Probability Langmuir-Hinshelwood based CO₂ photoreduction kinetic models

W.A. Thompson*, E. Sanchez Fernandez, M.M. Maroto-Valer

Research Centre for Carbon Solutions (RCCS), School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK

HIGHLIGHTS

- Experimental and data analysis protocols for high quality CO₂ photoreduction data.
- Probability Langmuir-Hinshelwood kinetic models for CO₂ photoreduction.
- Models accounted for deactivation and fractional coverage.

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ABSTRACT

For engineering solutions, scaling photoreactors and processes, kinetic models that describe the impact of process conditions on CO₂ photoreduction are critical to driving this technology forward. Probability Langmuir-Hinshelwood based CO₂ photoreduction kinetic models were developed after several criteria that included: a high purity photodifferential photoreactor with a high ratio of reagent gas volume to irradiated photocatalyst surface area and automated robust data collection and kinetic modelling using a MATLAB programme. Product distribution profiles indicated the dynamic changes occurring over the photocatalyst with an initial increase in H₂ product distribution, followed by an increase in CH₄ and finally CO product distribution, possibly due to the photocatalytic degradation of CH₂O and CH₂O₂ intermediates. Production of H₂ increased with a decrease in CH₄ when the partial pressure of H₂O was increased. Using the glyoxal mechanism, this is possibly explained via the formation of CH₃CO₂H from H₂O reacting with CH₃CHO that prevents the full conversion of CH₃CHO to CH₄. To account for deactivation, probability Langmuir-Hinshelwood based kinetic models were used to fit CO₂ photoreduction kinetic data for CH₄, CO and H₂ with low average standard errors of $3.44 \times 10^{-4}$, $1.54 \times 10^{-4}$ and $1.36 \times 10^{-4}$, respectively. The probability LH based kinetic model coefficients were estimated with low standard deviations, using a robust and repeatable numerical method using a trust-region and multi-start algorithm. The models were used to predict optimised selectivity of CH₄, CO and H₂.

1. Introduction

CO₂ photoreduction offers a potential solution to minimising the impacts from rising anthropogenic CO₂ concentration [1]. The use of relatively abundant CO₂ also offers an opportunity for industries to be created through the production of value added chemicals [2]. CO₂ photoreduction offers one such avenue for the production of solar fuels. CO₂ photoreduction also offers the potential to produce H₂ and CO syngas that can be converted into higher order hydrocarbon fuels using well established Fisher-Tropsch chemistry.

Low CO₂ photoreduction efficiency towards products such as CH₄, CO and H₂ has driven the focus on developing novel photocatalysts [3–6], with limited focus on understanding the CO₂ photoreduction mechanism [7,8] and the kinetics [9–17]. Standardisation of the practical aspects for collecting CO₂ photoreduction data is still under development. The impact of adventitious carbon from photocatalyst preparation, coating and photoreactor components on false positive production is a challenge for collecting CO₂ photoreduction data [18,19]. This challenge is compounded by not being able to quantitatively compare CO₂ photoreduction photocatalysts due to the wide variation in experimental protocols and photoreactors used [20]. In addition, analytical methods for tracking the reaction are not consistent with different purities of analytical gases and combination of detectors used [21]. For developing intrinsic CO₂ photoreduction kinetic models, the use of a photodiﬀerential photoreactor that increases the probability of equal participation of illuminated active sites has not been

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addressed for developing CO₂ photoreduction kinetic models [22]. Deactivation of the CO₂ photoreduction photocatalyst is a challenge that has been reported by a growing number of authors [7]. The current Langmuir-Hinshelwood (LH) based kinetic models assume that the availability of active sites is constant and does not account for the deactivation of the photocatalyst. In addition, previous LH based CO₂ photoreduction kinetic models have included fractional coverage of H₂O and CO₂ without considering the mole equivalents of a proposed elementary surface reaction. Numerical analysis has so far not been considered for evaluating the estimation of the CO₂ photoreduction kinetic model coefficients. This is a critical aspect as conclusions about the reaction parameters are made based on the coefficient values estimated. Nonlinear functions are often nonconvex with a large number of local minimum leading to a range of solutions and different coefficient values [23].

With the above challenges identified for developing intrinsic CO₂ photoreduction kinetic models, the five considerations for developing these models is described by the decision tree and was used to guide the kinetic model development presented in this work (Fig. 1).

