

PAPER • OPEN ACCESS

A kinetic model for the photocatalytic reduction of CO₂ to methanol pathways

To cite this article: H Abdullah *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **702** 012026

View the [article online](#) for updates and enhancements.

You may also like

- [REACTIVITY OF OH AND CH₃OH BETWEEN 22 AND 64 K: MODELING THE GAS PHASE PRODUCTION OF CH₃O IN BARNARD 1b](#)
M. Antiñolo, M. Agúndez, E. Jiménez et al.
- [Hyperfine structure of the hydroxyl free radical \(OH\) in electric and magnetic fields](#)
Kenji Maeda, Michael L Wall and Lincoln D Carr
- [Sensing mechanism of SnO₂/ZnO nanofibers for CH₃OH sensors: heterojunction effects](#)
Wei Tang



ECS The Electrochemical Society
Advancing solid state & electrochemical science & technology

242nd ECS Meeting

Oct 9 – 13, 2022 • Atlanta, GA, US

Presenting more than 2,400 technical abstracts in 50 symposia

Register now!

ECS Plenary Lecture featuring M. Stanley Whittingham,
Binghamton University
Nobel Laureate –
2019 Nobel Prize in Chemistry

The banner features the ECS logo, the meeting details, a portrait of M. Stanley Whittingham with his Nobel Prize medal, and a 'Register now!' button. The background includes images of a conference audience and a person interacting with a futuristic interface.

A kinetic model for the photocatalytic reduction of CO₂ to methanol pathways

H Abdullah^{1*}, M M R Khan¹, Z Yaakob² and N A Ismail¹

¹Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Pahang, Malaysia.

²Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia.

*E-mail: hamidah@ump.edu.my

Abstract. Carbon dioxide (CO₂) is one of the greenhouse gases that contribute to global warming. CO₂ could be converted to valuable products such as hydrocarbons through the photocatalytic process. The aim of this research was to develop the kinetic model for the photocatalytic reduction of CO₂ to methanol (CH₃OH) in liquid phase reaction using cerium oxide-titanium dioxide (CeO₂-TiO₂) catalyst. The Langmuir-Hinshelwood approach was used in developing rate laws for the catalytic reaction using the catalytic reaction mechanism proposed. The catalytic reaction mechanism is about the adsorption of reactant (CO₂ dissolved in the liquid phase), the reaction on catalyst surface and desorption of product. The experimental kinetic data were evaluated in the Polymath 6.1 software. In this study, two types of mechanism are proposed whereas one is considered the carbon monoxide (CO) oxidation while the other is not. Based on the model fitting, it was found that the model considers the CO oxidation is fitted well with the experimental data represents that the oxidation reaction of intermediate product, CO is the rate-determining step in the photocatalytic reduction of CO₂ to CH₃OH in liquid phase reaction.

1. Introduction

The technologies of reducing CO₂ emission is important to tackle the challenge of global climate change. Reduction of CO₂ to hydrocarbons using catalyst and photon as an energy which is called photocatalytic reaction has the potential to be parts of renewable energy as well as to reduce CO₂ emission. Titanium dioxide (TiO₂) catalyst has gained a lot of interest as potential photocatalyst due to its non-toxicity, low cost and excellent photochemical properties [1]. However, it has limitations such as has wide band gap which makes it only active under UV light and has high electron/hole pair recombination rate as compared to the rate of a chemical reaction [2]. Both factors lead to low activity and yield of the product. Therefore, various research has been studied in order to design the ideal catalyst for photocatalytic reduction of CO₂ to hydrocarbons such as doping TiO₂ with anions [3], doping TiO₂ with cation [4], coupling TiO₂ with another semiconductor [5] and etc. Koci et al. [11] found that modification of TiO₂ by doping with silver (Ag) could enhance the yield of methane (CH₄) and CH₃OH under visible light irradiation mainly caused by the narrow band gap and decreases of electron-hole recombination rate [6]. TiO₂ modified by doping with gold (Au) also improved the photocatalytic activity of CO₂ reduction due to the efficient electron-hole separation and surface plasmon response of Au-nanoparticles [7]. Among them, modifying TiO₂ with cation is widely investigated [8]. Cation as rare earth elements, instead of transition and noble metals, have caught the interest of researches because it is abundant, non-toxic and



Content from this work may be used under the terms of the [Creative Commons Attribution 3.0 licence](https://creativecommons.org/licenses/by/3.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

inexpensive. Moreover, it has a 4f electron configuration that contributes to lower the band gap and reduce the high electron/hole recombination rate problem [9].

