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Photoconversion of CO_2 into methanol over ZnO photocatalyst

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Abstract: The dependence on fossil fuels for energy production has led to increasing carbon dioxide (CO_2) gas concentration in the atmosphere from 280 ppm in the pre-industrial era to 406 ppm nowadays, causing the so-called global warming. Therefore, sustainable sources of energy are necessary to overcome this problem. In this paper, we report the photoreduction of CO_2 into hydrocarbons fuel over ZnO semiconductor. ZnO photocatalyst was prepared via modified thermal decomposition method where the X-ray diffraction pattern proved the fabrication of wurtzite hexagonal structure of ZnO nanoparticles. CO_2 photoreduction was operated in CO_2-saturated 0.5 M NaCl solution using 150 W mercury (Hg) lamp as the light source. Methanol and acetaldehyde were the main products in the experiment with the maximum production yield of 10.9 and 16 µmol/g respectively. The high photocatalytic activity would be related to the presence of Cl^- ions, which acted as hole scavenger which decreased the rate of charge carriers recombination

keywords: ZnO; CO2 reduction; methanol

1.Introduction

Since the discovery of fossil fuels, carbon dioxide (CO_2) concentration in the atmosphere has critically increased. The rising amounts of CO_2 has greatly enhanced the greenhouse effect which initiated a dramatic climate change. Therefore, decreasing this carbon footprint is crucial to prevent multiple disasters. The photocatalytic reduction of CO_2 is considered as one of the most promising routes for solving not only the ecological problem, but also the susceptibility for producing hydrocarbon fuels such as CH_3OH [1], [2]. According to their photocatalytic activity, semiconductors materials like metal oxides have been widely investigated for the photoreduction of CO_2. In 1979, Inoue et.al., converted CO_2 into methanol (CH_3OH) and formic acid (HCOOH) by photocatalytic reduction upon utilizing semiconductor materials like TiO_2, ZnO, CdS, SiC and GaP [3] which encouraged researchers to furtherly investigate this reaction. Unfortunately, the efficiency of photocatalytic reduction of CO_2 is still challenging and further investigations are mandatory to understand its mechanism.

Hence, we report the fabrication of ZnO photocatalyst through thermal decomposition method to be utilized for the photoreduction of CO_2 into C_1 and C_2 hydrocarbons in 0.5 M NaCl aqueous solution. The formation rate of methanol and acetaldehyde was estimated to be 2.7 and 4 µmol g^{-1} h^{-1} respectively. For this, to the best of our knowledge, that is the first time to obtain C_2 hydrocarbon in ZnO semiconductor material.

2. Experimental

2.1 Materials

Zinc carbonate basic laborchemie Apolda, and NaCl (POCH ≥ 99.5%) were used without any further purification.

2.2 Synthesis of ZnO nanoparticles

The synthesis of ZnO material was produced via modified thermal decomposition method [4]. In brief, Zinc carbonate basic reagent was heated in air at 350 °C for 3 h with a heating rate of 2 °C/min. A white powder was obtained in which it was washed several times with deionized water and finally dried at 90 °C for 8h.

2.3 Characterization instruments

The crystal structure and phase composition of ZnO was analyzed by X-ray powder diffraction (XRD) (Bruker, D8Advance, Germany) with copper inner shell-K□ (λ = 1.5406 Å) (40 mA, 40 kV). Moreover, surface topography and composition were analyzed by field emission scanning electron microscope (FE-SEM) using Quanta FEG-250 SEM at 20 kV. In addition, high resolution transmission electron microscope (HR-TEM, JEOL-JEM-1230, Tokyo, Japan) was used to identify the nanoparticles size and shapes. The hydrocarbon products from CO_2 photoreduction was detected by Gas chromatography-Mass spectrometry (GC-MS) instrument via Thermoscientific model, GC TRACE 1300 and TSQ 8000.

2.4 Photocatalytic reduction of CO_2

The photoconversion of CO_2 was made in a homemade Pyrex glass photoreactor. Briefly, 0.1 g of ZnO sample was suspended in 50 ml of 0.5 M NaCl solution inside the reactor chamber. Then, a pure CO_2 gas (99.99%) was purged inside the solution for an hour in the dark while maintaining stirring of the solution to remove any unnecessary gases inside the chamber. After that, while maintaining both stirring and purging of CO_2, the solution was irradiated by UV- light from 150 W Hg lamp for 4 h to initiate CO_2 photoreduction experiment. A liquid sample was withdrawn every 1 h to detect any liquid hydrocarbon product by GC-MS analysis. The product separation in GC was accomplished by using Trace TR-WaxMS GC column.

3. Results and discussions

3.1 Material Characterization

The XRD of ZnO sample was investigated as shown in Figure 1. The result indicated the acquisition of highly crystalline ZnO sample of hexagonal Wurtzite phase. The main observed signals at 2θ° 31.8°, 34.4° and 36.2° were ascribed to the planes (100), (002), and (101) respectively, which matching JCPDS card no. 89-0510 [5], [6]. There were no foreign signals in the pattern which indicated the presence of pure phase of ZnO. The crystallite size was estimated to be equal to 19 nm.