In this work, to limit the impact of adventitious carbon, slurry deposition of commercial P25 TiO₂ with H₂O onto stainless steel supports was tested in a chemically cleaned stainless steel based photoreactor setup (Fig. 1 Steps 1–2). To increase the probability of active site participation leading to an intrinsic kinetic model, a photodifferential photoreactor with a high ratio of reactor gas volume to illuminated photocatalyst area was employed (Fig. 1 Step 2). A robust gas chromatography analytical method using a combination of flame ionisation and thermal conductivity detectors, methaniser and variable valve timing was used for linear calibration for the expected CO₂ photoreduction products (Fig. 1 Step 3). To account for deactivation, using a novel probability approach, a probability LH based kinetic model was used to account for the loss of active sites during the reaction towards CH₄, CO and H₂ (Fig. 1 Step 4). This probability approach yielded a different explanation to the current LH based kinetic models for the change in fractional coverage and the loss of active sites during CO₂ photoreduction over time. A Weibull probability density function (PDF) was re-parametrised to include active illuminated sites and deactivation over time with a LH based model. Elementary surface reactions towards CH₄, CO and H₂ are used to account for the mole equivalents of the reaction in the kinetic model. A robust mean median multi-start trust-region numerical method is used to estimate the coefficients of the nonlinear probability LH based kinetic models (Fig. 1 Step 5).

2. Experimental

2.1. Catalyst coating

Stainless steel 80 gauge mesh (25 × 40 mm) was cleaned by sonication in 100 ml 1:9 70 % HNO₃ in DI H₂O, neutralized in 100 ml 0.6 M Na₂CO₃ in DI H₂O, washed with 3 × 20 ml DI H₂O and then dried at 80 °C for 12 h. The mesh was coated with a slurry of 4.7 g P25 TiO₂ (Evonik) in 12 ml DI H₂O. The slurry was covered and agitated in an ultrasound bath set at 50 °C for 60 min. The stainless steel mesh was sonicated in the catalyst slurry for 30 s before being dried at 140 °C for 3 h.

2.2. CO₂ photoreduction rate data

All CO₂ photoreduction experiments were performed under continuous flow conditions (Fig. 2).

The coated stainless steel mesh was placed in the middle of the photoreactor and sealed. Residual air in the system was evacuated via three repetitive steps of placing the system under vacuum to −1 bar and the vacuum released with CO₂ (99.995%) to +1 bar. The CO₂ was evacuated through the GC lines until approximately 0.2 bar, before the system was sealed and placed under vacuum again. The flow rate of CO₂ and Ar was set according to the experimental settings required and passed through the temperature controlled (± 0.1 °C) aluminium body saturator for at least 12 h to allow the system to equilibrate. The total flow of the reagent gas was set to 0.35 ml.min⁻¹. See the Supplementary
information for the flow rates of CO₂ and Ar used. Relative humidity
(± 1.8% RH) was measured using an inline Sensirion SH175 humidity
sensor potted (MG Chemicals 832HD) into a Swagelok 1/4” T-piece.
The temperature of the photoreactor was controlled using a hotplate
and the surface of the coated photocatalyst measured using a Radley’s
pyrometer (± 2.0°C). To prevent condensation at higher saturation
temperatures, the lines from the outlet of the saturator up until the inlet
of the H₂O trap were heated and temperature controlled (± 0.1 °C)
with a heating rope and thermocouple (Fig. 2). An OmniCure S2000
fitted with a 365 nm filter was used as the light source. The light source
was placed 30 mm above the surface of the coated meshes used. Please
refer to Supplementary information for a photo of the light source
setup. Irradiance at the exit of the fiber optic light guide was measured
before each experiment using an OmniCure R2000 radiometer (± 5%).
An inline GC (Agilent, Model 7890B series) with a Hayesep Q column
(1.5 m), 1/16 inch od, 1 mm id), MolSieve 13X (1.2 m), 1/16 inch od,
1 mm id), thermal conductivity detector (TCD), nickel catalysed me-
thanizer and flame ionization detector (FID) was used to analyze the
output of the photoreactor every four minutes. The GC was calibrated
using 1000 ppm calibration gas (H₂, CO, CO₂, O₂ and CH₄) in a balance
output of the photoreactor every four minutes. The GC was calibrated
before each experiment using an OmniCure R2000 radiometer (± 5%).

![Fig. 2. Overview of experimental setup used for collecting CO₂ photoreduction kinetic data (Not to scale).](image)

Table 1

| Exp. Name. | Partial pressure CO₂ (kPa) | Partial pressure H₂O (kPa) |
|------------|----------------------------|----------------------------|
| PCO₂-L     | 25.72                      | 2.66                       |
| PCO₂-I     | 48.44                      | 2.74                       |
| PCO₂-H     | 98.38                      | 2.62                       |
| PH₂O-L     | 25.72                      | 2.66                       |
| PH₂O-I     | 25.50                      | 3.47                       |
| PH₂O-H     | 24.67                      | 6.64                       |

3. Results

3.1. Experimental space investigated

The work investigates the impact of photocatalyst fractional cov-
ervation on CO₂ photoreduction kinetics. To accomplish this, a wide
experimental space of different partial pressures of CO₂ and H₂O, was
explored for collecting kinetic data for CO₂ photoreduction using P25
TiO₂ (Table 1). Low, intermediate and high settings, shown in bold text
on Table 1, were used for partial pressures of CO₂ (25.72, 48.44 and
98.38 kPa) and H₂O (2.66, 347 and 6.64 kPa). Temperature was kept
constant at 41.0 ± 2.0 °C and the irradiance was kept constant at 400
mW.cm⁻² ± 20 mW.cm⁻². A total of three hundred and fifty experi-
mental points were used to fit each CH₄, CO and H₂ kinetic model.
Previous CO₂ photoreduction kinetic studies have relied on several
discrete data points [9–17]. This is the first example describing CO₂
photoreduction kinetics using continuous experimental data points
collected under continuous flow conditions. In addition, previous ex-
amples have not factored in the requirements of the decision tree pro-
posed in this work for collecting CO₂ photoreduction kinetic data Fig. 1.

