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Kinetic modelling for photosynthesis of hydrogen and methane through catalytic reduction of carbon dioxide with water vapour

Seng Sing Tan [a,*], Linda Zou [b], Eric Hu [c]

[a] School of Engineering, Nanyang Polytechnic, Singapore 569830, Singapore
[b] Institute of Sustainability and Innovation, Victoria University, VIC 3000, Australia
[c] School of Engineering and Technology, Deakin University, VIC 3217, Australia

Abstract

In a photocatalytic reduction process when products formed are not effectively desorbed, they could hinder the diffusion of intermediates on the surface of the catalyst, as well as increase the chance of collisions among the products, resulting photo-oxidation in a reserve reaction on the surface. This paper analyses a simple kinetic model incorporating the coupled effect of the adsorptive photocatalytic reduction and oxidation. The development is based on Langmuir–Hinshelwood mechanism to model the formation rates of hydrogen and methane through photocatalytic reduction of carbon dioxide with water vapour. Experimental data obtained from literatures have achieved a very good fit. Such model could aid as a tool for related areas of studies. A comparative study using the model developed, showed that product concentration in term of ppm would be an effective measurement of product yields through photocatalytic reduction of carbon dioxide with water vapour.

Keywords: Kinetic model; Photocatalysis; Reduction of CO_2; Energy conversion

1. Introduction

The technologies of recycling CO_2, reducing CO_2 emission and CO_2 sequestration are equally important to tackle the challenge of global climate change. Using the photocatalytic process to reduce CO_2 with H_2O into hydrogen and hydrocarbons has the potential to be parts of a renewable energy system, as well as to control CO_2 emission from industrial processes and eventually eliminate it. However, the technology of recycling CO_2 is currently not ready to make a significant contribution to the reduction of CO_2 concentration in the atmosphere.

Previous work suggested that one of the possible main reasons for the inefficient reforming rate could be the rapid recombination of photo-excited electron/hole pairs as well as the reverse reaction. Many researchers have studied various possible effective remediation methods for the photocatalysis process [1]. No one has yet developed a comprehensive kinetic model for photosynthesis of hydrogen and methane through catalytic reduction of CO_2 with water vapour. It would be a useful tool to assist in analysing such processes. In this paper, a simple model incorporating the coupled effect of the adsorptive photocatalytic reduction and oxidation is developed, based on the assumption that the process is chemisorption and the controlling equation is a Langmuir–Hinshelwood type of kinetic equation. It is then analysed using experimental data obtained from literatures.

2. Langmuir–Hinshelwood mechanism

In heterogeneous catalysis, kinetic expressions could be developed by applying the principle of mass action in terms of the surface concentrations. Substituting relations from the adsorption isotherm with the knowledge that the total number of surface sites should be constant, the rate expressions could be obtained in terms of observable bulk [2]. The rates are often found to be proportional to the molar concentration of the reactants raised to a simple power. In the instances when two reactants, A and B, are competitively adsorbed molecularly for the same adsorption sites but with different rate constants for adsorption and desorption, and undergo a reaction to yield products, the reaction can be represented by a Langmuir–

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* Corresponding author. Tel.: +65 6550 0433; fax: +65 6454 9871.
E-mail address: tan_seng_sing@nyp.gov.sg (S.S. Tan).

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Hinshelwood mechanism. The reaction rate can be resolved into an expression (1), in terms of the partial pressures, p_A and p_B, where k is the relevant rate constant and θ_A and θ_B represent the fractional surface coverage of each reactant.

$$\text{Rate} = k\theta_A\theta_B = k\frac{ap_A bp_B}{(1 + ap_A + bp_B)^2} \quad (1)$$

The rate constant ratio parameters, a and b, and the relevant rate constant, k, are all temperature-dependent, so the overall temperature dependence of the rate may be strongly non-Arrhenius in the sense that the overall reaction rate is unlikely to be proportional to $e^{-E/RT}$ [3]. Another variation of adsorption conditions arises where the adsorbate undergoes dissociative adsorption, occupying two sites. Two adjacent empty sites are needed for adsorption to occur. Similarly, two adjacent occupied sites are needed for desorption to occur. If occupancy is random, the probability for adsorption is given [4] by the square of the fraction of the surface not covered, $(1-\theta)^2$ and for desorption is given by the square of the fraction of the surface covered, θ^2. Based on these analogies, a kinetic model of photocatalytic reduction of CO_2 with H_2O is being derived next.

