

Developing the glycerol carbonylation process using photocatalysis and 2-cyanopyridine as a water-reducing agent

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ABSTRACT

This study investigates the direct carbonylation of glycerol using a composite photocatalyst (TiO₂ loaded with cellulose) and 2-cyanopyridine as a water-reducing agent. In this research, the performance of the photocatalytic system was evaluated under different conditions, including various concentrations of 2-cyanopyridine, glycerol, and catalyst dosage, as well as changing the molar ratios of CO₂ to glycerol and reaction times. The optimal conditions for achieving high glycerol conversion and GlyCO₃ performance were determined, resulting in a glycerol conversion of 92.43% and a yield of 91.12% towards glycerol carbonate under these conditions. Increasing the concentration of 2-cyanopyridine up to 30 mmol enhanced GlyCO₃ production. However, excessive amounts led to decreased yields due to catalyst site blockage. The influence of the CO₂ to glycerol molar ratio on GlyCO₃ yield was marginal within a certain concentration range, indicating a non-limiting CO₂ supply. Catalyst loading significantly affected product yield, with higher concentrations promoting greater GlyCO₃ formation. However, catalyst reusability tests revealed a decline in activity after recycling, attributed to drying-induced deactivation. These findings provide valuable insights into optimizing the cellulose-TiO₂ photocatalyst for efficient glycerol carbonylation, contributing to the advancement of sustainable chemical processes.

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1. Introduction

There are several methods of chemical reduction and artificial use of CO₂ that can be used to convert it into high-value materials. Examples of such methods comprise the methanol synthesis process, urea synthesis process, carboxylation of epoxides, carboxylation of pyrrole, glycerol carbonylation, and phenols carboxylation (Liu et al., 2016). Research is currently being conducted on the glycerol carbonylation process and the synthesis of glycerol carbonate. The goal is to develop an innovative application program that aims to convert greenhouse gas CO₂ into materials that have a high added value. Glycerol carbonate, also known as glycerin carbonate (4-hydroxymethyl-2-oxo-1,3-dioxolane), is an organic chemical compound with diverse applications. It boasts several desirable physical

properties, including a high boiling point of 110-115°C at 0.1 mmHg, a high flash point of 190°C, low volatility with a vapor pressure of 8 mbar at 177°C, and solubility in water. Moreover, it exhibits low toxicity and is biodegradable. Its hydroxyl group and the 2-oxo-1,3-dioxolane group confer broad reactivity, rendering it useful as a solvent, chemical mediator, monomer for polymers, and carrier in batteries. Currently, two primary methods exist for converting glycerol to glycerol carbonate: indirect transesterification with carbonate sources, and direct carbonylation with carbonyl agents such as phosgene, carbon monoxide, or carbon dioxide (Sonnati et al., 2013). The transesterification process, involving the reaction of glycerol with either dimethyl carbonate or ethylene carbonate, can be enhanced



using various catalysts. These catalysts encompass metal oxide-based catalysts, hydrocatalyst-based catalysts, and ionic liquids. However, this process can be costly and often necessitates solvents or non-reusable homogeneous catalysts. Similarly, synthesizing glycerol carbonate from glycerol and urea can be achieved using diverse catalysts like metal oxide catalysts, gold-based zeolite, and heteropoly tungstate exchanged with samarium. Nevertheless, this process yields ammonia as a byproduct and entails a complex purification process that bears negative ecological and economic consequences (Liu et al., 2019).

On the other hand, direct carbonylation of glycerol with CO₂ emerges as a green and appealing route for glycerol carbonate synthesis. This method is advantageous as it employs the greenhouse gas CO₂ as an inexpensive carbon source, while glycerol is commercially available at a low cost. Additionally, the direct carbonylation approach offers a straightforward and efficient means to produce glycerol carbonate, unlike the aforementioned synthesis methods, which possess certain drawbacks (Liu et al., 2016). Thermodynamic analyses of the carbonylation of glycerol with CO₂ suggest that producing glycerol carbonate yields a low output. This is primarily due to the constraints imposed by thermodynamic equilibrium. However, the use of catalysts in the process shows promise, and the efficiency of these catalysts can be enhanced by employing metal oxide bases and hydrocatalysts, as well as ionic liquids (Ozorio et al., 2015; Li et al., 2015). Efficiency can also be improved by increasing the CO₂ pressure, the reaction time, the reaction temperature, or by adding a water-reducing agent or a coupling agent to activate the CO₂ carbonyl bond. These measures help mitigate the thermodynamic limitations of direct glycerol carbonylation (Ozorio et al., 2015). For example, recently, the production of glycerol carbonate over CO₂ catalysts was conducted in the presence of 2-cyanopyridine as a water-reducing agent (Hu et al., 2021). The results indicated that 2-cyanopyridine is an excellent water-reducing agent in the catalytic process of glycerol carbonylation. This method can yield a selectivity of glycerol-to-glycerol carbonate higher than 95%, with the efficiency of glycerol carbonate reaching 78.9% (Liu et al., 2016). Among the types of photocatalysts, classic semiconductors such as TiO₂, WO₃, CeO₂, M₂O₃, Bi₂S₃, MO₂C, SiC, C₃N₄, ZnWO₄, and ZnO are capable of reducing CO₂ through