Table 2

| Control type | Inert gas | CO₂ | Light | Photocatalyst | H₂O |
|--------------|-----------|-----|-------|---------------|-----|
| Type I       | I         | X   | 1     | 1             | 1   |
| Type II      | I         | X   | 1     | 1             | 1   |
| Type III     | I         | 1   | 1     | X             | 1   |
| Type IV      | I         | 1   | 1     | 1             | X   |
We performed Type I-IV controls with only the Type I control yielding CO$_2$ photoreduction products CH$_4$, CO, and H$_2$. It is very difficult to completely remove all traces of the slow-moving CO$_2$ gas when performing a Type I control experiment. Using a 3× vacuum purge similar to the one described to prepare the CO$_2$ photoreduction test (Section 2.2) where Ar was used to release the vacuum instead of CO$_2$ and post purge flow rates of 15.13 mL·min$^{-1}$ Ar for 16 h yielded between 2530–7380 ppm CO$_2$ that remained in the system. Dilla reported maximum CO$_2$ photoreduction, using P25 TiO$_2$, when using very low partial pressures of CO$_2$ with a maximum production reported when using 1000 ppm CO$_2$ [29]. Ideally, the amount of CO$_2$ should be zero to use a Type I control experiment as evidence for CO$_2$ being the carbon source for CO$_2$ photoreduction. Under atmospheric like conditions (400 ppm CO$_2$), CO$_2$ was shown to form a HCO$_3$ layer on TiO$_2$ (110) which was stable at temperatures below 400 K [30]. HCO$_3$ is a potential intermediate for CO production [7] and the formation of this layer is very likely to occur during the preparation and storage of the photocatalyst [30]. In this work, we did not attempt to pre-clean the photocatalyst or subtract production under control Type I conditions as the deconvolution of the potential impact of adsorbed HCO$_3$, adventitious carbon and CO$_2$ photoreduction at low partial pressures of CO$_2$ is too complex.

P25 TiO$_2$ was chosen as a photocatalyst for this study as it is commercially available and well studied [3,31,32]. P25 TiO$_2$ is very pure with limited adventitious carbon able to survive the oxidative AEROXIDE® manufacturing process using temperatures of 1000–2400 °C. To limit the impact of adventitious carbon, stainless steel mesh was used as a photocatalyst support. P25 TiO$_2$ was coated onto the stainless steel supports using a P25 TiO$_2$/DI H$_2$O slurry deposition. Coverage of the coating was estimated using Otsu thresholding as we have previously described (Fig. 3) [33]. A consistent pattern of cracks was observed when using a slurry deposition that yielded 12.80, 54.21 and 84.70 mg dry loading of P25 TiO$_2$ onto the mesh, with very similar coverage of 90.97%, 90.06% and 90.47% respectively (Fig. 3). The area of the exposed photocatalyst on the coated meshes was independent of the dry loading mass of P25 TiO$_2$ and likely to yield an equal probability of illuminated surface area between the different meshes used. Therefore it is assumed that the Step 1 in Fig. 1 is met with P25 TiO$_2$ already scaled for production, a reproducible coating method with equal coverage and a simple scalable DI H$_2$O slurry deposition method that limits the impact of adventitious carbon.

3.3. Analytical methods and photodifferential photoreactor

3.3.1. Analytical methods

Tracking the CO$_2$ photoreduction reaction by an inline GC minimizes the impact of sample contamination and allows for a continuous flow CO$_2$ photoreduction process. For collecting accurate kinetic data, a linear calibration that includes the expected production range is critical. The CO and CH$_4$ kinetic data reported herein was interpolated from the calibration curves included in the Supplementary information. H$_2$ kinetic data and monitoring of O$_2$ and N$_2$ was extrapolated from the calibration curves (Supplementary information) due to the very low values observed and difficulty in calibration down to these levels with a loss of linearity. Air contamination is likely to impact the TCD area recorded for O$_2$ and N$_2$, especially as the diluted calibration gas approaches the concentrations of O$_2$ and N$_2$ contamination from air during the calibration.

