Malaysian Journal of Fundamental and Applied Sciences Vol. 11, No. 3 (2015) 102-105

MJFAS Malaysian Journal of Fundamental and Applied Sciences
ISSN:2289-5981 e-ISSN:2289-599X
UTM UNIVERSITI TEKNOLOGI MALAYSIA

Copper modified TiO_2 and $g\text{-}C_3N_4$ catalysts for photoreduction of CO_2 to methanol using different reaction mediums

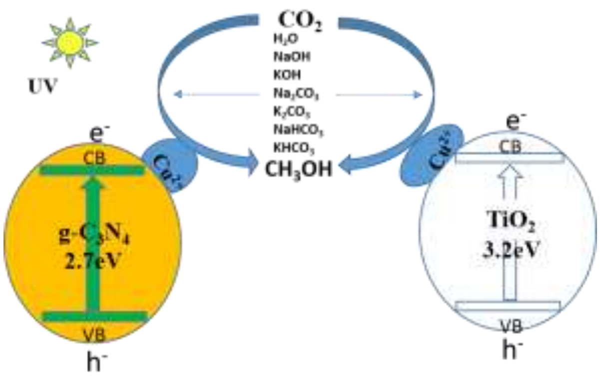
Adekoya Oluwatobi David[1], Muhammad Tahir[1], Nor Aishah Saidina Amin[1*]

[1] Chemical Reaction Engineering Group (CREG)/Low Carbon Energy Group, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.
[2]Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

[*]Corresponding Author: noraishah@cheme.utm.my

GRAPHICAL ABSTRACT

Article history :
Received 25 October 2015
Accepted 13 November 2015



ABSTRACT

In this study, Cu/TiO_2 and $Cu/g\text{-}C_3N_4$ catalysts were tested for CO_2 reduction to methanol. The catalysts were prepared by the wet impregnation method and, characterized by XRD and FESEM. The product identification and yield were determined using a GC with FID. The CO_2 photoreduction process was performed in each of the following reaction mediums: H_2O, NaOH, KOH, Na_2CO_3, K_2CO_3, $NaHCO_3$ and $KHCO_3$. The efficiency was studied by comparing the methanol yield for each. A slurry type photoreactor with a UV lamp of 365 nm wavelength was used. CO_2 photoreduction to methanol using NaOH as the reaction medium registered the highest yield of 431.65 μmole/g-cat•hr. This is due to the higher solubility of CO_2 in the alkali as compared to that of the other reaction mediums, the ability of NaOH to serve as a hole scavenger owing to the formation of OH• ions and the higher selectivity of NaOH solution for CO_2 photoreduction to methanol. It was obvious the choice of reaction medium affected the photoreduction of CO_2 to methanol. The trend of results indicated the use of NaOH as a reaction medium improved the efficiency of the photoreduction process. The findings from this research could promote research in the field of photocatalysis by improving the yield which will encourage the support for methanol economy.

Keywords: methanol, titanium dioxide, carbon nitride, copper

http://dx.doi.org/10.11113/mjfas.v11n3.376

1. INTRODUCTION

The world today is experiencing two major problems global warming and the rising demand of energy. Global warming is due to the rapid increase of CO_2 in the atmosphere while the geometric progression of population growth in the world is the reason for the rising demand of energy. One of the most prominent strategies embraced by scientists is Carbon Dioxide Capture and Storage (CCS) which involves the storage of these captured CO_2 in deep oceans, depleted oil or gas wells etc. [1] Carbon dioxide Capture and Recycle (CCR) is the conversion/reduction of the captured CO_2 to hydrocarbon fuels. This is a better approach because it ends in a win-win situation. Since this initiative was executed in 1979 by employing semiconductors (TiO_2, SiC, GaP, WO_3) to photoreduce CO_2 to simple C_1 products (CH_3OH, HCHO, HCOOH and trace amounts of CH_4), researchers have focused more on it [2, 3]. Methanol is the most desired product from the photoreduction process of CO_2 amongst others because it can be easily/directly used as a liquid fuel [4].

The properties of methanol reveal numerous benefits which makes it a viable and prospective feedstock in industries [5]. The photoreduction process is dependent on some operating parameters which affects its efficiency and hence the yield and selectivity. One of the key parameters is type of reaction medium [6]. Researchers have used different types of reaction mediums such as H_2O [7], NaOH [8], $NaHCO_3$ [9], and $KHCO_3$ [10] for CO_2 photoreduction. Water is the most abundant, readily available, inexpensive, and environment friendly of all the reaction mediums but it is faced with one draw-back which is its low solubility with CO_2 (2g/L) [11-13]. There is a need for reaction mediums (sacrificial electron donors) capable of improving the process efficiency.