photocatalysis (Chamanehpour et al., 2022; Mao et al., 2013).

TiO₂, a solid semiconductor photocatalyst, is widely utilized due to its high performance under UV light, non-toxicity, low cost, and excellent stability (Sayadi et al., 2021). However, the photocatalytic performance of TiO₂ is hindered by several factors, including its wide energy band gap, high electron-hole recombination rate, and small surface area. The wide energy band gap of TiO₂, ranging from 3 to 2.3 eV, limits its ability to efficiently utilize sunlight, as it only responds to ultraviolet light, which constitutes only 3 to 5% of sunlight. This implies that a significant portion of visible light, approximately 45%, remains unused (Ahmadpour et al., 2024). To expand the light absorption range of TiO₂ to encompass the visible light spectrum, it can be modified by incorporating metallic and non-metallic elements, as well as employing dye-sensitizing techniques. TiO₂ loaded with non-metallic elements is more effective in absorbing light in the visible light range. Compared to TiO₂ loaded with metal and color-sensitive techniques, TiO₂ loaded with non-metallic elements (such as carbon) is more resistant and has greater durability against corrosion and thermal instability (Kargar et al., 2021). This study aims to the development of an effective photocatalytic system capable of converting glycerol and CO₂ into glycerol carbonate.

2. Material and Methods

2.1. Materials

TiO₂ (Ti [OCH(CH₃)₂]₄) (97%) and acetylacetone (99%) from Sigma Aldrich, USA, and microcrystalline cellulose, isopropyl alcohol, from Merck, Germany was purchased.

2.2. Synthesis of the cellulose-TiO₂

Aligned with the advancement of a photocatalytic system and drawing upon the previously optimized results of photocatalyst synthesis, including cellulose loading and sample treatment times, among other factors, as documented in prior research, this study similarly employed the sol-gel-microwave technique for synthesizing the cellulose-TiO₂ composite (Ahmadizadegan, 2017). Initially, equal amounts of titanium (IV) isopropoxide and acetylacetone were combined at room temperature to mitigate the pace of hydrolysis and condensation reactions. The incorporation of carbon onto TiO₂ was accomplished by adding microcrystalline cellulose powder at a

weight ratio of 10% to the titanium isopropoxide solution with acetylacetone. Next, 120 mL of Nanopure water was gradually introduced into the cellulose suspension while vigorously stirring, followed by the addition of 80 ml of isopropyl alcohol. The resulting mixture was left at room temperature for an hour before being transferred to a specialized container for microwave irradiation for 4 minutes. Subsequently, the cellulose-TiO₂ composite mixture underwent centrifugation, followed by multiple washes with deionized water, and was then dried at 80°C for 8 hours. Finally, the cellulose-TiO₂ composite was subjected to calcination at 500°C for 2 hours.

2.3. Photocatalyst characterization instrument

The crystallite structures of the cellulose-TiO₂ samples were analyzed using powder X-ray diffraction (XRD). This was performed on a Rigaku D/Max-2500 diffractometer with Cu K α radiation, scanning at a rate of 10° per minute. Scanning electron microscopy (SEM) was used to examine the morphology and structure of the photocatalyst. X-ray Energy Dispersive Spectroscopy (EDS) was utilized for elemental and compositional analysis. Fourier transform infrared spectroscopy (FTIR) was utilized to analyze the chemical composition of the sample surface. The spectra were acquired using a Nicolet NEXUS 470 FT-IR spectrometer. XPS measurements were performed using a PHI Quantera Scanning X-ray Microprobe with monochromatic Al K α radiation. Thermogravimetric analysis (TGA) was conducted using the SDT-Q600 instrument from TA Instruments. The surface area of the samples was determined via N₂ adsorption-desorption at -196°C using a Micromeritics Tristar 3000 instrument. Computations were based on the Brunauer-Emmett-Teller (BET) method, while pore volume and size distribution were analyzed using the Barrett, Joyner, and Halenda (BJH) method.