3.3.2. Photodifferential photoreactor

An intrinsic CO$_2$ photoreduction kinetic model ideally describes kinetic data that is not impacted by scale. To develop an intrinsic kinetic model, all active sites must ideally have the same probability of participating in the CO$_2$ photoreduction reaction. To achieve this, a photodifferential photoreactor that increases the probability of equal participation of active sites by uniform light distribution, is critical for recording kinetic data. The photoreactor used for collecting kinetic data

![SEM images](image1.png)

Fig. 3. SEM images in top row and coating coverage (%) estimated using Otsu thresholding in bottom row for low, intermediate and high loading of P25 TiO$_2$, using a slurry deposition method onto 80 gauge stainless steel mesh used in this study.
Temperature is likely to impact the adsorption/desorption equilibrium of gases on the photocatalysts surface, the surface diffusion of the reagent gases H₂O and CO₂ and possible intermediates that include: CH₂O, CH₂O₂, CH₃OH, CH₃CO₂H and CO₃²⁻ [7]. Temperature is also very likely to facilitate CO₂ photoreduction by overcoming thermal energy barriers [34]. Without consensus on the mechanism of CO₂ photoreduction and the possible intermediates, temperature is assumed to impact all photocatalytic reactions occurring on the surface of the photocatalyst. In this work, the impact of partial pressures of the reagent gases on the fractional coverage was investigated with temperature kept constant. The high heat capacity of the thick based (h = 2 cm) stainless steel photoreactor and measurement of the photocatalyst surface temperature with a pyrometer ensured high quality kinetic data was collected. This type of photocatalyst increased the uniformity of light and heat distribution. The light source was placed parallel and 30 mm above the surface of coated mesh inside the photoreactor.

To maximise the saturation of reagent CO₂ gas with H₂O, the CO₂ gas passed through a coil shaped copper tube in an aluminium body impinger with a PTFE insert (Fig. 4a). Saturation of CO₂ with H₂O was measured using a low cost inline humidity sensor. The sensor recorded both % Rh and °C with standard deviations of 0.21 for relative humidity measurements (%RH) and 0.08 for temperature measurements (°C). A representative example of the humidity sensors measurements and a more detailed setup description is shown in the Supplementary information.

Kinetic models can be impacted if the mass of photocatalyst is used to describe kinetic data in units of μmol.g⁻¹.cat⁻¹.h⁻¹. Using mass of photocatalyst in the kinetic data units, the kinetic data is no longer a description of CO₂ photoreduction occurring at illuminated photocatalyst active sites but an average that includes the bulk of non-illuminated and non-participating photocatalyst sites inside the non illuminated photocatalyst. Using this kinetic data will yield an extrinsic kinetic model. With a photodifferential photoreactor, units of μmol.cm⁻².h⁻¹ that described the kinetic data over area illuminated were used in this study. Assuming active sites are only on the photocatalyst surface, using area illuminated instead of the mass of the photocatalyst allowed for developing kinetic models that are scalable with respect to light and attempts to only include participating active sites. The coverage estimated (Fig. 3) was used to calculate the kinetic data rates.

3.4. Probability Langmuir-Hinshelwood based kinetic model

The majority of the current examples describing CO₂ photoreduction kinetics use the LH or a derivative of the LH based kinetic model as shown by Eq. (1) [9–15,35].

$$ r = kI^n \prod_{i=1}^{z} \frac{(K_i R_i)^{\alpha_i}}{1 + \sum_{i=1}^{z} K_i R_i} $$

where: $r$ is the rate of the reaction (μmol.g⁻¹.cat⁻¹.h⁻¹); $k$ is the rate constant (μmol.g⁻¹.cat⁻¹.h⁻¹); $I$ is the light intensity (mW.cm⁻²); $n$ is the reaction order of light intensity (dimensionless); $K_i$ represent the equilibrium adsorption constants for reactants and products (bar⁻¹); $P$ refer to the partial pressures for reactants and products (bar); $z$ indicates the number of reactants that are involved in the assumed surface reaction and $a_i$ is the number of moles for each reactant from the assumed surface reaction and $z$ indicates the number of all reactants and products.

According to the LH model Eq. (1), the rate of CO₂ photoreduction is directly proportional to the fractional coverage of the reagent gases. Under the assumption that all sites being equal and monolayer formation, the fractional coverage of the reagent gases involved in the elementary surface reaction should reach a steady state under continuous flow conditions in a photodifferential photoreactor at constant temperature and irradiance. However the LH based kinetic model does not account for deactivation of the photocatalyst, especially under continuous flow conditions, as described by a growing number of reports [36–41,33,42–44]. To account for this deactivation, the change in production over time needs to be considered in the kinetic model along with a parameter that describes the deactivation leading to a decrease in active sites over time. The primary cause of deactivation is an ongoing investigation with evidence of the formation of bidentate carbonate species, peroxy and peroxocarbonate species on the photocatalysts surface possibly leading to deactivation [7,42]. One option to explain the deactivation over time is to assume elementary surface reactions that permanently deactivate the active sites. Integrating the rate
of these surface deactivation reactions over time, allows to estimate the concentration of sites that deactivate over time and modify the fractional coverage. To account for the deactivation observed over time, a number of different derivatives of the LH based kinetic model Eq. (1) that included the concentration of deactivated sites over time have been developed and can be found in the Supplementary information. Initial attempts to fit the experimental data did not succeed due to lack of knowledge of the causes of deactivation.

