



TiO₂ supported one-dimensional low silica zeolite for the high-efficiency production of pure methane via Photocatalytic reduction of CO₂ gas



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Abstract

Abstract: Due to the depletion of crude oil, scientists must search for a renewable source of energy. Photocatalytic reduction of CO₂ to methane gas as a hydrocarbon fuel seems to be a promising technique to produce solar fuel and reduce global warming for improved sustainability. A gas flow reactor was made from a quartz tube packed with TiO₂ thin-film deposited on different substrates; one dimensional zeolite beads and glass sheets. At ambient temperature, TiO₂ was prepared by the Sol-Gel method using ethylenediaminetetraacetic acid (EDTA) as a precipitating agent. The effect of calcination temperature was also studied at different temperatures: 200, 400, and 550°C. TiO₂-supported one-dimensional zeolite was characterized by X-Ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and FT-IR and Raman spectroscopy. The prepared materials were used in the photocatalytic reduction of CO₂ (5 ml/min flow rate) in the presence of water vapor at 80°C using a simple gas flow reactor (20 cm in length and 2.5 cm in diameter). The gaseous products were analyzed by gas chromatography. The analysis confirmed the production of pure methane gas. The highest yield of CH₄ gas was achieved after four hours of irradiation with a continuous flow of CO₂ gas. The maximum concentration of methane was 1404 ppm using TiO₂/zeolite calcined at 550°C. The results were compared with those of unsupported TiO₂ prepared under the same conditions. The order of activity was TiO₂/Z 550 > TiO₂/Z 400 > TiO₂/Z 200T > TiO₂/glass sheets > TiO₂ powder.

Keywords: photocatalytic reduction; One dimensional Zeolite; Carbon dioxide, methane gas; water vapor.

Introduction

Fossil fuel utilization creates a social challenge. On the other hand, about 90% of our present energy needs coal, natural gas, and oil used for combustion. However, for every 1 ton of equivalent carbon burned, it creates and releases more than 3.5 tons of carbon dioxide (CO₂). [1]. Furthermore, the Earth's surface temperature has risen by about 0.6 K throughout the last century, with a particularly significant rising in the last 20 years. Fossil fuels are popular for various reasons: they are available in various forms practically everywhere in the world; people have discovered how to use them successfully to supply energy for various uses, and they are relatively cheap and easy to transport. In our modern global energy economy, it is obvious that greater quality of life entails more energy use [2].

Nowadays Carbon dioxide emission reduction strategies are mostly focused on carbon capture and storage (CCS). Carbon capture is the process of removing CO₂ from flue gas before it is discharged into the environment through gas separation, whereas

carbon sequestration (storage) is the process of isolating CO₂ from the atmosphere. There are three methods for reducing CO₂ emissions exist, the First is pre-combustion capturing, the second is post-combustion capturing, and the third is oxy-fuel combustion [3]. The fourth alternative of this study is the utilization of collected CO₂ exhausts to synthesize sustainable hydrocarbon fuels [4]. Two major advantages are the fundamental chemical energy content of liquid fuels (such as petroleum, diesel, and others) and the ease with which they may be stored and transferred. Although it is conceivable to reduce CO₂ emissions by using hydrogen or even electricity to create sustainable fuels, the renewable source that must be employed to convert CO₂ gas into fuels would not contribute to net CO₂ emissions.

A growing number of scientists are taking an interest in CO₂ as a low-cost and accessible source of carbon in the atmosphere, as well as one of the greenhouse gases that contribute to global warming. This is primarily used to convert it into useful fuels and other compounds, which have received a lot of

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attention in recent years. However, because CO₂ is a relatively inert and stable molecule, it is extremely difficult to change CO₂ from a thermodynamic standpoint. Several attempts have been made to improve CO₂ conversion efficiency, including catalytic-hydrogenation, electro-catalysis, photocatalytic degradation, thermolysis, and bio-catalysis [1, 2]. Photocatalytic conversions have lately been a popular area of research owing to their resemblance to the photosynthesis process, which is one of the most environmentally beneficial, mild, and simple-to-manage reactions. As a result, several photo-catalysts, such as carbon-based nanomaterials, sulfide, oxide semiconductors, and others, have been developed for CO₂ conversion [3-5]. Along with the extensive research into carbon dioxide conversion, new research studies of photo-catalysts are now being developed and tested to boost efficiency. Photo-reactors, on the other hand, plays another important role in the low CO₂ conversion efficiency. Several scientists have created monolith reactors, optical fiber reactor designs, fluidized bed reactors, annular batching power plant reactors, and other photocatalytic reactors for CO₂ conversion [6, 7].