2.4. Catalytic reaction

To investigate the influence of 2-cyanopyridine as a water-reducing agent on the photocatalytic direct carbonylation of glycerol using a cellulose-TiO₂ photocatalyst loaded with carbon, optimal values of 2-cyanopyridine concentration and other reaction parameters were determined. In a stepwise manner, varying concentrations of 2-cyanopyridine (0, 15, 30,

45, and 60 mmol), glycerol aqueous solutions with varying concentrations (7, 10, 12, and 15 mmol), and different photocatalyst dosages (0, 0.15, 0.30, 0.50, 0.90, 1.05, and 1.20 g) were added to the photoreactor, along with 10 ml of dimethylformamide (as a solvent). The suspensions were continuously stirred in the dark for 30 minutes to facilitate the complete absorption of glycerol onto the photocatalyst's surface. Then, CO₂ gas was introduced into the photoreactor at room temperature with an initial pressure of 3.0 MPa. The schematic representation of the experimental setup for photocatalysis can be found in the supplementary material (SM 1). Simultaneously, the suspensions were irradiated with a 400 W metal halide lamp outside the reactor. The light intensity on the photoreactor surface was 104 Lux. At specific intervals (1, 2, 4, 6, 8, and 10 hours) during irradiation, 5 mL samples were taken from the photoreactor and filtered using a centrifuge to separate the photocatalyst. Glycerol conversion and product yields were determined using high-performance liquid chromatography (HPLC, Agilent 1100).

The determination of glycerol conversion and product yields was conducted using Equations 1 and 2, respectively (Liu et al, 2016).

$$X_{\text{Glycerol}} (\%) = \frac{X_{\text{Glycerol}(i)} - X_{\text{Glycerol}(f)}}{X_{\text{Glycerol}(i)}} \times 100$$

(1)

$$Y_{\text{GC}} (\%) = \frac{X_{\text{GC}}}{X_{\text{Glycerol}(i)}} \times 100$$

(2)

where Glycerol conversion (X_{Glycerol}) and GlyCO₃ yield (Y_{GC}) are defined based on the initial molar concentration of glycerol ($X_{\text{Glycerol}(i)}$) and its final molar concentration after the reaction ($X_{\text{Glycerol}(f)}$). X_{GC} represents the molar concentration of the GlyCO₃ product. The catalyst was tested for reusability at 150°C and a CO₂/amine ratio of 8.1 for 6 hours. Following the initial run, the catalyst was separated via centrifugation and underwent a washing process with deionized water and acetone to eliminate adsorbed species. Subsequently, the catalyst was subjected to a drying process at 150°C for 7 hours, followed by calcination at 600°C for 5 hours. This regeneration procedure was implemented before each recycling experiment.

3. Results and discussion

3.1. Characterization

The corresponding scanning electron microscopy (SEM) images of cellulose-TiO₂ particles, synthesized via the cell-microwave method, are depicted in supplementary material SM2. The images reveal small clusters with irregular shapes, indicating the profound impact of the synthesis process and microwave treatment on the morphology and shape of the particles. Extending the microwave treatment duration resulted in alterations in particle size and shape, leading to the formation of clusters with diverse shapes. Moreover, the incorporation of cellulose as a carrier material enhanced particle distribution and stability, potentially influencing the formation of clusters with varied structures. The EDS graph derived from the SEM images for analyzing the elemental composition of the photocatalyst is depicted in supplementary material SM3. The analysis of the EDX chart for the photocatalyst sample revealed the presence of crucial phases (like C and Ti) and confirmed its high purity. Carbon and titanium comprised 10% and 52% of the mass, respectively, aligning with results from other tests. Incorporating microcellulose as a carbon source in photocatalyst synthesis has enhanced the sample's properties and purity.

3.1.1. X-ray diffraction (XRD)

The X-ray diffraction (XRD) analysis presented in supplementary material SM 4 (a) reveals the phase composition and crystal structures of cellulose-TiO₂ photocatalyst samples. The synthesized TiO₂ photocatalyst exclusively exhibits the anatase phase, evident from diffraction peaks observed at specific angles and distances. Notably, peaks are observed at approximately 25.2°, 37.9°, 48.3°, 53.8°, 55.3°, and 62.7°, corresponding to the (101), (103), (200), (105), and (213) planes (JCPDS 21–1272), respectively (Sayadi et al., 2021). The anatase crystal size of cellulose-TiO₂ nanoparticles was calculated using the Debye-Scherrer equation, $D = K\lambda / \beta \cos\theta$, where D is the crystal size of the nanoparticles, K represents the Scherrer constant (0.98), λ represents the wavelength (1.54), and β represents the wavelength and Full Width at Half Maximum. The results show that the Cel-TiO₂ sample obtained using the Debye-Scherrer