However, the physical properties of the catalyst are not enough to describe the net photocatalytic activity since the photocatalytic reduction of CO₂ has a multistep process such as CO₂ adsorption, activation and dissociation of the C-O bond [10]. Moreover, the photocatalytic reduction of CO₂ to CH₃OH also has various pathway [11]. Therefore, understand the kinetics of a photocatalytic reaction is important in order to determine the rate-determining step and the right pathway. Besides, kinetic study is vital to develop the photocatalytic system as well as practical application in the future.

Thus, the objective of this study is to develop a kinetic model based on the Langmuir-Hinshelwood model using CeO₂-TiO₂ catalyst in order to determine the kinetic parameters and to provide fundamental insights on the possible reaction mechanism.

2. Materials and Method

2.1. Materials

The CeO₂-TiO₂ (2 wt % CeO₂ loading) catalyst used was prepared as per the reported procedure [12]. The sodium hydroxide (NaOH) with 99 % purity was purchased from R & M Chemicals. Purified carbon dioxide (99.98 %) was supplied by Siad Technical Gases, Malaysia.

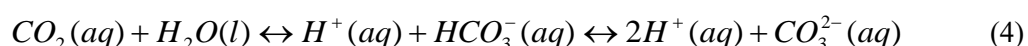
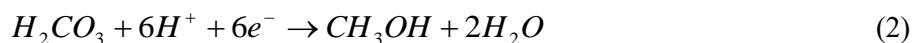
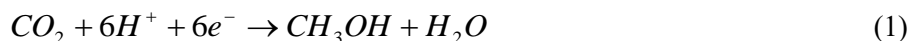
2.2. Kinetic Measurement

The photocatalytic reduction of CO₂ was performed according to the procedure reported elsewhere [13]. The CO₂ with 0.4 L/min was bubbled through the 300 ml of 0.1 M NaOH solution in the reactor. Then, 0.3 g CeO₂-TiO₂ catalyst was dispersed in the reactor. The solution was agitated under the visible light irradiation for 6 hours. The gas and liquid samples were taken every 1 hour and analyzed using a gas chromatography (GC-Agilent Technologies 6890N) with a thermal conductivity detector (TCD) and flame ionization detector (FID), respectively.

The experimental kinetic data, which is the concentration of CH₃OH for each interval in 6 hours reaction, were evaluated using non-linear regression method (Levenberg-Marquardt) in the Polymath 6.1 software to estimate the unknown kinetic constants.

3. Results and Discussion

Based on the previous result [12], the CH₃OH was observed as the main product in the reaction. The CH₃OH is possibly produced by the reduction of CO₂ in gas and CO₂ which dissolved in water and form carbonate as equations 1 to 3. The carbonate formed was supported by the result shown in figure 1. It shows that the pH dropped drastically from pH 12.4 to 6.87 in the first 10 minutes and then remain stable. The carbonic acid (H₂CO₃), ion bicarbonate (HCO₃⁻) and ion carbonate (CO₃²⁻) were formed and in equilibrium as in equation 4 when a CO₂ is dissolved in solution [14].



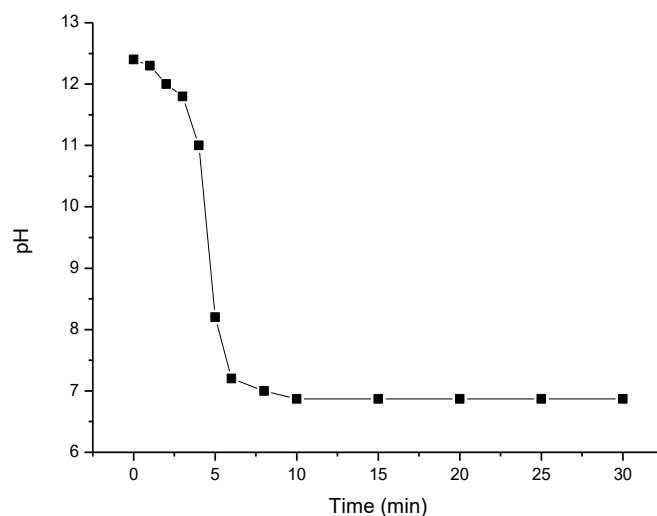
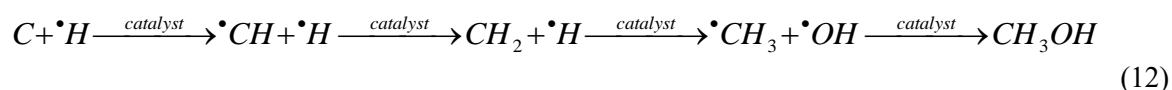
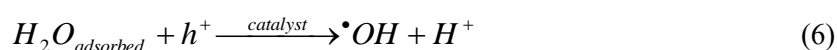
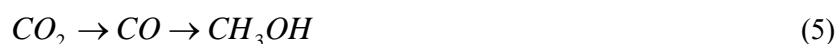


