels but also iron and steel production and cement production (Figure 1.2).

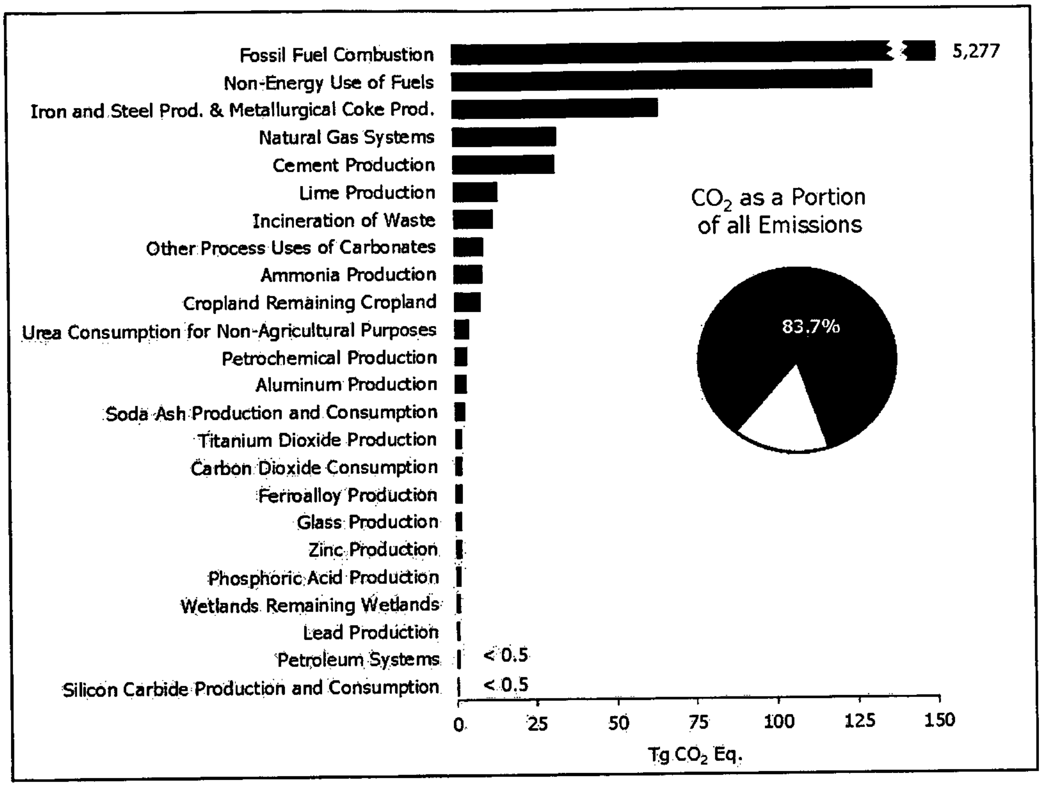

Figure 1.2. Sources of CO_2 emissions, Tg CO_2 Eq. = million metric tons CO_2 equivalent (IPCC, 2011).

1.3 CO_2 conversion for global sustainability

Reducing the CO_2 concentration and emission in the atmosphere is among the most important concerns for environmental protection and also global climate change. Under this circumstance, revolutionary approaches with innovative ideas are needed for green living environment as long term solution. The use of CO_2 as feedstock for producing chemicals is not only interesting for mitigation of GHGs emission, but is an interesting challenge to explore new concepts and opportunities for catalysis and industrial chemistry. Products that can be made from CO_2 include methanol, synthetic gas, dimethyl ether, ethylene, propylene, dimethyl carbonate, cyclic carbonate, and a variety of others (Alizadeh et al., 2009; Lee et al., 2008; Lu et al., 2004; Ma et al., 2009; Ramin et al., 2005; Zhang et al., 2006).