Wu et al. [8] have used an optical-fiber reactor to convert CO₂ to methanol using the NiO/InTaO₄ photo-catalyst achieving the highest conversion rate. With the Cu/In co-doped TiO₂ photo-catalyst and H₂ as the redox mediator, Muhammad Tahir and Nor Aishah Saidina Amin [9] used a mono-lith photo-reactor and the main product was CO. The photo-reduction data showed that the monolith photo-reactor produced 12 times more CO than the EU cell-type photo-reactor in Brno, Czech Republic, from October 14th to October 16th, 2015. Yuan et al. [10] used an optical-fiber monolith reactor to convert CO₂ into fuels; the novel reactor significantly enhanced CO₂ to methanol conversion. Qiu-ye et al. [11] used Pt/TiO₂ Nano-sheet Porous Film to convert CO₂ to methane. Kwak et al. (2015) [12] convert CO₂ into methane over Ni-TiO₂ and a photo reactor-gas circulator. Gao et al. [13] reported the formation of methane from the photo-reduction of CO₂ using visible light.

A novel twin reactor was constructed and used for the conversion of CO₂ to CH₃OH with a mixture of CO₂ and CO as the feed, the results showed a sharp increase in the conversion of CO₂ as reported by Cheng et al. [14].

Aluminum silicates with a highly organized crystal structure are known as zeolites. The three-dimensional network of SiO₄- and AlO₄-tetrahedral creates the zeolite's cavities [15, 16]. The nano-sized zeolites were developed based on several features of zeolite functions such as acidity, selectivity character, and filling abilities, and it became a challenge to get unique features compared to micro-crystalline zeolite with a high surface area and a tiny particle size with

less than 100 nm [17,18]. In many applications, such as fluid catalytic cracking, Nano-crystalline Y- zeolite with extra acid sites on the surface and a bulky volume display increased stability and activity because of its good diffusion [19, 20]. A three-dimensional structure of Faujasite type structure of Zeolite Y, which has pores that are perpendicular to each other in the directions of x, y, and z. It is made up of sodalite cages with a crystalline cubic structure and pores that measure 7.4Å. It can also be distinguished by its silica to alumina ratio of 4 to 6, which differs from the other Faujasite type, Zeolite X, which has a ratio of 2 to 3, whilst type A has a ratio of 2.

Although many studies on CO₂ conversion with various photo-catalysts were conducted, the majority of the reactors contained both liquid and gas phases, or only liquid or gas with a sacrificial agent. In this work, we designed a pure gas phase-catalytic reactor for CO₂ conversion to fuels, and the optimal conditions for the CO₂ conversion were investigated in the presence of titanium dioxide thin films supported by glass sheets and zeolite pellets.

2. Experimental

2.1. Synthesis of TiO₂ thin films

At room temperature, 40 ml of titanium (IV) butoxide Ti(OCH₂CH₂CH₂CH₃)₄ was dissolved in 120 ml of butanol and stirred for 2 h to form nanostructured TiO₂ thin films supported zeolite. 30 g of one-dimensional zeolite was added to the prepared solution. Then ethylene-diamine-tetra-acetic acid was added dropwise to the solution containing zeolite with continuous stirring for 2 h. The white precipitate was transferred to a Teflon-lined and left in the oven at 160°C for 8 h. The precipitate, combined with zeolite, was washed with ethanol and double distilled water, then dried at 100°C for 3 h and calcined at different temperatures: 200°C, 400°C, and 600°C for 2 h.