Figure 1. pH as function of time in NaOH solution under the bubbling of CO₂.

Sasirekha et al. [15] proposed that the CH₃OH was formed from the intermediate product (CO) as equation (5) [15]. The details proposed mechanisms are as equations 6 to 12. Besides, the using of NaOH in the reaction also contribute to the formation of CH₃OH. The oxidation of OH ions in NaOH solution could form OH radicals, thus supplying more OH radicals for CH₃OH formation. Tseng [17] reported that the CH₃OH yield from the photocatalytic reduction of CO₂ increases after adding NaOH in solution [16-17].



Thus, the proposed mechanisms with a combination of the Langmuir Hinshelwood (L-H) model were used in this study as the basis in developing the kinetic model. The reactants and products were assumed to be adsorbed on the same active sites as equation (13) [18-19].

$$r_{reduction} = k_{reduction} I^\alpha \frac{K_{H_2O} C_{H_2O} K_{CO_2} C_{CO_2}}{(1 + K_{CO_2} C_{CO_2} + K_{H_2O} C_{H_2O} + K_{CH_3OH} C_{CH_3OH} + K_{CO} C_{CO} + K_{O_2} C_{O_2})^2} \quad (13)$$

The rate of reduction equation can be deduced as equation (14) by using this assumption:

- i) the reaction rate is proportional to the fraction of the surface covered by CO₂
- ii) H₂O, CH₃OH, and O₂ are weakly adsorbed over the catalyst
- iii) CO₂ and CO are moderately adsorbed. However, the reaction was observed to be very fast at the beginning and become slow after a certain time of reaction. Besides, CO was not observed. Thus, it indicates that the CO formed is not effectively desorbed from the catalyst surface and accumulated ($K_{CO} C_{CO} \gg 1 + K_{CO_2} C_{CO_2}$)

$$r_{reduction} = k_1 \frac{K_{H_2O} C_{H_2O} K_{CO_2} C_{CO_2}}{(K_{CO} C_{CO})^2} \quad (14)$$

where k_1 is the photoreduction rate constant affected by temperature and light intensity ($k_1 = r_{reduction} I^\alpha$) and K_{CO_2} , K_{H_2O} , K_{CO} are the ratios of the rate constant for adsorption of CO₂, H₂O, and desorption of CO, respectively. Since H₂O was in great excess and CO₂ was continuously feed into the reactor, the concentration of CO₂ and H₂O can be assumed constant. Thus, the rate of reaction becomes as per equation (15).

$$r_{reduction} = k_2 \frac{1}{(K_{CO} C_{CO})^2} \quad (15)$$

$$\text{where } k_2 = k_1 K_{H_2O} C_{H_2O} K_{CO_2} C_{CO_2}$$

Based on equation (15), it can be said that the rate of formation of products is dependent on CO conversion and/or desorption over the catalyst surface. Tan et al. [18] proposed that the CO also sometimes undergoes partial oxidation with oxygen [18, 20]. They suggested that the CO oxidation undergoes dissociative adsorption process. The rate of photo-oxidation of CO could also be evaluated by L-H model as equation (16).