Without consensus on the driving force behind the deactivation of the photocatalyst, a macroscopic view of the kinetic model is introduced here to describe this change with time.

All the phenomenon involved in the photocatalytic process can be approximated by the chance of photons reaching sites that remain active. Instead of assuming a rate of decay of active fractional coverage, we assume that the fractional coverage is constant and replace the irradiance term ($I^x$) in Eq. (1) with a probability of photons as a probability density function (PDF) being able to reach the active sites. The probability decreases over time as in Eq. (2).

$$r = k_{PDF}(t) \left( \prod_{i=1}^{n} (K_i, P_i)^{\eta_i} \right) \left( 1 + \sum_{i=1}^{n} K_i P_i \right)^{-\beta}$$

where: $t$ is time (s, min or h) and $PDF$ is a probability density function

A Weibull PDF was used to describe the deactivation of a Co containing catalysts for Fisher-Trosh processes [45]. The two parameter Weibull PDF is shown by Eq. (3).

$$PDF(t) = \frac{\eta}{\gamma} \frac{t^{\eta-1}}{\gamma} \exp \left( \frac{t}{\gamma} \right)^{\eta}$$

where PDF($t$) is the probability density function; $\eta$ is the shape parameter (Dimensionless); $\gamma$ is the scale parameter (Dimensionless) and $t$ is time (h, s or min).

The scale parameter $\gamma$ and shape parameter $\eta$ have an impact on the shape and height of the Weibull PDF (Fig. 5 a), where increasing $\gamma$ broadens the Weibull PDF and increasing $\eta$ increases the height of the Weibull PDF.

For modelling the deactivation of CO$_2$ photoreduction with a Weibull PDF, the Weibull PDF needs to be re-parametrised to include illuminated active sites and a deactivation term. The Weibull PDF scale parameter $\eta$ is analogous to the impact of deactivation ($\eta$$_d$) where a larger scale parameter increases the probability of photons reaching sites favouring a steady state of production.

$$\beta = I^x$$

The Weibull PDF shape parameter $\beta$ term (Fig. 5b) is analogous to the impact of irradiance of illuminated sites successfully catalysing the reaction Eq. (4) where if more irradiance is successfully utilised in the CO$_2$ photoreduction process then a higher rate of production will be observed with the shape parameter $\beta$ having an impact on the height of the PDF and less of an impact on the shape of the PDF (Fig. 5b).

The two parameter Weibull function can be re-parametrised and used to describe the change in sites over time ($t$) shown by Eq. (5) which can then be used towards the probability LH based kinetic model Eq. (6).

$$PDF(t) = \frac{\gamma}{\eta_d} \frac{t^{\eta-1}}{\gamma_d} \exp \left( \frac{t}{\gamma_d} \right)^{\eta_d}$$

$$r = \frac{\gamma}{\eta_d} \frac{t^{\eta-1}}{\gamma_d} \exp \left( \frac{t}{\gamma_d} \right)^{\eta_d} \left( 1 + \sum_{i=1}^{n} K_i P_i \right)^{-\beta}$$

where $r$ is the rate of reaction (mol.cm$^{-2}$.h$^{-1}$); $k$ is the rate constant (mol.cm$^{-2}$.h$^{-1}$); $t$ is time (h); $I = \frac{I^x}{I_{in}}$ is the irradiance (Dimensionless)$\gamma$ is the reaction order of light intensity (Dimensionless); $\eta$$_d$ is the deactivation scale parameter (Dimensionless); $K_i$ represent the equilibrium adsorption constants for reactants and products (bar$^{-1}$); $P_i$ refer to the partial pressures for reactants and products (bar); $\alpha$ indicates the number of reactants that are involved in the assumed surface reaction and; $a_i$ is the number of moles for each reactant from the assumed surface reaction and $z$ indicates the number of all reactants and products.

The inclusion of time and the flexible Weibull PDF allows for the dynamic kinetic modelling of CO$_2$ photoreduction over time which still includes a LH component.

3.5. Numerical methods for developing CO$_2$ photoreduction kinetic models

For the systematic and reproducible treatment of the CO$_2$ photoreduction kinetic data, a program (Fig. 6) was developed in MATLAB to extract the GC data (GCIt), followed by a numerical method (numIt) to estimate the probability LH based kinetic model coefficients (Section 3.4).