In this paper, the efficiency of different reaction mediums used for CO_2 photoreduction is compared. Also, the efficiency of the two catalysts used is compared and the effect of reaction medium on the efficiency of the catalysts is discussed. Cu/TiO_2 has long been considered the best catalyst for methanol photosynthesis [14]. It is envisaged that doping TiO_2 with Cu^{2+}could lower its band gap due to the lower redox potential of copper ions. The electron-hole recombination rate could be effectively reduced [15]. g-C_3N_4 was selected because of its low band gap of 2.7 eV amidst its several other properties which makes it almost perfect as a metal free heterogeneous catalyst [16]. Meanwhile, the reaction mediums were H_2O, NaOH, KOH, Na_2CO_3, K_2CO_3, $NaHCO_3$ and $KHCO_3$. A slurry type photoreactor equipped with a UV light source of 365 nm was used for the process. The catalysts were characterized using XRD and FESEM while a GC with FID was used to separate and identify the products.

2. EXPERIMENTS

2.1 Catalyst Preparation

TiO_2 (anatase, Sigma Aldrich, >99% trace metals basis), $Cu(NO_3)_2.3H_2O$ (Emory, 99%) the copper salt used for metal doping, and melamine (99% Sigma Aldrich) were used as the precursor for preparing carbon nitride. Both catalysts were prepared by the wet impregnation method. In a typical method, 4 g of TiO_2 was dissolved in a solution of 0.456 g of copper nitrate $Cu(NO_3)_2.3H_2O$. The mixture was stirred for 1h using a magnetic stirrer after which it was put in a water bath to evaporate the solvent at 80°C for 3h. The sample was oven dried at 120°C for 12h and then calcined for 5h at 450°C and grinded into powder form to give 3 wt % Cu doped TiO_2 [17, 18]. g-C_3N_4 was synthesized by the thermal decomposition of melamine in a furnace at 550°C for 2h [19]. 3wt% Cu doped g-C_3N_4 was synthesized by a method similar to that of Cu/TiO_2 but with a slight modification where TiO_2 was replaced with g-C_3N_4. 1 M of the different reaction mediums (NaOH, KOH, Na_2CO_3 and K_2CO_3) were prepared conventionally.

2.2. Characterization

The crystalline structure of the as-prepared catalysts were determined with X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Kα radiation source in the range of $2\theta = 5\text{-}80°$ and a step size of 0.05° and counting time of 5s. The surface morphology was examined using field-emission scanning electron microscopy (FESEM JEOL model JSM-6700F, Japan).

2.3. Photocatalytic Activity Test

The photocatalytic reaction was conducted in a 1L jacketed Pyrex glass beaker mounted on a FAVORIT Stirring Hotplate HS0707V2. A 365nm UV lamp was used as the solar light source and a black casing was used for the reactor to shield against the radiation. 0.2g of the as-prepared powder form photocatalyst was placed in the slurry type reactor with 400ml of each reaction medium one after the other. CO_2 gas was first injected into the solution for 30mins at a flow rate of 20 cc/min with the light off. This is to allow full adsorption of CO_2 into the solution. The solution was then irradiated under the UV lamp light for 2h each. Sample was collected after 2h, separated with a 0.45µ filter and analyzed using a GC with FID. Blank experiments were conducted to ensure that the product formed was due to the photoreduction of CO_2.

