Copper modified TiO$_2$ and g-C$_3$N$_4$ catalysts for photoreduction of CO$_2$ to methanol using different reaction mediums

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GRAPHICAL ABSTRACT

ABSTRACT

In this study, Cu/TiO$_2$ and Cu/g-C$_3$N$_4$ 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$_2$O, NaOH, KOH, Na$_2$CO$_3$, K$_2$CO$_3$, 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 μmol/g-cat/hr. This is due to the higher solubility of CO$_2$ in the alkaline 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 to 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

1. INTRODUCTION

The world today is experiencing two major problems: global warming and the rising demand for 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$_3$OH, 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$_2$O [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$^+$ 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-C3N4 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 H2O, NaOH, KOH, Na2CO3, K2CO3, NaHCO3 and KHCO3. 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

TiO2 (anatase, Sigma Aldrich, >99% trace metals basis), Cu(NO3)2·3H2O (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 TiO2 was dissolved in a solution of 0.456 g of copper nitrate Cu(NO3)2·3H2O. The mixture was stirred for 1 h using a magnetic stirrer after which it was put in a water bath to evaporate the solvent at 80°C for 3 h. The sample was oven dried at 120°C for 12 h and then calcined for 5 h at 450°C and grinded into powder form to give 3 wt % Cu doped TiO2 [17, 18]. g-C3N4 was synthesized by the thermal decomposition of melamine in a furnace at 550°C for 2 h [19]. 3wt% Cu doped g-C3N4 was synthesized by a method similar to that of Cu/TiO2 but with a slight modification where TiO2 was replaced with g-C3N4. 1 M of the different reaction mediums (NaOH, KOH, Na2CO3 and K2CO3) 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 2θ = 5-80° and a step size of 0.05° and counting time of 5 s. 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 1 L jacketed Pyrex glass beaker mounted on a FAVORIT Stirring Hotplate HS0707V2. A 365 nm UV lamp was used as the solar light source and a black casing was used for the reactor to shield against the radiation. 0.2 g of the as-prepared powder form photocatalyst was placed in the slurry type reactor with 400 ml of each reaction medium one after the other. CO2 gas was first injected into the solution for 30 mins at a flow rate of 20 cc/min with the light off. This is to allow full adsorption of CO2 into the solution. The solution was then irradiated under the UV lamp light for 2 h each. Sample was collected after 2 h, separated with a 0.45 μm filter and analyzed using a GC with FID. Blank experiments were conducted to ensure that the product formed was due to the photoreduction of CO2.

3. RESULTS AND DISCUSSION

Fig. 1 exhibits the XRD patterns of the Cu/g-C3N4 and Cu/TiO2. 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-C3N4 framework. Nevertheless, there is no peak attributable to the Cu metal. This could be due to its low dopant percentage of just (3 wt %) or that the metal dopant was firmly bonded to the g-C3N4 support. This could be due to nucleophilic nitrogen surrounding the unique 2-dimensional layered structure of g-C3N4. This could have aided hybridization with other components. In the case of Cu/TiO2, a single anatase phase TiO2 was formed. The peaks at 20 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 TiO2 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/TiO2 is more crystalline compared to the Cu in the Cu/g-C3N4. 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](image-url)
In order to investigate the morphology of the two photocatalysts used, FESEM analysis was performed. From Fig. 2a illustrates the Cu/TiO₂ 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-C₃N₄ image indicates lamellar structure with high porosity.

![FESEM images of (a) 3% Cu/TiO₂ and (b) 3% Cu/g-C₃N₄](image)

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 CO₂ in NaOH. The solubility of CO₂ in water at room temperature is only 2g/L [15, 16]. More CO₂ 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 CO₂ producing CO₃²⁻ ions but in the case of NaOH the flow was rather slower because as more CO₂ was added to the NaOH solution the carbonic acid was converted to bicarbonate producing HCO₃⁻ ions.

![Yield of methanol in various reaction mediums](image)

Table 1 Yield of methanol from CO₂ photoreduction using Cu/TiO₂ and Cu/g-C₃N₄ using different reaction mediums

<table>
<thead>
<tr>
<th>Reaction medium</th>
<th>MeOH yield using Cu/TiO₂ (µmole/g cat-hr)</th>
<th>MeOH yield using Cu/g-C₃N₄ (µmole/g cat-hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃</td>
<td>1.05</td>
<td>180.9</td>
</tr>
<tr>
<td>KOH</td>
<td>1.70</td>
<td>230.69</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>17.68</td>
<td>259.60</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>41.89</td>
<td>271.70</td>
</tr>
<tr>
<td>H₂O</td>
<td>46.08</td>
<td>323.72</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>61.39</td>
<td>375.65</td>
</tr>
<tr>
<td>NaOH</td>
<td>139.34</td>
<td>431.65</td>
</tr>
</tbody>
</table>

The potential can be lowered by nearly 0.7V when CO₂ was changed to CO₃²⁻ or HCO₃⁻ [20]. The HCO₃⁻ (or CO₃²⁻) ions were anchored to the photocatalyst surfaces which efficiently received the electrons, and converted to CH₃OH after protonation [21]. The use of water as a reaction medium favors water splitting leading to H₂ production instead of CO₂•⁻ radical anions which allows formation of the methoxy (•OCH₃) radicals needed for CH₃OH. This is because the electrode potential for water splitting is lesser than that of CO₂ 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. CO₂ is also more soluble in Na₂CO₃ 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. KHCO₃ is an exception because its solubility is fairly higher compared to NaHCO₃ [22].

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-C₃N₄ is more than 3 times higher than that of Cu/TiO₂ with NaOH as the reaction medium. This is so because of the suitable band gap of g-C₃N₄ compared to that of TiO₂ 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-C₃N₄, 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-C₃N₄.

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 CH₃OH [23]. The carbonate and hydrogen carbonates formed from the dissolution of CO₂ 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 spoted a similar trend for both catalysts. The Cu/g-C₃N₄ gives a better yield compared to Cu/TiO₂ due to its suitable band gap for photocatalytic reactions even though the crystallinity of Cu on g-C₃N₄ did not give much effect on its activity. It is evident that NaOH is a better reaction medium for CO₂ photoreduction to methanol due to the high solubility of CO₂ in NaOH and the selectivity of NaOH towards CO₂ photoreduction to methanol. The NaOH serves as a hole scavenger, its OH• radical helps foster the reduction of CO₂ 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 CO₂ and the competition between water splitting and CO₂ reduction hampers its efficiency as a reaction medium for CO₂ reduction.

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