$$r_{oxidation} = k_3 \frac{K_{CO} C_{CO} \sqrt{K_{O_2} C_{O_2}}}{(1 + K_{CO} C_{CO} + \sqrt{K_{O_2} C_{O_2}})^2} \quad (16)$$

where k_3 is the kinetic constant of oxidation while K_{CO} and K_{O_2} are the ratios of rate constants for adsorption and desorption of CO and O₂, respectively. Equation 16 is simplified to equation 17 by assuming that all active sites are occupied by CO due to the CO being strongly bound to the catalyst surface ($K_{CO} C_{CO} \gg 1$)

$$r_{oxidation} = k_3 \frac{\sqrt{K_{O_2} C_{O_2}}}{K_{CO} C_{CO}} \quad (17)$$

In this study, two types of mechanism are proposed. One is considered the CO oxidation while the other is not. The rate of CH₃OH formation that does not consider the CO oxidation is per equation (15) while the net rate of reduction by considering the CO oxidation is shown in equation (18).

$$r_{netreduction} = k_2 \frac{1}{(K_{CO} C_{CO})^2} - k_3 \frac{\sqrt{K_{O_2} C_{O_2}}}{K_{CO} C_{CO}} \quad (18)$$

Both equations can be simplified to equations (19) and (20) by assuming that the concentration of CO (C_{CO}) and O₂ (C_{O_2}) is proportional to the concentration of CH₃OH (C_{CH_3OH})

$$\frac{dC_{CH_3OH}}{dt} = k_4 \frac{1}{(C_{CH_3OH})^2} \quad (19)$$

$$\frac{dC_{CH_3OH}}{dt} = k_4 \frac{1}{(C_{CH_3OH})^2} - \frac{k_5}{\sqrt{C_{CH_3OH}}} \quad (20)$$

where $k_4 = \frac{k_2}{K_{CH_3OH}^2}$ and $k_5 = k_3 \frac{\sqrt{K_{O_2}}}{K_{CO}}$

Equations 19 and 20 were integrated and arranged as equations (21) and (22), respectively.

$$t = \frac{(C_{CH_3OH})^3}{3k_4} \quad (21)$$

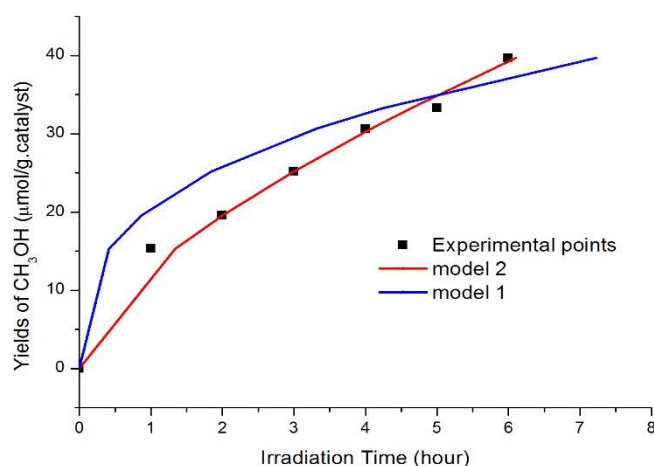
$$t = k_6 \lg(1 - k_7 (C_{CH_3OH})^{3/2}) + k_8 (C_{CH_3OH})^{3/2} \quad (22)$$

where $k_6 = \frac{-2k_4}{3k_5^2}$, $k_7 = \frac{k_5}{k_4}$, $k_8 = \frac{-2}{3k_5}$

k_4, k_6, k_7, k_8 are the kinetic constant related to reaction rate constants, adsorption-desorption ratio constants and light intensity. The unknown kinetic constants were estimated with a non-linear least square regression method (Levenberg-Marquardt) using Polymath 6.1 software. The CeO₂-TiO₂ performance has been explored in the proposed kinetic model. Table 1 shows the summary results of the processing of kinetic data using the method of non-linear regression. The experimental data of photocatalytic reduction of CO₂ to CH₃OH were compared with the data calculated according to both equations. The profiles of CH₃OH formation for both proposed models and experimental data are shown in figure 2. It is clearly seen that model 2 fit well with the experimental data when compared to model 1. Moreover, the correlation coefficients in table 2 also show that the model 2 is suitable for CH₃OH formation rate using CeO₂-TiO₂ catalyst in liquid phase reaction. Thus, it is confirmed that CO is produced as an intermediate product, the CO was oxidized with O₂, and the reaction of CO to CH₃OH is the rate-determining step in the photocatalytic reduction of CO₂ to CH₃OH in liquid phase reaction. It is different if the reaction is occur in the gas phase reaction whereas the rate-determining step is the adsorption of the reactants and desorption of products over the catalyst surface [21].