3. RESULTS AND DISCUSSION

Fig. 1 exhibits the XRD patterns of the Cu/g-C_3N_4 and Cu/TiO_2. The wide-angle peak at 27.5° was characteristic of an interlayer stacking of conjugated aromatic systems. A minor diffraction peak was found at 13.35°, which was indexed to the (1 0 0) plane and assigned to the in-plane structural packing of aromatic systems. The presence of these two characteristic peaks confirmed the formation of g-C_3N_4 framework. Nevertheless, there is no peak attributable to the Cu metal. This could be due to its low dopant percentage of just (3wt %) or that the metal dopant was firmly bonded to the g-C_3N_4 support. This could be due to nucleophilic nitrogen surrounding the unique 2-dimensional layered structure of g-C_3N_4. This could have aided hybridization with other components. In the case of Cu/TiO_2, a single anatase phase TiO_2 was formed. The peaks at 2θ values of 25.26°, 37.77°, 48.0°, 53.84°, 55.02°, 62.62°, 68.67°, 70.25° and 75.0° were identified by comparing with literature data and confirming the particles are crystalline anatase TiO_2 and Cu peak (43.2°). All peaks are in good agreement with the standard spectrum (JCPDS no 01-075-2246). From the XRD diffractograms, it is obvious that the Cu in Cu/TiO_2 is more crystalline compared to the Cu in the Cu/g-C_3N_4. Graphitic carbon nitride is the most stable of all the allotropes of carbon nitride under ambient conditions. Its amorphous structure and high reactivity makes it an efficient photocatalyst for water splitting even without noble metal doping. It allows the transfer of charges maximally thereby reacting very well with the reaction mediums and stabilizing the electrons and holes.

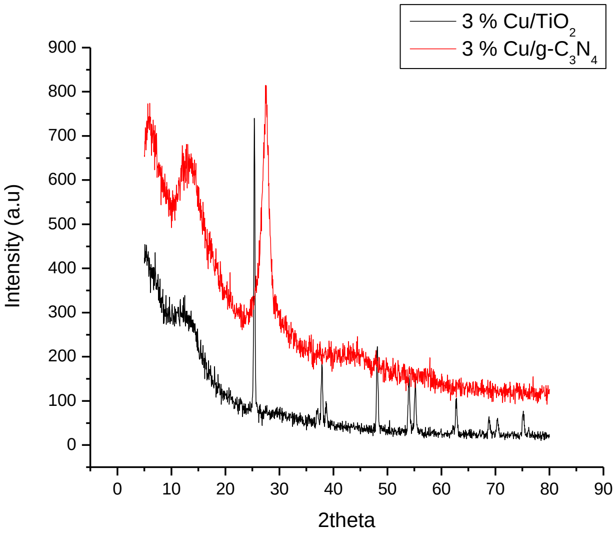


Fig. 1 XRD patterns of the samples

In order to investigate the morphology of the two photocatalysts used, FESEM analysis was performed. From Fig. 2a illustrates the Cu/TiO_2, sample consists of agglomerated nanosized particles and the metal dopant was most probably incorporated into the support. In the case of Fig. 2b, $Cu/g\text{-}C_3N_4$ image indicates lamellar structure with high porosity.

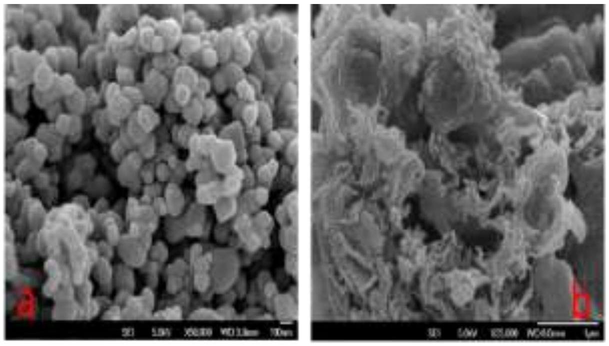


Fig. 2 FESEM images of (a) 3% Cu/TiO_2 and (b) 3% $Cu/g\text{-}C_3N_4$

From the results summarized in Table 1 and illustrated in Fig 3, it is obvious that in considering the reaction mediums and their yield of methanol, 1 M NaOH solution registered the best result and this can be traced to the solubility of CO_2 in NaOH. The solubility of CO_2 in water at room temperature is only 2g/L [15, 16]. More CO_2 is converted when NaOH was used as the reaction medium. This was seen during the process by observing the rapid flow of exit gas from the process while using water. This was due to the immediate formation of carbonic acid between water and CO_2 producing CO_3^{2-} ions but in the case of NaOH the flow was rather slower because as more CO_2 was added to the NaOH solution the carbonic acid was converted to bicarbonate producing HCO_3^- ions.