2.2. Characterization of the prepared samples

X-ray diffraction (XRD) patterns were measured on an X'Pert Philips diffractometer (Cu K α radiation with a 2 θ range of 5–90°, a step size of 0.08°, an accelerating voltage of 40 kV, and an applied current of 40 mA. The surface morphology of the sample was analyzed by scanning electron microscopy (SEM; model quanta 250 FEG (Field Emission Gun) attached with an EDX unit (Energy Dispersive X-ray Analysis) for chemical analysis with an accelerating voltage of 30 KV, magnification of 14x up to 100 000, and resolution for the gun is 1n), FEI company, Netherlands. A high-resolution transmission electron microscope (HRTEM) was carried out using (JEM-2010, JEOL Co., Japan).

2.3. Experiment of photocatalytic reduction of CO₂

The experiments were carried out in a homemade gas flow reactor in the presence of water vapor, as in

Figure 1. The gas flow reactor consists of a quartz tube surrounded by a quartz jacket. Two light sources of 254 nm, 6 watts each, and intensity of 35.6 watts/m² were fixed so that the light falls perpendicular to the quartz tube. The quartz tube and the lamp were placed in a box covered with aluminum foil so they reflected all the radiation into the reactor again. The distance between the light source and the quartz jacket is 2.5 cm. The temperature of the flow reactor was raised by the aid of hot air passing in between the quartz tube and the jacket. Purged with a rate of 20 ml/min, CO₂ of purity 99.999% was purged. 3 moles of CO₂ were purged with 1 mole of H₂O with constant stirring and heating.

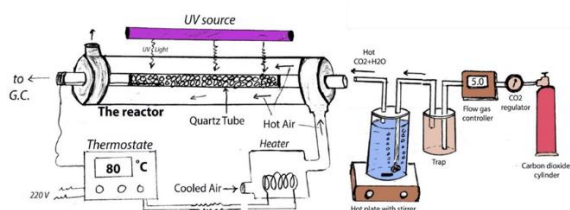


Figure 1: Schematic design of the gas flow reactor

2.4. Photo-catalytic Activity Evaluation.

The photocatalytic reduction of CO₂ was conducted in a flat, closed reactor. Before the run started, the design was evacuated by using a circulating vacuum pump. The prepared TiO₂ thin film was located in the center of the reactor, and then the gaseous CO₂ and water vapor flowed through the reactor for 2 h to achieve the adsorption-desorption equilibrium. Before, the reactor was sealed. The light source was a UV lamp with a precise measurement of incident light intensity. The photocatalytic reaction was typically performed at room temperature for 6 hrs. The products were measured by gas chromatography (GC). The comparison tests consisted of a reaction under light without the catalysts and a reaction in the dark with the catalysts. The results indicated that there was almost no methane production in the comparison experiments.

3. Results and discussion

Figure 2 shows the XRD of the prepared materials, it shows the presence of diffraction peaks at $2\theta=6.2(111)$, $10.1(220)$, $11.8(331)$, $20.2(440)$, $23.5^\circ(533)$, $26.9^\circ(642)$, $30.5^\circ(822)$, $31.2^\circ(555)$, and $32.2^\circ(840)$. The presence of the high-intensity diffraction peak at $2\theta=7.1$ of the zeolite, indicates a high crystallinity. The insight Figure shows the XRD of the powdered TiO₂. The Figure shows the presence of the anatase phase of TiO₂.