equation has a crystal size of anatase 6.2 nm. Upon examination of the XRD patterns, it is evident that carbon loading enhances the crystallinity of the anatase phase compared to cellulose-TiO₂. This heightened crystallinity suggests a potential enhancement in the photocatalytic performance of the samples. Furthermore, the size of the anatase crystals is determined from the most prominent diffraction peak (101), providing valuable insights for analyzing and interpreting the structural characteristics of the samples (Ahmadizadegan, 2017).

3.1.2. Transform Infrared Spectroscopy (FTIR)

The surface of the chemical photocatalytic samples was carefully examined by FTIR analysis, and the bands related to the functional groups were separately identified. Comparing the FTIR spectra of carbon-loaded TiO₂ photocatalyst to that of TiO₂ without carbon loading, as well as the FTIR spectrum of cellulose and TiO₂ without carbon loading, revealed a notable reduction in FTIR peaks within the wavelength range of 3000 to 3600 cm⁻¹ and the disappearance of absorption peaks upon loading TiO₂ with carbon (Plermjai et al., 2019).

A broad absorption peak at 3380 cm⁻¹ was identified, corresponding to the hydroxyl (O-H) groups in the cellulose structure. Additionally, the absorption peak at 2900 cm⁻¹ was attributed to the stretching vibration of the C-H bond in the molecular structure of cellulose. The minor absorption peaks at 1440 cm⁻¹ and 1370 cm⁻¹ were attributed to the presence of -CH₂ and C-H bending, respectively, within the molecular structure of cellulose. Furthermore, the small absorption peaks at 1160, 1030, and 1110 cm⁻¹ were associated with the C-O, C-O, C=C, and C-O bonds in the cellulose structure, respectively. An absorption peak at 900 cm⁻¹ was associated with C-O-C bond stretching (Hamad et al., 2018). This indicates the destruction of the molecular structure of cellulose due to heat treatment with microwave irradiation and calcination, as no significant stretching peak of the O-H functional group was observed in the carbon-loaded TiO₂ photocatalyst. However, the small absorption peaks at 1630 cm⁻¹ indicated the presence of the O-H group due to water adsorption on the photocatalyst surface (Plermjai et al., 2019). Additionally, in the TiO₂ photocatalyst sample

loaded with carbon, the Ti-O absorption peak at 760 cm^{-1} was lower than in TiO_2 without carbon loading, which is related to the presence of a carbon layer on the TiO_2 surface (see supplementary material SM 4(b)).

3.1.3. TGA

The TGA thermal analysis of the cellulose- TiO_2 photocatalyst sample reveals significant insights. Initially, weight loss between 26 and 100 degrees Celsius suggests potential water release or alterations in the molecular structure of cellulose or TiO_2 (Sugashini et al., 2022). These changes may stem from processes like water absorption, molecular decomposition, or phase transitions within this temperature range. Subsequently, weight loss between 100 and 250 degrees Celsius may result from functional group depletion, organic decomposition, or the dissolution of TiO_2 and cellulose. Factors such as organic carbon decomposition, oxidation, or TiO_2 structural modifications can contribute to weight loss within this temperature span. The substantial weight loss observed from 250 to 900 degrees Celsius, accounting for 60.9% of the total, likely indicates cellulose breakdown, complete TiO_2 dissolution, or final oxidation and decomposition processes. During this stage, weight loss likely occurs due to the ultimate decomposition and dissolution of materials within the photocatalyst. In summary, the TGA thermal analysis underscores weight loss across distinct temperature stages, driven by varied processes including phase transitions, functional group depletion, organic decomposition, dissolution, and final decomposition, all of which potentially enhance photocatalyst performance (see supplementary material SM 4(c)).

3.1.4. BET analysis

The cellulose- TiO_2 photocatalyst underwent analysis using nitrogen adsorption and desorption spectrometry, along with BET analysis (see supplementary material SM 4(d)). According to the IUPAC classification, the sample exhibited type IV characteristics, indicating the presence of irregular mesopores with distinct capillary condensation steps in the pressure range of 0.3 to 1.0. The BET surface area of the cellulose- TiO_2 photocatalyst sample was approximately $47.067\text{ m}^2/\text{g}$, suggesting ample surface area for interaction with active agents and environmental elements. This

attribute can potentially enhance photocatalytic performance and pollutant absorption in the surrounding milieu (Gulbrandson et al., 2023). The BET analysis revealed favorable structural traits in the cellulose- TiO_2 photocatalyst sample, contributing to its superior performance in photocatalytic reactions.