3. Mechanism of photocatalysis

In our previous experiment conducted recently, the results showed that the titanium oxide catalyst pellet could be used in photoreduction of CO_2 with H_2O. It showed that when short wave ultra-violet (UVC) radiation was used, a total yield of CH_4 obtained in the experiment after 65 h of continuous irradiation was 8.3 μmol. Some H_2 and CO were also observed [5]. The reaction scheme in Fig. 1 was proposed from our previous study [6]. The mechanism of this proposed photocatalysis process forms the basis in developing the kinetic model.

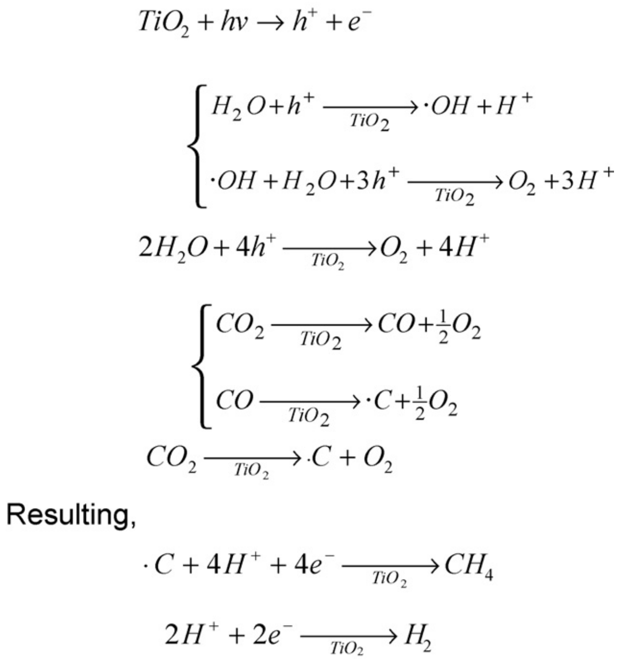

Fig. 1. Reaction scheme for photocatalytic reduction of CO_2 with H_2O on TiO_2 pellets.

The results obtained in this previous experimental study showed good correspondence with other reports [7–9] and suggested that the process has splitted the water and led to photo-produce hydrogen and as well as photo-reduced CO_2 into CH_4 through the following reaction.

$$2H_2O + 3CO_2 \xrightarrow[TiO_2]{} CH_4 + 2CO + 3O_2$$

$$2H_2O \xrightarrow[TiO_2]{} 2H_2 + O_2$$

Some of the products could have been photo-adsorbed, blocked the active sites and slow down the reformation. Some of these products could have recombined in a reserve reaction. It was noted that no oxygen could be detected in the gaseous production mixture. Saladin reported the similar observation and deduced that oxygen together with some other oxygen-containing products such as CO could have been photo-adsorbed and hindered the diffusion of intermediates on the surface of the catalyst [7]. Based on the other related studies [10] which reported observation of O_2 in the reduction products of CO_2, there should be no doubt that O_2 was produced in our experiments. As we failed to detect any oxygen during the illumination, the missing oxygen could be due to the photo-adsorption.

In separate studies, TiO_2 catalyst has been widely explored to investigate photocatalytic oxidation of gas-phase organics for air pollution study [11]. Thus, when CO and O_2 were formed and not effectively desorbed from the catalyst surface in the photocatalytic reduction of CO_2 with H_2O process, the build up of concentrations of the products on the catalyst surface could lead to photo-oxidation of CO back into carbon dioxide in the reverse reaction. Such oxidation process, taking place at the same time, could have affected the reduction process and limited the reduction yields. The simple modelling to be developed here simulating the reaction process will incorporate the coupled effect of the adsorptive photocatalytic reduction and oxidation processes in the photo-activities.

4. Model development

Based on the reaction scheme for the photo-reduction of CO_2 with H_2O on TiO_2 catalyst proposed in our previous study [6] and using the rate law of a reaction which is an equation expressing the reaction rate in terms of molar concentrations of the species involved in the reaction, a simple model could be developed. In the very initial state when no product exists, the reaction rate expression could be represented as follows, by applying the Langmuir–Hinshelwood model from (1).

$$\text{Rate of reduction} = k_1\frac{ap_{CO_2} bp_{H_2O}}{(1 + ap_{CO_2} + bp_{H_2O})^2}$$

where a and b are the ratio of rate constants for adsorption and desorption of CO_2 and H_2O, respectively. According to most of the experimental setup in this area of research, having the operating temperature at room conditions, the partial pressure of water vapour in the reactor would be relatively low in comparison with the concentration of CO_2. Assuming the CO_2 covered most of the surface, $a p_{CO_2} \gg 1$, the reaction rate can be simplified as follows:

$$\text{Rate of reduction} = k_1 \frac{b p_{H_2O}}{a p_{CO_2}}.$$

At some stage when the products begin to form, the denominator of the above expression is revised to include the products covering some of the catalyst surface as well. Similar expression can be derived with these inclusions. As proposed previously [7,12], the products, CO and O_2, were adsorbed and photo-oxidized in a reverse reaction since they, especially CO, were not effectively desorbed and diffused from the catalyst surface. CO oxidation reaction with O_2, which undergoes dissociative adsorption, can be derived and the following expression is obtained.