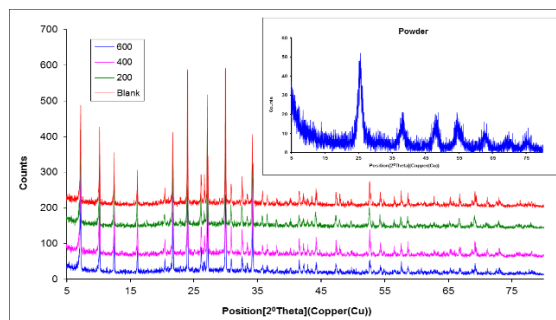


Figure 2: XRD of pure TiO₂, TiO₂/zeolite calcined at 200, 400, and 600 °C

By employing the FTIR method and the KBr-disk approach, the functional groups could be identified. In Figure 3, the FTIR spectra of synthetic TiO₂/zeolites are shown. The synthesized Zeolites A were shown to have several functional groups like O-H groups, which manifested as stretching vibrations at 3450 cm⁻¹ and bending vibrations at 1610–1639 cm⁻¹. Asymmetric stretch vibration can be seen in the wavenumber between 1010 and 1033.88 cm⁻¹ (Si-O-Al). The peak at 457–462 cm⁻¹ displays a collapsing vibration of (Si-O-Si) or (O-Si-O), and the peak at 663.53 cm⁻¹ indicates a symmetric stretching vibration of (Si-O-Al). Zeolites are known for having T-O-T bonds such as Si-O-Si, Al-O-Al, or Si-O-Al. Figure 3 shows also the TiO₂/zeolite after the photocatalytic reduction of CO₂. It is obvious that no additional groups were formed after the photo-reduction process.

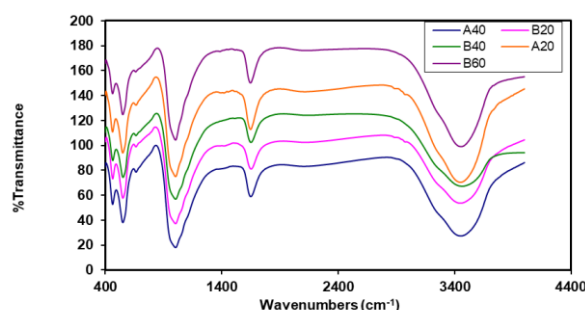


Figure 3: FTIR of TiO₂/zeolite A at different temperatures before and after the photo-reduction process.

Figure 4 displays the HRTEM of 5–8 nm-sized pure well-crystalline TiO₂. Figure 4B depicts the existence of zeolite in the form of rod-like particles, but the image also depicts the deposition of TiO₂ on the walls of the zeolites following TiO₂ precipitation (Figure 4 C). When the temperature reaches 600 C, the rods' forms somewhat distort (Figure 5 D).

Figure 5A depicts the surface morphology of pure zeolites, indicating the zeolites' proven structural identity. Figure 5B shows the TiO₂ incubation in the voids of the zeolites in a spherical form with an excellent homogeneous distribution on the surface at a greater magnification. The mixture includes both

flakes and spheres. According to the elemental analysis, the prepared substance includes Ca, O, Mg, Al, Ti, Si, and C. (Table 1).