GCIt (Fig. 6) included importing raw GC data, fitting calibration
curves, integrating peaks, calculating ppm and finally producing a matrix of the experimental settings (Irradiance, partial pressures of CO2 and H2O and time) and a matrix of the CO2 photoreduction kinetic data towards CH4, CO and H2. These two matrices were then used in the numIt programme for kinetic modelling. To find a global solution to the nonlinear probability LH based CO2 photoreduction kinetic model, we developed a numerical method that estimated the coefficient value using the median value from the iterations of a trust-region and multi-start numerical method. numIt (Fig. 6) iterated over a user selected number of multi-start points \(MS_i\); and a global solution to the nonlinear fitting exercise where a single model is determined by a compromise between computation time and accuracy.

### Table 3

Upper and lower constraints for the multi-start trust region method used for estimating the probability LH based kinetic model coefficients.

| Lower constraint | Upper constraint |
|-----------------|-----------------|
| \(k\)            | \(\eta_d\)       |
| \(\alpha\)       | \(K_{\text{H}_2\text{O}}\) | \(K_{\text{CO}_2}\) |
partial pressures of CO₂ and H₂O over time. The probability LH based kinetic models were dynamic and were able to model both a steady and deactivated state for the production of CH₄, CO and H₂ for different partial pressures of CO₂ and H₂O. (Figs. 7 and 8).

Perfect line fits are not uncommon when fitting generalised models and this was highlighted by the less than perfect fits to the H₂ production data when changing the partial pressure of CO₂ (Fig. 7 c). The H₂ kinetic model was still able to account for differences in maximum production and also a delayed but similar trend to the experimental values. It is also important to note that H₂ production did not vary when changing the partial pressure of CO₂ and the generalised H₂ kinetic model may not have been able to account for these very slight variations.

### 3.7. Impact of partial pressure CO₂

Production of CO and CH₄ increased when lower partial pressure of CO₂ was used (Fig. 7). This has previously been explained by an increase in competition between CO₂ and H₂O for active sites on the catalyst [10,12] or by a reduction in photogenerated charge carriers on the photocatalyst surface [29]. To investigate the impact of partial pressure of CO₂, the product distribution trends of CH₄, CO and H₂ over time were evaluated using Eq. (8).

$$PD = \frac{n_{D,i}}{\sum_{i=1}^{n} n_{A,i}}$$  \hspace{1cm} (8)$$

where PD is the product distribution of the desired product as a fraction; n₀D is the molar flow rate of the desired product (μmol. h⁻¹); nᵢA is the molar flow rate of desired and undesired products (μmol. h⁻¹) and n is the number of desired and undesired products.

During ≈ 0–1 h, the product distribution of CO decreased (Fig. 9 b) whilst the product distribution of H₂ and CH₄ increased (Fig. 9 c,a).

During the initial reaction times (≈ 0–2 h), the product distribution towards H₂ was favoured over CH₄ (Fig. 9 c,a) with the product distribution of CH₄ and CO rising (Fig. 9 c,a). CO₂ photoreduction towards H₂ was favoured over CH₄ (Fig. 9 c,a) with the product distribution of CH₄ and CO rising.

### Table 4

| Product | Assumed surface reaction | PDF LH model |
|---------|--------------------------|--------------|
| CH₄     | $8 \times TiO_2 + h^+ \rightarrow h^+ + e^-$ $4H_2 + 8h^+ \rightarrow 8H^+ + 2O_2$ $CO_2 + 4H^+ + 4e^- \rightarrow CH_4 + 2H_2O$ | $r_{CH_4} = kPDF(t)(K_{H_2}P_{H_2}K_{CO_2}P_{CO_2})^{2}$ |
| CO      | $2 \times TiO_2 + h^+ \rightarrow h^+ + e^-$ $H_2 + 2H^+ \rightarrow 2H^+ + \frac{1}{2}O_2$ $CO_2 + 2H^+ + 4e^- \rightarrow CO + H_2O$ | $r_{CO} = kPDF(t)(K_{H_2}P_{H_2}K_{CO_2}P_{CO_2})^{2}$ |
| H₂      | $4 \times TiO_2 + h^+ \rightarrow h^+ + e^-$ $2H_2 + 4h^+ \rightarrow 4H^+ + O_2$ $4H^+ + 4e^- \rightarrow 2H_2$ | $r_{H_2} = kPDF(t)(K_{H_2}P_{H_2}K_{CO_2}P_{CO_2})^{2}$ |

### Table 5

| Product | $k$ | $n_D$ | α | $K_{CO_2}$ | $K_{H_2}$ |
|---------|-----|-------|---|------------|-----------|
| CH₄     | $7.16 \times 10^{-1}$ | 4.81 | 7.37 $\times 10^{-2}$ | 99.99 | 3.21 |
| CO      | $4.62 \times 10^{-1}$ | 19.80 | 3.51 $\times 10^{-2}$ | 79.33 | 22.65 |
| H₂      | $3.43 \times 10^{-2}$ | 2.78 | 1.06 $\times 10^{-7}$ | 77.22 | 12.54 |