$$\text{Rate of oxidation} = k_2 \theta_{CO} \theta_{O_2} = k_2 \frac{c p_{CO} \sqrt{d p_{O_2}}}{(1 + c p_{CO} + \sqrt{d p_{O_2}})^2}$$

where c and d are the ratio of rate constants for adsorption and desorption of CO and O_2, respectively. As the CO is so strongly bound to the catalyst surface that dominates the denominator of the expressions, ($c p_{co} \gg 1$), both expressions for reduction and oxidation can be simplified and combined as follows:

$$\text{Rate of reduction} = k_1 \frac{a p_{CO_2} b p_{H_2O}}{(c p_{CO})^2}$$

and

$$\text{Rate of oxidation} = k_2 \frac{\sqrt{d p_{O_2}}}{c p_{CO}}.$$

Therefore,

$$\text{Net reduction rate} = k_1 \frac{a p_{CO_2} b p_{H_2O}}{(c p_{CO})^2} - k_2 \frac{\sqrt{d p_{O_2}}}{c p_{CO}}.$$

The resultant rate of reaction will be the net rate of the reduction process less the reverse oxidation process. In order for the expression to be solvable, certain limits and boundary conditions shall be set for a proposed system.

5. Model solution of proposed system

Assuming the ideal gas law applies, the partial pressure of water vapour in the reactor can be determined from the operating temperature. In most of the experimental setups at steady state, it should be constant as long as the operating conditions in the reactor remain unchanged, ignoring the initial transient state. If highly purified CO_2 is presented with saturated water condition, and the pressure and temperature conditions are presumably remained steady throughout the reaction cycle, p_{CO_2} and p_{H_2O} can be assumed constant. Thus:

$$\text{Net reduction rate} = k_3 \frac{1}{(p_{CO})^2} - k_4 \frac{\sqrt{p_{O_2}}}{p_{CO}}.$$

In order to further simplify, we assume that $p_{O_2} \propto p$ and $p_{CO} \propto p$ at steady state, where p is the partial pressure or the concentration of the interested product. As a result, the rate equation can be resolved as follows:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{k_5}{p^2} - \frac{k_6}{\sqrt{p}}$$

$$\mathrm{d}t = \frac{p^2}{k_5 - k_6 p^{3/2}} \mathrm{d}p$$

After integrating and substituting the initial conditions, the following solution is obtained, applicable to simulate photocatalysis process of CO_2 reduction in most experimental setups.

$$t - t_0 = k_7 \ln\left[1 - \left(\frac{p}{p_{\max}}\right)^{3/2}\right] + k_8 p^{3/2} \qquad (3)$$

where,

k_7 and k_8 are the kinetic constants related to the rate constants and the experimental conditions of the setup, $p_{\max}$ is the maximum yield of the interested product, and t_0 is the time delay of photo-activities due to the transient state.

If a few data could be obtained in an experimental setup, the model could be used to fit into the data by iterating the two kinetic constants. The expression obtained would be a good representation of the whole profile of the reactivities. The reaction rate and the product formation for any duration of irradiation could then be predictable based on the expression.

6. Model validation

Alxneit and Corboz [12] conducted a study on photosynthetic reduction of CO_2 at the surface of catalyst in presence of water. The experiments were performed with TiO_2 (Degussa P25) an average crystallite size of 21 nm, a specific surface area of 50 $m^2\ g^{-1}$. About 200 μg of TiO_2 were deposited onto sapphire windows as dense, optically homogeneous layers of normally 600 nm thickness. A 200 W Hg/Xe-lamp was used as a light source. Radiation was blocked by a cooled water filter passing light with wavelength less than 900 nm. Their experimental results showed a fast initial increase of CH_4 cumulative yield. The rate of CH_4 formation decreases drastically after long duration of irradiation. No further increase of the yield can be measured after about 4 h of irradiation. The maximum product yield obtained from this experiment was 21.5 μmol g^{-1}. A curve representing the profile of the CH_4 yield could be generated as a function of irradiation time using our proposed kinetic model to fit with the experimental data. Comparison of the product formation profiles between the proposed model and the experimental data can be observed as shown in Fig. 2.