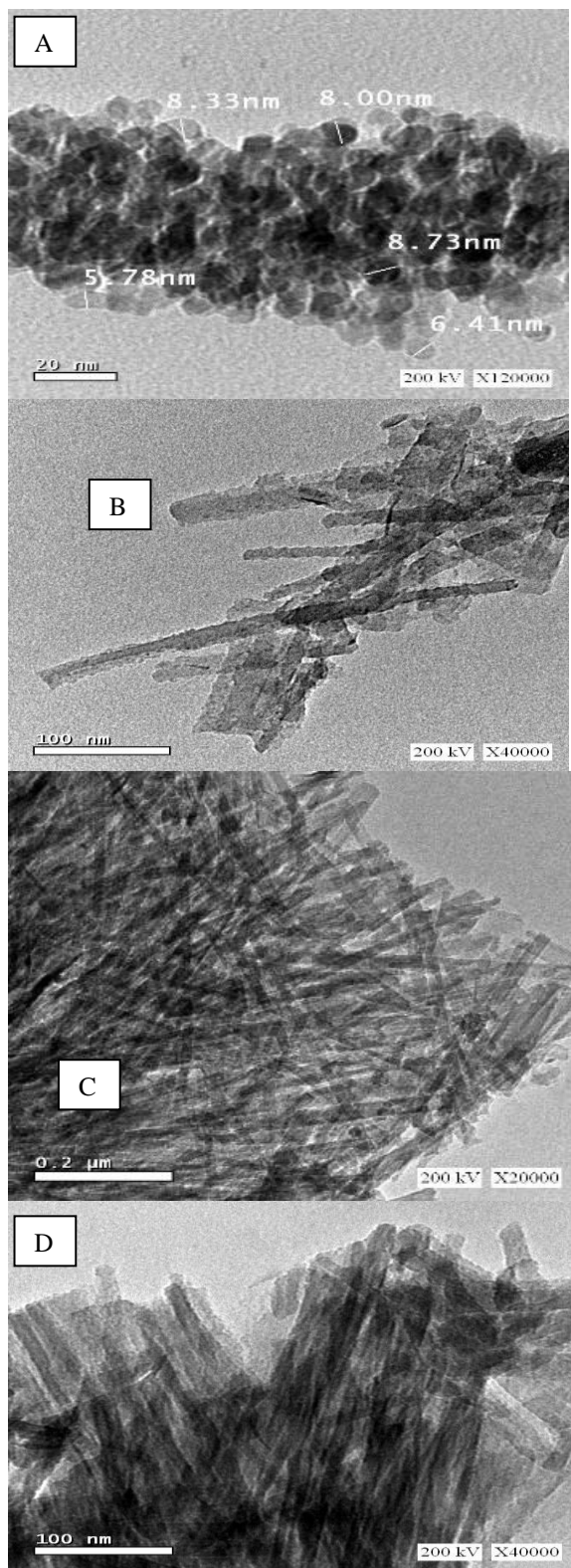


Figure 4: HRTEM of pure TiO₂, zeolites, and TiO₂/zeolite at different temperatures of 400 and 600° C.

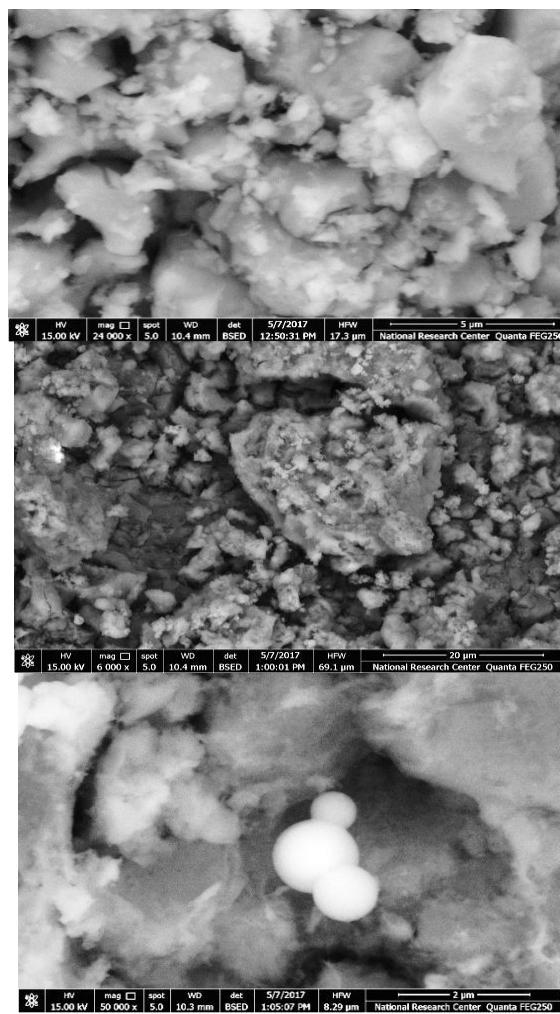
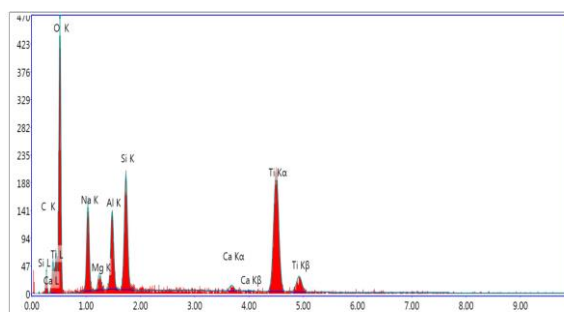


Figure 5: SEM images of zeolites (A), TiO₂/Zeolites (B) at 600°C, and TiO₂/zeolites (C) at different magnification.