3.1.5. X-ray photoelectron spectroscopy (XPS)

For a deeper analysis of the photocatalyst sample's composition, XPS was used to examine the obtained curves. The C (1s) region XPS spectrum was divided into four peaks at 285 eV, 285.08 eV, 286.58 eV, and 288.18 eV, representing C-H, C-C/C=C, C-O/C-N, and C=O bonds, respectively. The C-C/C=C group peak had the largest area and atomic percentage. Additionally, the presence of C-O and C=O bonds in the C(1s) region confirmed carbon's integration into the TiO_2 atomic network (Li et al., 2020). The high-resolution XPS spectrum of the Ti(2p) region exhibited six peaks. The peaks at 460 eV and 466 eV are notable as they correspond to tetravalent Ti^{+4} species within the atomic lattice. In the $\text{Ti}2p_{1/2}$ and $\text{Ti}2p_{3/2}$ regions, two peaks at 459 eV and 464 eV show an enhanced bond energy compared to standard peaks, indicating Ti atom repulsion towards adjacent oxygen atoms in the crystal structure. This phenomenon is attributed to oxygen vacancies carrying a high positive charge, resulting in shortened Ti-O bonds (Sayadi et al., 2021). The high-resolution XPS spectrum of the (1s)O region of the carbon-loaded TiO_2 photocatalyst revealed three distinct peaks. The peaks at 532 eV and 532.5 eV are associated with the atomic lattice oxygen of TiO_2 (Ti-O-Ti), while the third peak at 533 eV is attributed to Ti-O-C bonds or oxygen vacancies within the photocatalyst's crystal structure (see supplementary material SM 5(a-d)).

3.2. Optimization Study

3.2.1. Influence of 2-Cyanopyridine

Fig. 1(a) shows how using 2-cyanopyridine as a dehydrating agent affects the reaction. Without it, the reaction is limited by chemical equilibrium, but using a dehydrating agent can push the equilibrium towards product formation by removing water. Increasing 2-cyanopyridine concentration from 1 to 30 mmol led to higher GlyCO_3 yields, from 3.2% to

20.55%. However, going beyond 30 mmol saw a slight drop in glycerol conversion and GlyCO₃ yield, likely due to 2-cyanopyridine blocking active sites on the catalyst at higher amounts (Teng et al., 2021).

3.2.2. Influence of reaction time

To determine the optimal duration for the photocatalytic reaction of direct glycerol carbonylation with CO₂ using a TiO₂ photocatalyst loaded with carbon and 2-cyanopyridine as a water-reducing agent, the system's performance was assessed across various time intervals. According to Fig. 1(b), the carbonylation process was carried out between 0 and 10 hours at a temperature of 150°C and under 40 bar CO₂ pressure. Increasing the reaction time from 1 to 6 hours notably elevated glycerol conversion and GlyCO₃ yield from 47.94% to 91.49% and from 47.34% to 90.72%, respectively. However, a minimal increase in glycerol conversion coupled with a decline in GlyCO₃ yield was observed beyond 6 hours, specifically from 5 to 7 hours. These findings indicate that glycerol carbonylation with CO₂ is time-sensitive, with the optimal reaction window occurring between 1 and 6 hours at 150°C and 40 bar CO₂ pressure. Beyond this timeframe, prolonging the reaction does not significantly enhance overall yield. Further investigations are warranted to elucidate reaction kinetics and mechanisms, facilitating the fine-tuning of reaction conditions to maximize product yields (Procopio and Di Gooia, 2022).

3.2.3. Influence of the CO₂ to Glycerol Mole Ratio

The variation in glycerol concentration not only affects the molar ratio of CO₂ to glycerol but also influences the overall reaction kinetics and product yield. As shown in Fig. 1(c), increasing the concentration of glycerol leads to a decrease in the molar ratio of CO₂ to glycerol. This change in stoichiometry can impact the reaction equilibrium and subsequent product formation. From the results, it's evident that as the glycerol concentration rises from 7 to 15 mmol,

corresponding to a decrease in the CO₂ to glycerol ratio from 19.72 to 8.64, there is only a marginal decrease in GlyCO₃ yield from 19.44% to 8.24%. This suggests that within this concentration range, the reaction may still be operating within an optimal regime where the CO₂ supply is not significantly limiting (Hu et al., 2021). However, further increasing the glycerol concentration to 15 mmol, resulting in a lower CO₂ to glycerol ratio of 8.64, leads to a more substantial decrease in GlyCO₃ yield from 19.44% to 8.24%. This significant drop indicates that the reaction may become more limited by CO₂ availability at higher glycerol concentrations, resulting in reduced conversion and product yield (Lima et al., 2022).