### Table 6

| Partial pressure CO₂ (kPa) | CH₄ (μmol. cm⁻². h⁻¹) | CO (μmol. cm⁻². h⁻¹) | H₂ (μmol. cm⁻². h⁻¹) |
|----------------------------|------------------------|-----------------------|----------------------|
| 25.72                      | $4.90 \times 10^{-4}$  | $1.58 \times 10^{-4}$ | $8.85 \times 10^{-5}$ |
| 48.44                      | $4.33 \times 10^{-4}$  | $1.98 \times 10^{-4}$ | $1.94 \times 10^{-5}$ |
| 98.38                      | $2.01 \times 10^{-4}$  | $1.34 \times 10^{-4}$ | $2.51 \times 10^{-4}$ |

| Partial pressure H₂O (kPa) | CH₄ (μmol. cm⁻². h⁻¹) | CO (μmol. cm⁻². h⁻¹) | H₂ (μmol. cm⁻². h⁻¹) |
|----------------------------|------------------------|-----------------------|----------------------|
| 2.66                       | $4.90 \times 10^{-4}$  | $1.58 \times 10^{-4}$ | $8.85 \times 10^{-5}$ |
| 3.47                       | $1.82 \times 10^{-4}$  | $1.21 \times 10^{-4}$ | $7.28 \times 10^{-5}$ |
| 6.64                       | $2.66 \times 10^{-4}$  | $1.52 \times 10^{-4}$ | $1.19 \times 10^{-4}$ |

Average SE error $3.44 \times 10^{-4}$ $1.54 \times 10^{-4}$ $1.36 \times 10^{-4}$
this time, CO₂ is being converted to CH₄ intermediates.

During the latter stages of the reaction (≈ 5 h), the increase in product distribution of CO and decrease in product distribution for H₂ and CH₄ is likely related to deactivation where active sites conducive to the production of H₂ and CH₄ decrease with time. Overall the product distribution profiles provide evidence for the following: initially, a layer of H₂O dominates active sites due to increased hydrophilicity of TiO₂ when irradiated with UV-light [46]. During this time, H₂O oxidation is favoured with production of H⁺ and H₂. H⁺ is then used for CO₂ reduction towards surface intermediates and eventually to the delayed, relative to H₂ production, CH₄ production. The types of surface intermediates formed during this stage is very likely to include CH₂O and CH₂O₂ H [7]. Both CH₂O and CH₂O₂ are known to undergo photocatalytic degradation on TiO₂ leading to the production of CO during the latter stages of the CO₂ photoreduction reaction [47,48].

Coefficients α and ηᵣ were placed in the re-parametrised Weibull PDF Eq. (5) with impacts on the shape and height of the fitted kinetic models (Fig. 5). The shape of the curves for CH₄, CO and H₂ production were all different and would impact the estimation of both the α and ηᵣ coefficients. Attempts at decoupling this possibility by placing the ηᵣ term outside the PDF term (Please see Supplementary information) were unsuccessful where the modified function was unstable and did not always converge to a solution.

Bigger ηᵣ coefficients would indicate less deactivation (Fig. 5). The production of CH₄, CO and H₂ followed the trend of CO > CH₄ > H₂ in terms of stability (Fig. 7, 8). Stability was defined as the period for which the photocatalyst produced a particular compound before apparent deactivation causing a drop in production. This correlated with a decrease in the deactivation scale parameter ηᵣ where CO > CH₄ > H₂ (Table 5). The α coefficient values estimated followed the trend of H₂ > CH₄ > CO with an inverse relationship to ηᵣ (Table 5). This is expected as increasing α values, at constant irradiance, also impact the shape of the model with increasing values yielding sharper peaks with larger heights but also with a greater deactivation trend (Fig. 5). Irradiance is possibly playing a role in the deactivation of the photocatalyst with different relative impacts on CH₄, CO and H₂ production. This was reflected in the different α coefficients estimated for CH₄, CO and H₂ (Table 5).

For the probability LH based CH₄, CO and H₂ kinetic models, the adsorption equilibrium constant values (K_H₂O and K_CO₂) for H₂O and CO₂ were reasonably close with average values of 85.51 and 12.80 bar⁻¹, respectively. The large adsorption coefficient for H₂O is very likely explained by the increase in TiO₂ hydrophilicity under UV-light [46].

3.8. Impact of partial pressure H₂O

There are limited examples, testing the impact of H₂O on CO₂ photoreduction [12,49]. Increasing partial pressure of H₂O from 2.66, 3.47 and 6.64 kPa did not impact the production of CO greatly (Fig. 8). However, increasing the partial pressure of H₂O increased the production of H₂ and decreased the production of CH₄ (Fig. 8).
for deactivation (CO > CH4 > H2) and product distribution (Fig. 10) at different partial pressures of H2O was similar for the different partial pressures of CO2 experiments (Section 3.7).

The decrease in CH4 with increasing partial pressure of H2O could possibly be explained by an increase in competition for active sites, as explained in Section 3.7, between H2O and CO2 [12,29]. In addition, another explanation exists using the glyoxal mechanism, which is a speculative mechanism for CO2 photoreduction (Fig. 11)[7].