Table 1. The results of the kinetic data by non-linear regression.

Equation	Constant	95 % interval of reliability	Correlation coefficient	Variance
(21) (Model 1)	$k_4 = 0.00034$	$\pm 8.745 \times 10^{-5}$	0.805	0.912
(22) (Model 2)	$k_6 = -0.078$ $k_7 = -3.020$ $k_8 = -0.078$	± 0.00035 ± 0.08060 $\pm 5.627 \times 10^{-6}$	0.991	0.064

**Figure 2.** Comparison of model fitting with the experimental data for the formation of CH₃OH on the CeO₂-TiO₂ catalyst.

4. Conclusions

The experimental data obtained in this research were used to validate the model and it was fitted very well with the proposed model that considered the CO oxidation occur in the reaction. Thus, a kinetic model simulating the CH₃OH formations by photocatalytic reduction of CO₂ in NaOH solution on CeO₂-TiO₂ catalyst has been developed in this study and the kinetic constants have been determined with correlation coefficient of 0.991.

Acknowledgement

Funding from Universiti Malaysia Pahang (RDU 1603127) is gratefully acknowledged.

References

- [1] Anandan S, Ikuma Y and Niwa K 2010 *Solid State Phenom.* **162** 239–60
- [2] Ola O and Maroto-Valer M M 2015 *J Photochem. Photobiol. C Photochem. Rev.* **24** 16–42
- [3] Patil S B, Basavarajappa P S, Ganganagappa N, Jyothi M S, Raghu A V and Reddy K R 2019 *Int. J. Hydrogen Energy* **44** (26) 13022–39.
- [4] Ambrozova N, Reli M, Sihor M, Kustrowski P, Wu J C S and Koci K 2018 *Appl. Surf. Sci.* **430** 475–87.
- [5] Biswas M R U D, Ali A, Cho K Y and Oh W-C 2018 *Ultrason. Sonochem.* **42** 738–46.
- [6] Koci K, Mateju K, Obalova L, Krejcikova S, Lacny Z, Placha D, et al. 2010 *Appl. Catal. B Environ.* **96** (3–4) 239–44.
- [7] Tahir M, Tahir B and Amin N A S 2015 *Appl. Surf. Sci.* **356** 1289–99.
- [8] Daghrir R, Drogui P and Robert D 2013 *Ind. Eng. Chem. Res.* **52** (10) 3581–99.

- [9] Tong T, Zhang J, Tian B, Chen F, He D and Anpo M 2007 *J. Colloid Interface Sci.* **315** (1) 382–8.
- [10] Liu L and Li Y 2014 *Aerosol Air Qual. Res.* **14** (2) 453–69.
- [11] Koci K, Obalova L, Solcova O 2010 *Chem. Process Eng.* **31** 395–407.
- [12] Abdullah H, Khan MR, Pudukudy M, Yaakob Z and Ismail N A 2015 *J Rare Earths* **33** (11) 1155–61.
- [13] Michalkiewicz B, Majewska J, Kądziołka G, Bubacz K, Mozia S and Morawski A W 2014 *J CO₂ Util.* **5** 47–52.
- [14] Zhong H, Fujii K, Nakano Y and Jin F 2015 *J. Phys. Chem. C* **119** (1) 55–61.
- [15] Sasirekha N, Basha S and Shanthi K 2006 *Appl. Catal. B Environ* **62** (1–2) 169–80.
- [16] Tseng I-H and Wu JC-S 2004 *Catal. Today* **97**(2–3) 113–9
- [17] Tseng I-H, Chang W-C and Wu J C S 2002 *Appl. Catal. B Environ.* **37**(1) 37–48.
- [18] Tan S S, Zou L and Hu E 2008 *Catal. Today* **131**(1–4) 125–9.
- [19] Tahir M and Amin N S 2013 *Appl. Catal A Gen* **467** 483–96.
- [20] Tan S S, Zou L, Hu E 2006 *Catal. Today* **115**(1–4) 269–73.
- [21] Delavari S, Amin N A S 2015 *Appl. Energy* **162** 1171-85.