3.2.4. Influence of Catalyst Loading

The influence of varying catalyst concentrations on the synthesis of GlyCO₃ was investigated under the conditions of 150°C and 40 bar CO₂ pressure. The outcomes are presented in Fig. 1(d). Increasing the catalyst concentration from 0.15 to 1.2 g resulted in a linear increase in GlyCO₃ yield from 18.96% to 91.12%. Notably, further increases in catalyst concentration did not yield significant changes in product yield. A higher catalyst concentration provides more active sites for the reaction to occur, thereby promoting the conversion of glycerol to GlyCO₃. This leads to more efficient utilization of the available reactants and ultimately higher product yields. This study underscores the substantial influence of catalyst quantity on both conversion and product yield. Additionally, as discussed earlier, higher concentrations of 2-cyanopyridine can hinder conversion by blocking active sites. Furthermore, the potential inhibition of conversion at higher concentrations of 2-cyanopyridine, as mentioned earlier, could counteract the positive effects of increased catalyst concentration beyond a certain point (Reza et al., 2022). However, the combination of ample catalyst and a dehydrating agent notably enhanced glycerol conversion to GlyCO₃.

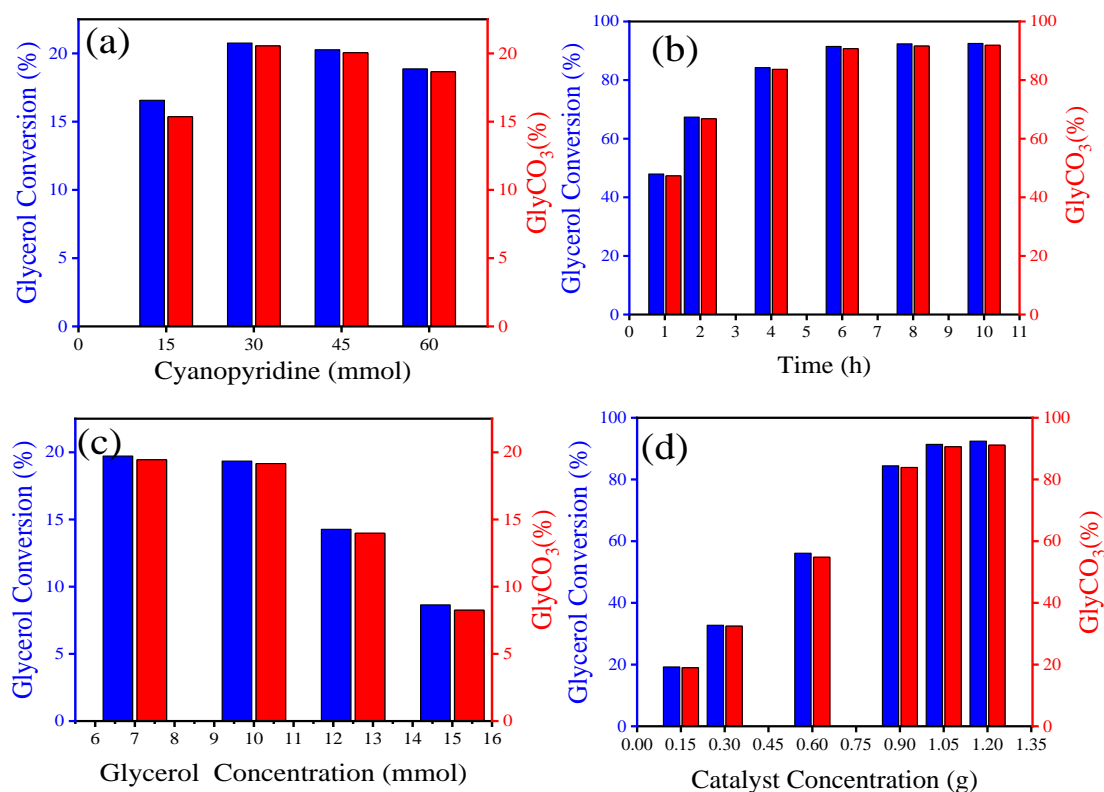


Fig. 1. a) the impact of 2-cyanopyridine on catalytic activity, b) the influence of reaction time on catalytic activity, c) the Impact of CO₂ to glycerol mole ratio on catalytic activity, and d) the Impact of loading of cellulose-TiO₂ catalyst on catalytic activity.