Table 1 Yield of methanol from CO_2 photoreduction using Cu/TiO_2 and $Cu/g\text{-}C_3N_4$ using different reaction mediums

Reaction medium	**MeOH yield using Cu/TiO_2 (μmole/g cat•hr)**	**MeOH yield using $Cu/g\text{-}C_3N_4$ (μmole/g-cat•hr)**
K_2CO_3	1.05	180.9
KOH	1.70	230.69
$NaHCO_3$	17.68	259.60
$KHCO_3$	41.89	271.70
H_2O	46.08	323.72
Na_2CO_3	61.39	375.65
NaOH	139.34	431.65

The potential can be lowered by nearly 0.7V when CO_2 was changed to CO_3^{2-} or HCO_3^- [20]. The HCO_3^- (or CO_3^{2-}) ions were anchored to the photocatalyst surfaces which efficiently received the electrons, and converted to CH_3OH after protonation [21]. The use of water as a reaction medium favors water splitting leading to H_2 production instead of $CO_2^{\bullet\,-}$ radical anions which allows formation of the methoxy ($\bullet OCH_3$) radicals needed for CH_3OH. This is because the electrode potential for water splitting is lesser than that of CO_2 reduction showing that water splitting is thermodynamically easier [6]. The NaOH also serves as a hole scavenger due to the formation of the OH• ions. CO_2 is also more soluble in Na_2CO_3 compared to water and gave a better result [6]. The low yield of methanol in the case of the potassium salts may be attributed to the decrease in the ionization enthalpies of the alkali metals as the atomic number increases down the group of the periodic table due to decrease in lattice enthalpies. The removal of a valence electron from sodium is higher than that of potassium and since there is a need for electrons in the photoreduction process the sodium salts should give a better performance. $KHCO_3$ is an exception because its solubility is fairly higher compared to $NaHCO_3$ [22].

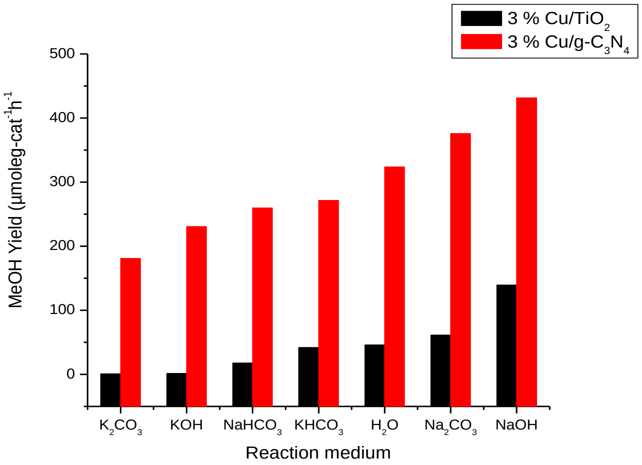


Fig. 3 Yield of methanol in various reaction mediums

The effect of doping on catalysts with Cu metal can be seen in Fig. 4. For both catalyst supports there is an increase in the efficiency of the process visible from the yield of methanol. This is obviously due to the ability of the Cu ions to act as electron trapping agents while still maintaining the mobility of photoelectrons. The yield of methanol from $Cu/g\text{-}C_3N_4$ is more than 3 times higher than that of Cu/TiO_2 with NaOH as the reaction medium. This is so because of the suitable band gap of $g\text{-}C_3N_4$ compared to that of TiO_2 and it is expected that the yield of methanol would be higher in the case of the former even after metal doping. The lamellar structure of the $Cu/g\text{-}C_3N_4$, as evident from FESEM, is characterized by a mesoporous morphology which is possibly responsible for the slight increase in its yield as compared to that of pure $g\text{-}C_3N_4$.

Another interesting observation from this study is the fact that the trend in the result obtained for both catalysts is similar. The results of the photocatalytic test indicated that for both catalysts, the methanol yield prevailed in NaOH compared to the other reaction mediums. The concentration of the surface OH• groups was found to play a role in the selectivity for the formation of CH_3OH [23]. The carbonate and hydrogen carbonates formed from the dissolution of CO_2 in NaOH assisted to increase the efficiency of the process.

