Effect of monometallic copper on zeolitic imidazolate framework-8 synthesized by hydrothermal method

Sonam Goyal\textsuperscript{1*}, Maizatul S Shaharun\textsuperscript{1}, Chong F Kait\textsuperscript{1} and Bawadi Abdullah\textsuperscript{2}

\textsuperscript{1}Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
\textsuperscript{2}Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

*Corresponding author: sonam_g03236@utp.edu.my

Abstract. Metal-organic frameworks (MOFs), which are self-assembled and can be synthesized by the coordination of metal cation/clusters with organics linkers. Copper/zeolitic imidazolate framework-8 (Cu/ZIF-8) MOF catalyst was successfully synthesized by reaction of metal sulfates of Cu with ZIF-8 via hydrothermal method. Thermogravimetric analysis (TGA) exhibits the excellent thermal stability up to 450°C of the Cu/ZIF-8 catalyst. Fourier transform infrared spectroscopy (FTIR) confirmed the ZIF-8 structure and the addition of copper metal. Field emission scanning electron microscopy (FESEM) images exhibit great morphologies which confirms the synthesis of Cu/ZIF-8 catalyst. UV-Vis (Ultraviolet-visible) spectroscopy and DRS (diffuse reflectance spectroscopy) show more absorbance in the visible region of Cu/ZIF-8 and lower band gap energy respectively, which leads to photocatalytic support. Our discoveries investigated a basic and intense approach to photocatalyst without losing their properties.

1. Introduction
The production of methanol from synthesis gas is a well-known process. In the last few years, researchers are trying to use abundantly available carbon dioxide (CO\textsubscript{2}) as an alternative feedstock for methanol production. This could open the way for a large-scale utilization of CO\textsubscript{2}. There is various catalytic system used for methanol synthesis from CO\textsubscript{2}. However, methanol synthesis from CO\textsubscript{2} under visible light irradiation are not explored well and limited research is reported until now. There is a very limited series of MOFs catalysts that have been utilized for methanol production from CO\textsubscript{2} and water in visible light region. One of the primary approaches copper-imidazolate (Cu-Im) framework with a crystalline structure reported by Li. et. al. who employed hydrothermal method to synthesize this Cu-Im framework for methanol production under mild aqueous conditions [1]. Thus, few experts have built up this province with a specific end goal to synthesize MOFs based catalysts [2], metal oxide catalyst [3] but due to their low efficiency in visible region and little chemical stabilities of catalysts, researchers still finding better MOFs catalysts. Currently, the new generation catalyst called MOFs have great potential for CO\textsubscript{2} capture and storage and have potential application in broad areas, such as catalysis, gas storage, sensors, nonlinear optics, and molecular recognition and separation [4-8]. Among various available and commercial MOFs, the zeolitic imidazolate frameworks (ZIFs) have some promising properties such high thermal and chemical stabilities [9]. ZIF-8 showed thermal and chemical stability, high porosity and chemical resistance to boiling alkaline water and organic
solvents [10]. However, the methods used for MOFs is time consuming and expensive on commercial scale. In recent years, researchers are trying to improve different methods for the controllable combination of ZIFs with fascinating crystal structure and morphologies, and for diminishing the excessive amounts of organic ligands and solvents utilized as a part of the synthesis process to reduce the cost and environmental impacts [11]. Few metal organic frameworks such as Cu/ZnO@MOF-5 [2], ZIF-8/Zn₂GeO₄ nanorods [12], etc. have been explored for photoreduction of CO₂ into fuels. To explore the potential of new catalyst formulation for methanol synthesis from CO₂, a metal-organic framework was used in the present study as Cu/ZIF-8 catalyst. This paper deals with the synthesis and characterization of newly reported, Cu/ZIF-8 via hydrothermal method, containing the preparation of ZIF-8 by attractive morphologies. The aim of this work is to develop an effective photocatalyst for methanol production. The application of methanol production from Cu/ZIF-8 catalyst is novel because, there has been no report in the literature so far. The focus will be given to the synthesis of Cu/ZIF-8 as the photocatalyst.

2. Synthesis
ZIF-8 crystals were synthesized in a purely aqueous system using already reported method [13]. Briefly, 1.17 g zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (Sigma-Aldrich) was dissolved in 10 mL deionized water in one beaker and 22.70 g of 2-methylimidazole (2Hmim) was dissolved in 80 mL deionized water in another beaker. Solution of zinc nitrate was added into 2Hmim solution under vigorous stirring at room temperature. 10 minutes later, collected product was centrifuged to follow washing with deionized water for 4-5 times. The product was dried at 85˚C for overnight in an oven.

To synthesizing Cu/ZIF-8, we used reported method by Li. et. al. [1], 0.25 g amount of ZIF-8 and 0.5 g copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) dissolved in deionized water were mixed under continuous stirring. Then required amount of 4M ammonium hydroxide solution was added to produce a 25 mL of solution. The mixture was poured into Teflon-lined stainless-steel autoclave and hydrothermally treated at 110˚C for 48 h. The solid product collected by filtration and washed with deionized water for 3–4 times. The prepared catalyst was finally dried at 85˚C for overnight. This method is reported by Li et. al. [1] with some little changes in our work.

