DEVELOPMENT OF TiO_2 LOADED $CuFe_2O_4$ PHOTOCATALYST FOR CO_2 CONVERSION INTO METHANOL UNDER VISIBLE LIGHT IRRADIATION

MD. RAHIM UDDIN

MASTER OF ENGINEERING

(CHEMICAL)

UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG

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MD. RAHIM UDDIN

Thesis submitted in fulfilment of the requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

February, 2016

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LIST OF ABBREVIATIONS

BET	Brunauer–Emmett–Teller
CB	Conduction Band
C	Concentration
EDX	Energy dispersive X-ray spectrometer
FE-SEM	Field emission scanning electron microscopy
FWH	Full width at half-maximum
GC-FID	Agilent gas chromatography (GC); flame ionization detector (FID)
NHE	Normal Hydrogen Electrode
PL	Photoluminescence
TGA	Thermogravimetric analysis
TPES	Total Primary Energy Supply
UV	Ultra-Violet
UV-Vis	Ultra-violet visible
VB	Valence Band
VLR	Visible Light Responsive
WL	Weight loss
XRD	X-ray diffraction

LIST OF SYMBOLS

E_g	Band gap Energy
e^-	Electron
h^+	Holes
λ	Wavelength
ΔG0	Gibb's free energy
eV	Electron Volt
MPa	Mega pascal
V	Standard Potential
µg	Microgram
g	Gram
µm	Micrometer
W	Watt
M	Molarity
Nm	Nanometer
2θ	Scattering angle
D	Coherent scattering length
B	Width of peak
K	Constant related to crystallite shape
Å	Angstrom, m
Wt	Weight
%	Percentage

Cm	Centimeter
M	Meter
^{o}C	Degree Celcius (Temperature)
μmol	Micro-moles
g_{cat}	Gram catalysts
L	Litre
H	Hour
T	Treatment Time
P	Positive type juction
N	Negative type junction
Β	FWHM (in radians)
ΔE	Redox potential
Θ	Diffraction angle
μg	Microgram
2θ	Scattering angle

ABSTRACT

The production of methanol through CO_2 photoreduction under visible light irradiation, has gained tremendous attention in recent times due to the limited availability of fossil-fuel resources and global climate change caused by rising CO_2 level in the atmosphere. The present study aimed to explore visible light active photocatalyst for carbon dioxide (CO_2) conversion to methanol in aqueous phase. In this context, copper ferrite ($CuFe_2O_4$) and TiO_2 loaded copper ferrite ($CuFe_2O_4/TiO_2$) were synthesized following sol–gel method. The effect of different parameters, such as TiO_2 to $CuFe_2O_4$ weight ratio, calcination temperature, light intensity, irradiation time and catalyst loading was investigated to evaluate the activity of the catalyst to produce methanol. Methanol was observed as the main product over $CuFe_2O_4$, but loading with TiO_2 remarkably increased the methanol yield. The maximum methanol yield was obtained on $CuFe_2O_4/TiO_2$ calcined at 700 ^oC with a catalyst loading of 1g/L. The catalyst was characterized by XRD, FE-SEM, UV-Vis, photoluminescence (PL) spectrophotometer, and EDX. The XRD results confirmed the formation of spinel type tetragonal $CuFe_2O_4$ phases along with predominantly anatase phase of TiO_2 in the $CuFe_2O_4/TiO_2$ hetero-structure. UV-Vis absorption spectrum suggested the formation of the hetero-junction with relatively lower band gap than that of TiO_2. PL spectra analysis confirmed the slow-down of the recombination of electron–hole (e^-/h^+) pairs in the $CuFe_2O_4/TiO_2$ hetero-structure. The mechanism of the photocatalysis was proposed based on the fact that the predominant species of CO_2 in aqueous phase were dissolved CO_2 and HCO_3^- at pH ~5.9. It was obvious that the $CuFe_2O_4$ could harvest the electrons under visible light irradiation, which could further be injected to the conduction band of TiO_2 to increase the life time of the electron and facilitating the reactions of CO_2 to methanol. The developed catalyst showed good recycle ability up to four cycles where the loss of activity was ~25%. To increase the yield of methanol a periodic addition of catalyst into the reactor was proposed where the methanol yield could be raised significantly.

ABSTRAK

Sejak kebelakangan ini pengeluaran metanol melalui pengurangan foto CO_2 di bawah sinaran cahaya yang boleh dilihat, telah mendapat perhatian yang besar kerana sumber bahan api fosil yang terhad dan perubahan iklim seluruh dunia yang disebabkan oleh peningkatan tahap CO_2 di dalam atmosfera. Kajian ini bertujuan untuk meneroka cahaya yang boleh dilihat foto-katalis yang aktif untuk penukaran karbon dioksida (CO_2) kepada metanol. Dengan ini, ferit tembaga ($CuFe_2O_4$) dan TiO_2 ferit tembaga dimuatkan ($CuFe_2O_4/TiO_2$) telah disintesis mengikut kaedah "sol-gel". Parameter yang berbeza, seperti TiO_2 untuk $CuFe_2O_4$ nisbah berat badan, suhu pengkalsinan, keamatan cahaya, masa penyinaran dan pemangkin loading telah disiasat untuk menilai aktiviti pemangkin untuk menghasilkan metanol. Methanol diperhatikan sebagai produk utama untuk $CuFe_2O_4$ sistem, tetapi memuatkan dengan TiO_2, ia meningkat hasil metanol. Maksimum metanol diperolehi daripada $CuFe_2O_4/TiO_2$ calcined pada 700 ^oC dengan mangkin 1g / L. Pemangkin dicirikan oleh XRD, FE-SEM, UV-Vis, photoluminescence (PL) spektrofotometer, dan EDX. Keputusan XRD mengesahkan pembentukan jenis spinel fasa $CuFe_2O_4$ tetragonal bersama-sama dengan fasa fasa kebanyakannya anatase TiO_2 di $CuFe_2O_4/TiO_2$ hetero-struktur. UV-Vis spektrum penyerapan mencadangkan pembentukan simpang hetero dengan jurang jalur yang agak lebih rendah daripada TiO_2. PL analisis spektrum mengesahkan perlahankan penggabungan semula elektron-lubang (e^-/h^+) pasang dalam $CuFe_2O_4$ / TiO_2 hetero-struktur. Mekanisme foto-pemangkinan telah dicadangkan berdasarkan fakta bahawa spesies utama CO_2 dalam fasa akueus telah dibubarkan kepada CO_2 dan HCO_3^- pada pH ~ 5.9. Ia adalah jelas bahawa $CuFe_2O_4$ boleh menuai elektron di bawah penyinaran cahaya, dan boleh disuntik ke jalur konduksi TiO_2 untuk meningkatkan masa hayat elektron dan memudahkan reaksi CO_2 kepada metanol. Pemangkin dibangunkan menunjukkan kebolehan kitar semula yang baik sehingga empat kali di mana kehilangan aktiviti adalah ~ 25%. Tambahan lagi, untuk meningkatkan hasil methanol, panambahan pemangkin dalam reaktor telah dicadangkan untuk menigkatkan hasil metanol dengan ketara.