With the glyoxal mechanism in mind, the reactivity of the organic intermediate acetaldehyde (CH3CHO) (Fig. 11) can also be considered where the nucleophilic attack of H2O on the C = O group of CH3CHO towards acetic acid (CH3CO2H). The conversion of CH3CHO towards CH3CO2H has been shown to occur for the photocatalysis on TiO2 [50].

3.9. Optimising selectivity

Using the probability LH based kinetic models (Table 4) and coefficients estimated (5), the selectivity shown in Table 7 was optimised using an interior-point algorithm (MATLAB ‘fmincon’ function) and constraints using the minimum and maximum experimental range used for time, partial pressure of H2O and CO2.

The optimised values (Table 7) matched the observations made about the product distributions where H2 formation isfavoured initially, followed by CH4 and finally CO formation. To maximise CH4 selectivity (Table 7), the reaction would need to be stopped at 2.69 h with maximum partial pressure of CO2 (98.38 kPa) and at first glance a surprisingly a high partial pressure of H2O (5.44 kPa) as it would be expected more H2 would be produced. Increasing the partial pressure of H2O increased the production of H2 (Fig. 8c) with a decrease observed for CO (Fig. 8b). However, the production of H2 is made less significant by the more steady state production of CO over time. CO selectivity was maximised (Table 7), depending on the lower constraints used (Table 8), at a extremely short reaction time (7.31 × 10^-17 h) or at the maximum time (5 h). CO production is likely slowed down by the
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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.cej.2019.123356.

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Table 7

Optimised time, partial pressures of H2O and CO2 for the desired selectivity using the probability LH based kinetic models (Table 5). «Lower time bound 0.5 h used (Table 8).

| Selectivity to optimise | Time (h) | P_H2O (kPa) | P_CO2 (kPa) | Optimum selectivity |
|------------------------|---------|-------------|-------------|---------------------|
| CH4                    | 2.69    | 5.44        | 98.38       | 2.32                |
| CO2+H2O               | 7.31 × 10−17(S) | 2.66 | 98.38 | 0.70                |
| CH4+H2O               | 1.57    | 6.64        | 25.72       | 0.34                |

Table 8

Upper and lower constraints for interior-point algorithm for optimising the selectivity.

| Time (h) | P_H2O (kPa) | P_CO2 (kPa) |
|----------|-------------|-------------|
| Lower constraint 0 | 2.66     | 25.72       |
| Upper constraint 5 | 6.64    | 98.38       |

occupation of active sites towards H2 and the reaction intermediates towards CH4. Selectivity of H2 was optimised after a reaction time of 1.57 h, maximum partial pressure of H2O and minimum partial pressure setting of CO2 (Table 8). The reaction towards H2 is initially fast but does not last long.

4. Conclusion

Developing CO2 photoreduction kinetic models is a challenge due to addressing the challenges of limiting the impact of adventitious carbon, tracking the extremely low production of products and developing kinetic models with uncertainty about the mechanism that include the formation of several products and deactivation of the photocatalyst. This is the first example that addresses these challenges for developing CO2 photoreduction kinetic models.

A simply slurry deposition coating method, high purity setup with an inline humidity sensor to measure humidity, a photodifferential photoreactor with high reagent gas volume to photocatalyst area illuminated, a calibrated GC method for the quantification of O2, N2, CH4, CO and H2, a MATLAB programme for data collection and kinetic modelling was used to develop CO2 photoreduction kinetic models.

To account for deactivation, a flexible Weibull PDF was combined with a LH based kinetic model to describe CO2 photoreduction towards CH4, CO and H2 for different partial pressures of CO2 and H2O. Increasing the partial pressure of CO2 decreased the production of CO and CH4 and is most likely due to the competition between CO2 and H2O for adsorption to active sites. Increasing the partial pressure of H2O increased H2 production with a decrease in CH4 production. Using the glyoxal mechanism, one plausible explanation is the formation of CH3CO2H from CH3CHO and H2O preventing the formation of CH4.

The probability LH based kinetic model generalised well for describing the kinetics of CO2 photoreduction towards CH4, CO and H2 with low standard errors of 3.44 × 10−4, 1.54 × 10−4 and 1.36 × 10−4, respectively. The estimated deactivation term (τ_a) described the deactivation behaviour where in terms of stability, CO > CH4 > H2. Adsorption equilibrium constants of 85.51 and 12.80 bar−1 are tentatively assigned to H2O and CO2, respectively.

Product distribution profiles of CH4, CO and H2 showed that the CO2 photoreduction reaction was dynamic with an initial increase in H2 product distribution, followed by an increase in CH4 and finally CO product distribution. These changes are likely the result of different processes being favoured on the photocatalyst surface over time where initially H2O oxidation and the formation of intermediates leading to CH4 are favoured. Finally, CO formation is favoured due to the possible