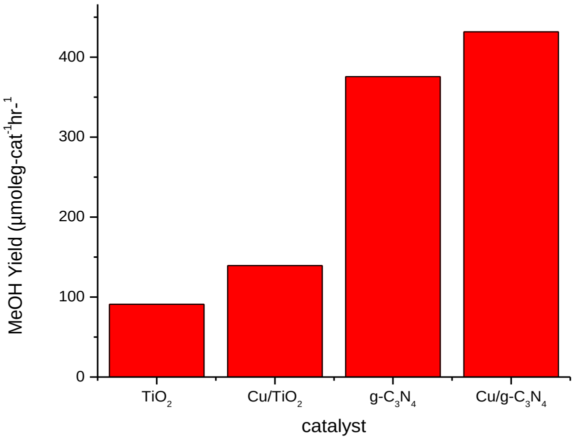


Fig. 4 Yield of methanol in NaOH reaction medium using different catalysts

4. CONCLUSION

From the results, NaOH exhibits the highest yield of methanol and other reaction mediums spotted a similar trend for both catalysts. The $Cu/g\text{-}C_3N_4$ gives a better yield compared to Cu/TiO_2 due to its suitable band gap for photocatalytic reactions even though the crystallinity of Cu on $g\text{-}C_3N_4$ did not give much effect on its activity. It is evident that NaOH is a better reaction medium for CO_2 photoreduction to methanol due to the high solubility of CO_2 in NaOH and the selectivity of NaOH towards CO_2 photoreduction to methanol. The NaOH serves as a hole scavenger, its OH• radical helps foster the reduction of CO_2 by extending the decay time of electrons. Although the cost of using water as a reaction medium is cheaper compared to others, its solubility for CO_2 and the competition between water splitting and CO_2 reduction hampers its efficiency as a reaction medium for CO_2 reduction.

ACKNOWLEDGEMENTS

This work is supported by Ministry of Higher Education (MOHE) Malaysia through Nanomite Long Term Research Grant Scheme (LRGS) No. R.J130000.7844.4L839.

REFERENCES

[1] Ganesh, I. Materials Science Forum. 2013. Trans Tech Publ.
[2] Tahir, M. and N.S. Amin, Appl. Catal. B: Environ. 142 (2013) 512.
[3] A. Dhakshinamoorthy, S. Navalon, A. Corma, H. Garci, Energy Environ. Sci. 5 (2012) 9217.
[4] M. Tahir, N.S. Amin, Renew. Sust. Energ. Rev. 25 (2013) 560.
[5] G.A. Olah, A. Goeppert, G.S. Prakash, Beyond oil and gas: the methanol economy. 2011: John Wiley & Sons.
[6] O. Ola, M.M. Maroto-Valer, J. Photochem. Photobiol. C: Photochem. Rev. 24 (2015) 16.
[7] H.W.N. Slamet, World Appl. Sci. J. 6 (2009) 112.
[8] H.-C. Yang, H.-Y. Lin, Y.-S. Chien, J. C.-S. Wu and H.-H. Wu, Catal. Lett. 131 (2009) 381.
[9] Q.D. Truong, J.-Y. Liu, C.-C. Chung Y.-C. Ling, Catal. Commun. 19 (2012) 85.
[10] H. W. Nasution, E. Purnama, S. Kosela J. Gunlazuardi, Catal. Commun. 6 (2005) 31331.
[11] P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, Ind. Eng. Chem. Res. 45 (2006) 2558.
[12] Indrakanti, V.P., J.D. Kubicki, H.H. Schobert, Energy Environ. Sci. 2 (2009) 745.
[13] S. Kaneco, Y. Shimizu, K. Ohta, T. Mizuno. J. Photochem. Photobiol. A: Chem. 115 (1998) 223.
[14] J.C. Wu, H.-M. Lin, C.-L. Lai, Appl. Catal. A: Gen. 296 (2005) 194.
[15] Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han, C. Li. Chem. Rev. (2014) 10043
[16] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O Müller, R. Schlögl, J. M. Carlsson, J. Mater. Chem. 18 (2008) 4893,
[17] L. Yoong, F.K. Chong, B.K. Dutta, Energy 34 (2009) 1652.
[18] Z. Ding, X. Chen, M. Antonietti, X. Wang. ChemSusChem 4 (2011) 274.
[19] J. Mao, T. Peng, X. Zhang, K. Li, L. Ye, L. Zan, Catal. Sci. Technol. 3 (2013) 1253.
[20] P.-W. Pan, Y.-W. Chen, Catal. Commun. 8 (2007) 1546.
21] Y. Y. Liu, B. B. Huang, Y. Dai, X. Y. Zhang, X. Y. Qin, M. H. Jiang, M. Whangbo, Catal. Commun. 11 (2009) 210.
[22] J.K. Stolaroff, No. LLNL-TR-644894. Lawrence Livermore National Laboratory (LLNL), Livermore, CA, 2013
[23] K. Ikeue, S. Nozaki, M. Ogawa, M. Anpo, Catalysis Today 74 (2002) 241.