Element	Weight %
C K	6.96
O K	49.87
NaK	10.63
MgK	1.47
AlK	5.17
SiK	6.9
CaK	0.64
TiK	18.37

Figure 6: EDX analysis and the corresponding Table of the elemental analysis

Photo-reduction of CO₂ to methane

The photocatalytic reduction of CO₂ was carried out using TiO₂ thin films loaded with different substrates such as; glass sheets, zeolites, and substrate-free (powder) at 200, 400, and 600° C.

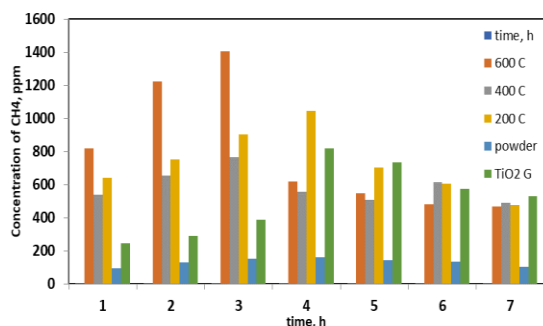


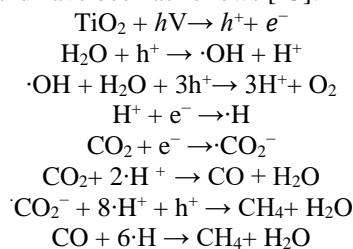
Figure 7: CH₄ yields using TiO₂ loaded on different supports at different temperatures.

Different versions of the complex CO₂ photo-reduction reaction can be found on different semiconductors, including CO, HCOOH, HCHO, CH₃OH, CH₄, and C₂H₆, with CH₄ and CH₃OH being the most desired. To prove that the reaction product is produced by photo-catalytic reduction of CO₂ with H₂O, an empty experiment in an environment containing N₂ and H₂O is necessary. No CH₄ is produced in the absence of UV light irradiation. When exposed to radiation, TiO₂ and TiO₂/Zeolites produce CH₄, which rises with exposure duration and then falls with additional exposure. The sample Ti/zeolite-600 conversion at its greatest level was attained. The generated CH₄ had a concentration of 1404 ppm.

Mechanism of Photo-reduction of CO₂ to Methane

Figure 7 shows the photo-conversion of CO₂ to methane on TiO₂/zeolite. According to the majority of specialists, this mechanism is based on proton-assisted multi-electron transfer rather than single electron transfer because a free electron transfer has an electrochemical potential of 2.14V compared to SCE. TiO₂ thin films develop the photon-generated electrons (e⁻) and holes (h⁺) on their surface when exposed to UV light. Excited holes produced hydroxyl radicals (OH) and hydrogen ions (H⁺) on the catalyst surface, which were then oxidized by OH radicals to create oxygen and hydrogen ions (O₂ and H⁺) [22]. H radicals are created when H⁺ and the energizing electrons interact. The lower Fermi energy level of support nanoparticles makes it simple for them to trap photo-generated electrons in TiO₂'s conduction band, which allows them to go swiftly to the absorbed CO₂ for photo-reduction. Excitons and CO₂ molecules would combine to create CO₂ radicals, which would then mix with H on the catalyst surface to create CH₄ [23, 24]. Since CH₄ is thermodynamically more viable and can be synthesized with the help of eight electrons, the

greater charge density on the created material nanoparticles should favor it. The possible course of action would have been as follows [25]:



Conclusion

The photocatalytic reduction of CO₂ to pure methane gas has successfully proceeded. TiO₂-supported one-dimensional zeolite beads were prepared by post-synthesis in presence of EDTA through the hydrothermal method. The used zeolite in the form of a rode-like structure contains low silica content as the silica/alumina ratio is around 1.5. The prepared material was calcined at different temperatures of 200, 400, and 550°C. The highest activity was the sample calcined at 550°C. The activity was compared with powered TiO₂ and TiO₂ thin film on glass sheets.

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