After iterating the two constants in the proposed expression (3), the model has fit well with the experimental data. The equation simulating the product formation was obtained using

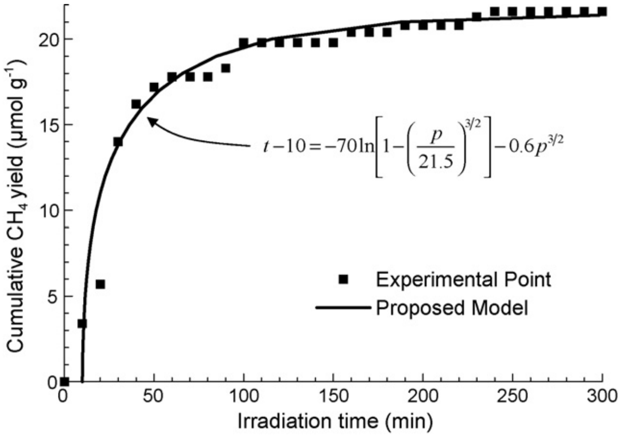

Fig. 2. Comparison of the proposed kinetic model fitting with the empirical profile of CH_4 formation from photocatalytic reduction of CO_2 with H_2O on TiO_2 surface.

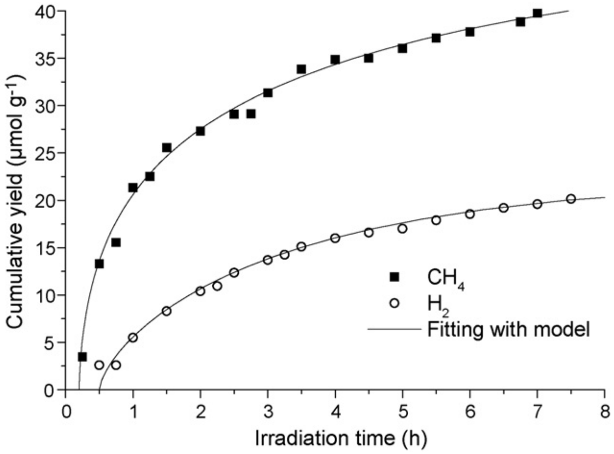

Fig. 3. Comparison of the proposed model fitting with the formation profiles of photosynthesised CH_4 and H_2 yields from photocatalytic reduction of CO_2 with gaseous H_2O.

the kinetic model with $k_7 = -70$ and $k_8 = -0.6$. The curve showed there was a time delay, $t_0 = 10$ min, at the initial state of reaction. Practically, there would have a transient state when the surface temperature of the catalyst increased gradually before steady state. Such similar phenomenon was observed in studies on photosynthesis of CH_4 at a TiO_2 surface from gaseous H_2O and CO_2 by Saladin and Alxneit [7]. In these studies, UV irradiation of the microcrystalline TiO_2 in the presence of H_2O and CO_2 led to photoreduction of CO_2 to form CO, H_2 and CH_4. All of these products were only detected a few minutes and even hours after irradiation started. Further validation could be done with any experiment data from this area of research.

7. Applications

Saladin conducted a study on photosynthesis of H_2 and CH_4 from gaseous H_2O and CO_2 using a miniaturised reactor [13]. The reactor consisted of two sapphire windows, which have the surface facing inside the reactor, coated with a thin layer of TiO_2 powder (Degussa P25). Approximately 80 μg TiO_2 was deposited on each window yielding dense homogeneously packed layers of nominally 0.24 μm thickness. CO_2 at 111 325 Pa at a flow rate of 2.0 mL min^{-1} was passed through a bubbler filled with water. The bubbler was kept in a thermostatic bath set to 291 K, thereby saturating the CO_2 stream with water, giving rise to a partial pressure of water vapour of 2058 Pa. Overall production yields of 40 and 20 micro-moles per gram of catalyst (μmol g^{-1}) were obtained for CH_4 and H_2, respectively, after 7.5 h of broadband irradiation. The products formation data were extracted from that study and our proposed model was used to explore the product yields beyond 7.5 h of irradiation. After iterating the two constants, k_7 and k_8, of the proposed model, the formation profiles of CH_4 and H_2 could be represented by the following expressions (4) and (5), respectively.

$$t - 0.2 = -9.5\ln\left[1 - \left(\frac{p}{48}\right)^{3/2}\right] - 0.025\,p^{3/2} \tag{4}$$

where p is CH_4 yield in μmol g^{-1}.

$$t - 0.5 = -3.8\ln\left[1 - \left(\frac{p}{22.5}\right)^{3/2}\right] \tag{5}$$

where p is H_2 yield in μmol g^{-1}.Using these two expressions, curves representing the formation profiles of CH_4 and H_2 can be graphically plotted as a function of irradiation time. Comparison of the product formation curves with the experimental data can be observed from the graph. As shown in Fig. 3, both curves could be fitted very well to the experimental data. It can be seen from the curves that the products formation have not ceased yet after 7.5 h of irradiation. It will be of interest for processes comparison to determine what the ultimate maximum product yields would be achievable if irradiation were to continue.