3.2.5. Proposed Photocatalytic Reaction Mechanism and Dehydration Pathways

Fig. 2 illustrates the process of glycerol conversion using a cellulose-TiO₂ photocatalyst under visible light. Initially, the C-doped TiO₂ photocatalyst absorbs visible light, providing the energy needed to activate electrons within the TiO₂ structure. This absorption leads to the generation of electron-hole pairs in the C-doped TiO₂ material, which then participate in photocatalytic reactions. Electrons from these pairs that move to the surface of the C-doped TiO₂ photocatalyst cause the activation of glycerol and CO₂ (Sugashini et al., 2022). During the synthesis of glycerol carbonate from glycerol and CO₂, the acid-base properties, consisting of the unsaturated metal cations Ti³⁺ (Lewis's acid sites as electron acceptors), oxide anions O²⁻ (Lewis's base sites as electron donors), and hydroxyl groups (Brønsted base centers), play an important and especially crucial role. One hydroxyl (OH) group of glycerol is adsorbed onto the acid sites of TiO₂, leading to the production of an intermediate ring through a

reaction known as Titanium glyceroxide. Subsequently, the activated CO₂ reacts with Titanium glyceroxide, forming seven-membered ring esters, ultimately yielding glycerol carbonate along with the release of water (H₂O). Given the limitations posed by CO₂ thermodynamics in the carbonylation of glycerol on the C-doped TiO₂ photocatalyst, coupling reactions or dehydrating agents are essential to tilt the equilibrium toward glycerol carbonate. To address this, it is conducted the carbonylation of glycerol with CO₂ for the first time, employing 2-Cyanopyridine on the C-doped TiO₂ photocatalyst. Subsequently, we assessed the photocatalytic performances in a batch photoreactor. In Fig. 2, the schematic illustrates the dehydrating pathways of the direct carbonylation process of glycerol by 2-cyanopyridine, acting as a water-reducing agent. As shown in the Fig. 2, 2-Cyanopyridine reacts with the formed H₂O of the direct carbonylation process, causing dehydration in the reaction system. Subsequently, 2-Cyanopyridine also reacts with OH⁻ and H⁺ groups existing on the TiO₂ to produce 2-Picolinamide.

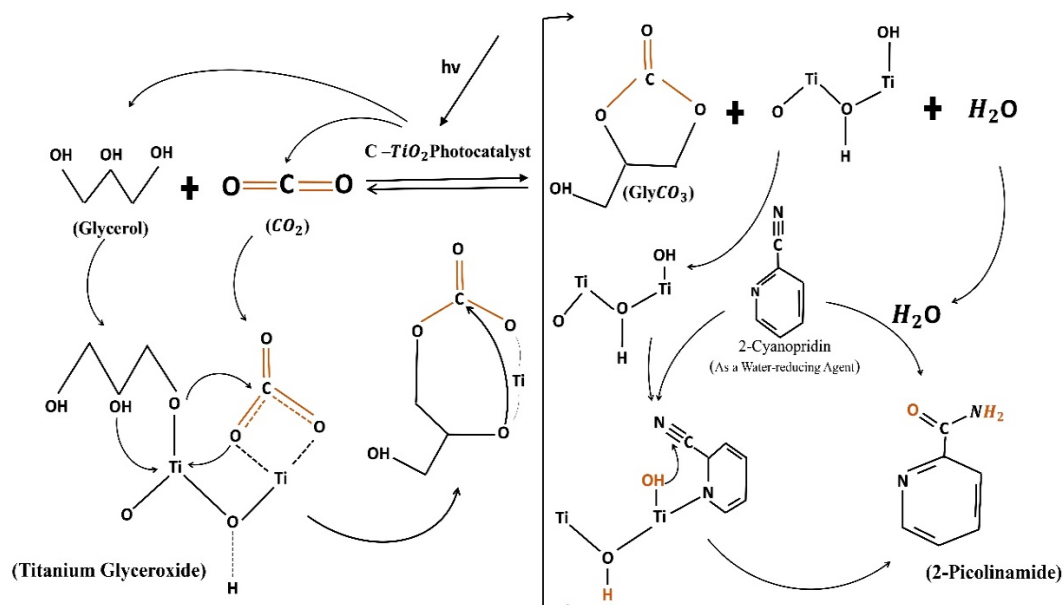


Fig. 2. Dehydration Reaction Mechanism 2-Cyanopyridine as a Water reducing Agent On C-doped TiO₂ photocatalyst under visible light.