3. Characterization
The UV-Vis spectroscopy (Agilent Cary 100 UV-Vis Spectrophotometer) and DRS is used to determine the optical absorption and band gap energy of catalyst respectively. UV-vis spectra of sample were noted in the range of 200-800 nm. A thermogravimetric analyzer (Perkin Elmer Pyris 1) was used to measure thermal stability of the sample, which occur under nitrogen flow at a heating rate of 10˚C/min from room temperature to 700˚C. FESEM, (JEOL6340) and electron microscope-energy dispersive X-ray (EDX) was used to investigate the morphology and elemental composition respectively. FT-IR Thermo Fisher Scientific Nicolet iS50 spectrometer with DTGS detector is used to identify the functional-groups in the catalyst by appearance of vibration bands.

4. Results and discussion
The morphological image of ZIF-8 and Cu/ZIF-8 catalyst is showed in figure 1. FESEM images shows that addition of Cu on ZIF-8 can affect the surface morphology of the catalyst, however there is no significant effect on the particle aggregation. The particle size of catalysts is uniform, ranging from 0.4 to 1.0 nm. It can be seen form figure 1 (a), that ZIF-8 particles image look-like hexagonal surfaces, which are analogous to entities reported by Pan and co-workers [13]. Cu/ZIF-8 FESEM image shown in figure 1 (b). It is well-defined rhombic dodecahedron structure, which is the characteristic of ZIF-8 morphology [8]. FESEM-EDX (figure 1c) of the Cu/ZIF-8 catalyst indicate that Cu, Zn, C and N were the main 4 components observed on the surface of sample.
Figure 1. FESEM images of (a) ZIF-8, (b) Cu/ZIF-8 and (c) EDX image of Cu/ZIF-8.

FTIR spectrum shows bonding vibrations of linkers in structure. The figure 2 shows the FTIR spectra of both samples, where a sharp peak at 423 cm⁻¹ attributing to Zn–N stretching mode, it screen that zinc molecules are linked to nitrogen atoms in 2Hmim linkers to form the ZIF coordination structure [14]. The absorption bands in the range from 1100 to 1300 cm⁻¹ are assigned to C–H vibrations, while the peak around 1390 cm⁻¹ is ascribed to C–C bonding [12]. The peaks distinguished at 1466 and 1470 cm⁻¹ attributed to C=N stretching vibration, while the peaks at 1229 and 1231 cm⁻¹ confirms the trembling of C-N in the imidazole ring. The presence of C-N and C=N groups specifies that the existence of imidazole molecules in the catalyst [15]. The Cu-N bonding vibration located between 550-620 cm⁻¹ in Cu/ZIF-8 catalyst [16].

Figure 2. FTIR vibration band spectrum of the ZIF-8 and Cu/ZIF-8.

The thermogravimetry analysis was used to study the thermal stability of the materials. The thermogram for both samples are represented in figure 3. The small weight loss in catalyst in region from 25 to 100°C is due to the loss of water. Very small change in weight loss was for Cu/ZIF-8
sample up to 450°C, following the same trend as ZIF-8 and then remain constant until 700°C. The obtained result confirmed that this synthesised catalyst has thermal stability up to 450°C. The rapid weight loss started of ZIF-8 observed upon increasing the temperature from 110 to 200°C (weight loss around 68%) [13]. Addition of monometallic copper into ZIF-8 increases thermal stability of the catalyst due to the higher melting point of copper cation than ZIF-8. It is also noteworthy to mention that Cu/ZIF-8 (residue remains 40%) catalyst reveal good thermal stability [1].

UV-Vis absorption spectra of the MOF’s recorded in the region from 200 to 800 nm region are shown in figure 4. DR-UV-Vis analysis was also performed to determine the band gap energy (figure 5). The band gap energies were obtained from the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), where $\alpha$ is the absorption coefficient [17]. The intercepts of plots (dash lines) on the energy axis confirmed the energy band gaps [1]. As observed in figure 5, the band gap value decreased from 4.0 eV to 3.45 eV with addition of copper into ZIF-8 which shows smaller band gap rather than stated by Schejn et. al. [8] and in this work ZIF-8 shows lower band gap energy than reported by Wang et. al. [18]. ZIF-8 shows a narrow absorption profile in visible region compares to Cu/ZIF-8. The band gap of ZIF-8 reduced after inclusion of copper on it and shifted to lower band gap energies with more absorbance and become active in visible region. The results suggest that Cu/ZIF-8 can be photoexcited to create more electron–hole pairs under visible light absorbance which could leads to higher photocatalytic efficiency [1, 19].

Figure 3. Thermal stability curve of ZIF-8 and Cu/ZIF-8.