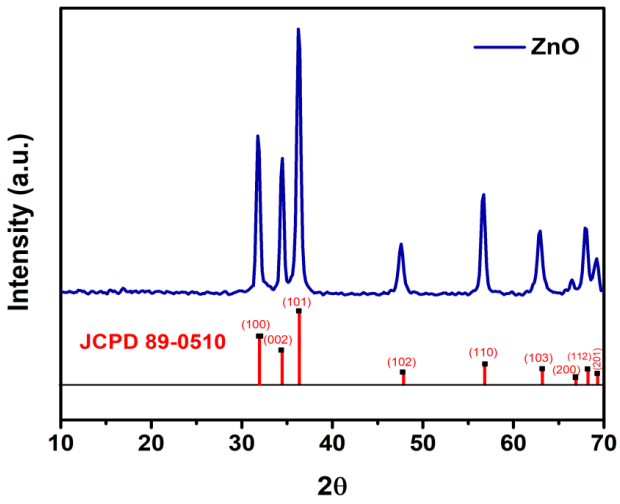

Figure 1 – X-ray diffraction pattern of ZnO.

The surface composition and structure of ZnO sample was investigated by FE-SEM as displayed in Figure **2**a. The analysis revealed the agglomeration of ZnO particles in an orientation that forming diamond-like shapes. However, HR-TEM analysis proved the accumulation of hexagonal nanoparticles structure of ZnO nanoparticles Figure **2**b, which is well matched with XRD result. The particle of ZnO nanoparticles was measure to be equal to ~19 nm.

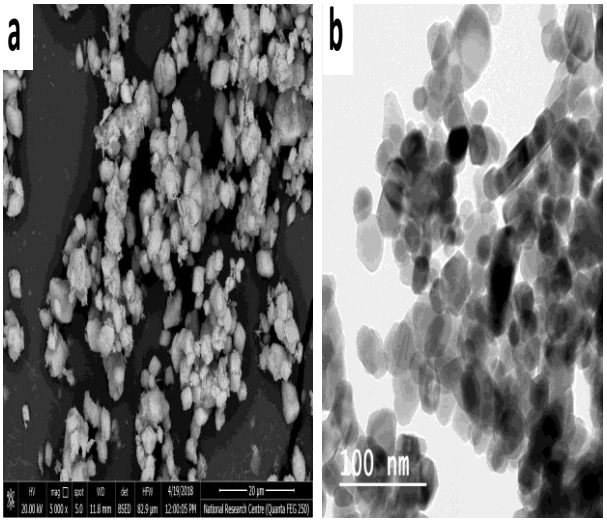

Figure 2 – a and b are the FE-SEM and HR-TEM images of ZnO respectively

3.2 CO_2 photoreduction in 0.5 M NaCl

The hydrocarbon products obtained from the photoconversion of CO_2 in 0.5 M NaCl solution at the surface of ZnO sample is illustrated in Figure 3. After 1 h irradiation, CO_2 reduction over ZnO showed the generation of acetaldehyde (CH_3CHO), while after 2 h

methanol (CH_3OH) was also detected. The maximum production yield of CH_3CHO and CH_3OH were ~10.9 and 16 µmol/g after 4 h respectively with estimated formation rate of 2.7 and 4 µmol g^{-1} h^{-1} respectively. Cl^- ions in NaCl solution improved the trapping of photogenerated holes by acting as a hole scavenger [7]. Moreover, the photoreduction of CO_2 into CH_3CHO and CH_3OH required 10 and 6 electrons respectively [7], [8],which indicating the large number of photogenerated electron on the surface of ZnO photocatalyst.

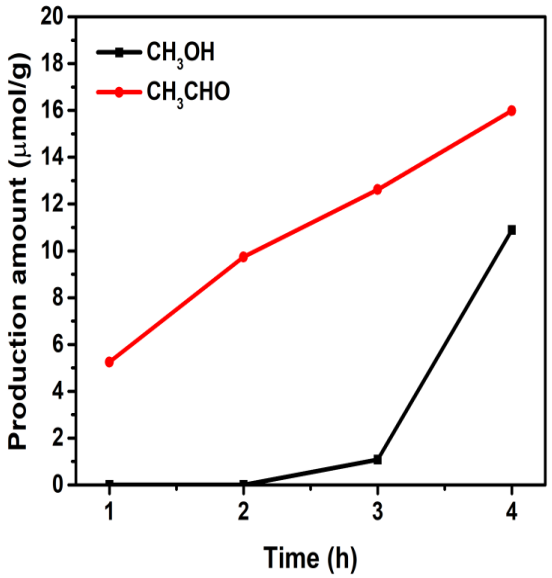

Figure 3 - Production yield over ZnO in 0.5 M a) $NaHCO_3$, b) NaOH, and c) NaCl aqueous solutions.

4. Conclusion

In this paper, we reported the synthesis of ZnO catalyst to investigate its photocatalytic activity towards CO_2 photoreduction. CH_3OH and CH_3CHO was formed in the experiment which indicated the high catalytic performance of ZnO photocatalyst. The superior performance of CO_2 photoreduction is related to the usage of NaCl as solvent. The presence of Cl^- ions in the solution acted as a hole scavenger that aided for longer lifetime of photogenerated electrons and higher reduction possibilities. Hence, our prepared catalyst showed high catalytic activity for CO_2 reduction to hydrocarbon and further studies are required to improve efficiency.

Acknowledgments

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