3.3. Catalyst Reusability Studies

Catalyst reusability trials were conducted using a cellulose-TiO₂ photocatalyst under conditions of 150°C and 40 bar CO₂ pressure, with 0.15 g of the catalyst used over 6 hours (as shown in Fig. 3(a)). At the start, the new catalyst achieved a glycerol conversion rate of 19.1% and yielded 18.9% GlyCO₃ after operating for 6 hours. However, a significant decrease in activity was observed in the catalyst after undergoing drying at 150°C during the recycling process. This decrease in activity may be attributed to the products strongly adhering to the active sites post-reaction. Therefore, rejuvenating the catalyst through calcination

which is crucial for efficiently rejuvenating its activity for future cycles in this reaction. Following regeneration, a minor decline of 2% in glycerol conversion was noted in the initial recycle, possibly due to the deactivation of a few active sites that were not completely rejuvenated during the post-reaction calcination process (Sugashini et al., 2022). Nevertheless, the catalyst maintained consistent performance up to the fourth recycle. XRD analysis verified that the catalyst's structural integrity remained consistent after completing four cycles (as illustrated in Fig. 3(b)), indicating significant reusability and structural stability in the glycerol carbonylation with CO₂ process.

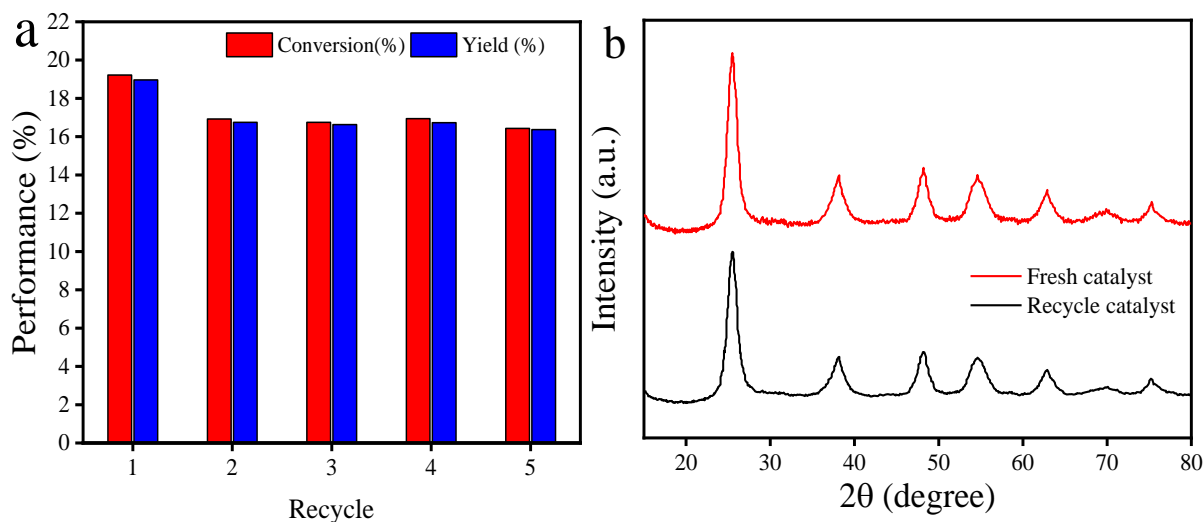


Fig. 3. (a) Reusability studies; condition: 150°C, 10mmol glycerol, 40 bar CO₂ pressure, 0.15g of cellulose-TiO₂ catalyst, 10 ml of DMF for 6 h; (b) XRD powder patterns of fresh and used catalyst after 5 cycles.

4. Conclusion

The study successfully utilized photocatalytic reactions to convert glycerol, a byproduct of biodiesel production, into valuable chemicals, demonstrating a straightforward, energy-efficient, and eco-friendly technology. Through photocatalysis, glycerol carbonate, a valuable chemical, was directly synthesized from CO₂ using a TiO₂ photocatalyst infused with carbon and 2-cyanopyridine as a water-reducing agent. Characterization tests confirmed the effectiveness of the synthesized photocatalyst, and the impact of various parameters on photocatalytic activity was investigated. The significant yield of glycerol carbonate, facilitated by the efficient hydration of 2-cyanopyridine, highlights the success of this process. Therefore, it presents a viable solution for addressing global warming and reducing greenhouse gas emissions, owing to its decreased energy consumption and environmental impact.

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