Based on the equations simulating the product formations obtained from the kinetic model, we could deduce the ultimate maximum yields of CH_4 and H_4 would be 48 and 22.5 μmol g^{-1} respectively. It is interesting to realise that such a model is applicable to both formations of H_2 and CH_4 through the photocatalytic reduction of CO_2 with H_2O and is useful to predict the ultimate achievable maximum product yields for a prolonged duration of irradiation. The model developed could be also useful to deduce the rate and product yield at any particular reaction time and could aid as a tool for future optimization study.

8. Comparison and discussion

As shown in Table 1, it became obvious that a much lower absolute yield in term of μmol with a small amount of catalyst could result a higher yield in term of μmol g^{-1}. Based on these two results obtained from P25 coated on sapphire windows in the miniaturised reactor, the setups were quite the same except that the thicknesses and the amounts of the TiO_2 coated were different. The product yield in μmol g^{-1} was approximately doubled when the amount of catalyst coated was reduced to slightly less than halved. However, it took a longer time to achieve the product yield. If sufficient time were given, the

Table 1
Comparison of CH_4 yields achieved in terms of ppm and μmol

Catalyst forms		P25 coated on sapphire	
Catalyst weight		160 μg	400 μg
UV duration		7 h	4 h
CH_4 yields	μmol g^{-1}	40	21.5
	μmol	0.0064	0.0086
	ppm	2612	3510
Max. CH_4 yields	μmol g^{-1}	48	21.5
	μmol	0.00768	0.0086
	ppm	3134	3510
Reactant quantity		2.45 μmol	

maximum CH_4 yields of the both experiments in term of μmol were in fact almost the same with a difference of about 10% only. Thus, using a small amount of catalyst would certainly result lower reforming rate but would still result similar amount of product yield if given sufficient reaction time. Therefore, μmol g^{-1} may not be an effective measurement, especially when the reaction rate is of concern.

The product yield of CH_4 from our study using Aerolyst 7708 showed a very significant high yield in term of μmol, as compared to other results. It was not simply due to the larger amount of catalyst used in our experiment. Using a larger amount of catalyst could only directly increase the rate of the reforming process but might not necessarily produce proportionally higher concentration of the product in term of ppm or high yield in term of μmol, especially in such redox reaction. Instead, it was mainly due to the fact that the amount of reactant in our reactor was relatively high compared with others experiments.

Considering the total amount of the reactants besides the amount of catalyst being used, it was noted that the capacity of our reactor was 1.1 L, which could be worked out to have approximately 45×10^3 μmoles of reactant based on the standard laboratory conditions, while the others used much lower amount of reactant, i.e. 2.45 μmol [12,13], 300 μmol [9] and 496 μmol [14] only. By using very small amounts of reactant and catalyst in laboratory, it might have favourable results in ppm, although the absolute amount of product was relatively small in μmol. However, such an analysis is only good for laboratory experimental studies. Experiments using a larger gas volume and more catalysts and measuring in ppm offered useful information and have more advantages. After all, the ability to use the product as a fuel depended on the concentration of CH_4. Thus, measuring product concentration in ppm would be a better choice. Although our product concentration in ppm was not as high as others, there is still more improvement that could be made on the design of the reactor and other configurations, based on the results obtained from this study.

9. Summary and conclusion

A kinetic model simulating the product formations through photocatalytic reduction of CO_2 with H_2O on TiO_2 surface has been developed in this study. The experimental data obtained from the literatures were used to validate the model and they fitted very well with our proposed model. It could be effectively used to estimate the reaction rate and the product formation from most of the photocatalytic reduction of CO_2 with gaseous H_2O. In applying the model to obtain the maximum achievable yields for comparison, it showed from the above studies that when effective use of catalysts in the system was the major concern, measuring product yields in μmol g^{-1} might favour results obtained from processes using very small amounts of catalyst in laboratory, but such configurations could not have good representation for a much bigger reactor from an application point of view. This comparative study showed that product concentration in term of ppm would be an effective measurement of reforming yields through photocatalytic reduction of carbon dioxide with water vapour.

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