Figure 4. UV-vis absorption spectra of ZIF-8 and Cu/ZIF-8.
5. Conclusion
Copper based zeolitic imidazolate framework-8 as a MOF were successfully synthesized under mild conditions using hydrothermal method and the incorporation of Cu into ZIF-8 confirmed with the FTIR spectra and FESEM-EDX analysis. It is found that the addition of Cu into ZIF-8 has increased thermal stability and reduces the band gap (4.0 to 3.45 eV) with more absorbance in visible region and making this framework active via UV as well as visible light. The results also concluded that increasing copper loading will increase absorption intensity. These outcomes will help researchers to improve metal organic frameworks with enhanced photocatalytic properties.

Acknowledgements
The authors acknowledge Financial support from Universiti Teknologi PETRONAS (UTP) and facilities within the UTP Centralized Analytical Laboratory (CAL).

References
[1] Li J, Luo D, Yang C, He S, Chen S, Lin J, et al. 2013 Copper (II) imidazolate frameworks as highly efficient photocatalysts for reduction of CO$_2$ into methanol under visible light irradiation. *J. Solid State Chem.* 203 154-59
[2] Müller M, Hermes S, Kähler K, van den Berg M W, Muhler M and Fischer R A 2008 Loading of MOF-5 with Cu and ZnO nanoparticles by gas-phase infiltration with organometallic precursors: properties of Cu/ZnO@MOF-5 as catalyst for methanol synthesis *Chem. Mater.* 20 4576-87
[3] Nasution H W, Purnama E, Kosela S and Gunlazuardi J 2005 Photocatalytic reduction of CO$_2$ on copper-doped titania catalysts prepared by improved-impregnation method *Catal. Commun.* 6 313-19
[4] Benmansour S, Atmani C, Settifi F, Triki S, Marchivie M and Gómez-Garcia C J 2010 Polynitrile anions as ligands: From magnetic polymeric architectures to spin crossover materials *Coord. Chem. Rev.* 254 1468-78
[5] Xiang Z, Cao D, Lan J, Wang W and Broom D P 2010 Multiscale simulation and modelling of adsorptive processes for energy gas storage and carbon dioxide capture in porous coordination frameworks *Energy Environ. Sci.* 3 1469-87
[6] Li J R, Kuppler R J and Zhou H C 2009 Selective gas adsorption and separation in metal–organic frameworks *Chem. Soc. Rev.* 38 1477-1504
[7] Britt D, Tranchemontagne D and Yaghi O M 2008 Metal-organic frameworks with high capacity and selectivity for harmful gases *Proc. Natl. Acad. Sci.* 105 11623-27
[8] Schein A, Aboulaich A, Balan L, Falk V, Lalévé J, Medjahdi G et al. 2015 Cu$^{2+}$-doped zeolitic imidazolate frameworks (ZIF-8): efficient and stable catalysts for cycloadditions and condensation reactions *Catal. Sci. Technol.* 5 1829-39
[9] Farha O K, Yazaydın A O, Eryazici I, Malliakas C D, Hauser B G, Kanatzidis M G, et al. 2010 De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities Nat. Chem. 2 944-48
[10] Park K S, Ni Z, Côté A P, Choi J Y, Huang R, Uribe-Romo F J et. al. 2006 Exceptional chemical and thermal stability of zeolitic imidazolate frameworks Proc. Natl. Acad. Sci. 103 10186-91
[11] Yao J, He M and Wang H 2015 Strategies for controlling crystal structure and reducing usage of organic ligand and solvents in the synthesis of zeolitic imidazolate frameworks CrystEngComm 17 4970-76
[12] Liu Q, Low Z X, Li L, Razmjou A, Wang K, Yao J et. al. 2013 ZIF-8/Zn2GeO4 nanorods with an enhanced CO2 adsorption property in an aqueous medium for photocatalytic synthesis of liquid fuel J. Mater. Chem. A 1 11563-69
[13] Pan Y, Liu Y, Zeng G, Zhao L and Lai Z 2011 Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system Chem. Commun. 47 2071-73
[14] Du Y, Chen R, Yao J and Wang H 2013 Facile fabrication of porous ZnO by thermal treatment of zeolitic imidazolate framework-8 and its photocatalytic activity J. Alloys Compd. 551 125-130
[15] Shaharun M S, Shaharun S and Al-Shaibani A 2016 Effect of zirconia on the physicochemical properties of copper (II) imidazolate frameworks in AIP Conference Proceedings 1787 050013
[16] Santos S X D and Cavalheiro E T 2014 Using of a graphite-polyurethane composite electrode modified with a Schiff base as a bio-inspired sensor in the dopamine determination J. Braz. Chem. Soc. 25 1071-1077
[17] Goyal S, Shaharun M S and Kait C F 2017 Characterization of copper (II)-zirconium (IV)-imidazolate framework synthesized by hydrothermal method in IJOAB J. 7 473-78
[18] Wang F, Liu Z S, Yang H, Tan Y X and Zhang J 2011 Hybrid zeolitic imidazolate frameworks with catalytically active TO4 building blocks Angew. Chem., Int. Ed. 50 450-453
[19] Jeyalakshmi V, Mahalakshmy R, Krishnamurthy K and Viswanathan B 2012 Titania based catalysts for photoreduction of carbon dioxide: Role of modifiers IJC-A 51A 1263-83