Photocatalytic conversion of CO$_2$ and CH$_4$ over immobilized titania nanoparticles coated on mesh: Optimization and kinetic study

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**Highlights**
- Optimization of photoreduction of CO$_2$ and CH$_4$ using RSM in conjunction with CCRD.
- Empirical model equations had satisfactory coefficients of $R^2$ and adjusted-$R^2$.
- Immobilized titania nanoparticles coated on mesh markedly increased CO$_2$ conversion.
- L–H model revealed high CO$_2$ and CH$_4$ adsorption on immobilized titania nanoparticles.

**Abstract**

The study on immobilized titania (TiO$_2$) nanoparticles semiconductor on stainless steel mesh for photocatalytic conversion of CO$_2$ and CH$_4$ has been investigated. Properties of commercial and calcinated photocatalysts on mesh surface were characterized using UV–vis spectra, BET, FESEM and XRD. The photoreduction products were identified with FTIR and GC. The process conditions was optimized using experimental design and process optimization tools to determine the maximum desired response via Response Surface Methodology (RSM) in conjunction with central composite rotatable design (CCRD). The experimental parameters were stainless steel mesh size, amount of titania nanoparticles, calcination temperature, UV light power and initial ratios of CO$_2$:CH$_4$:N$_2$ in feed. Calcination of coated titania nanoparticles increased the absorption of UV–vis light while uniform photocatalyst structure commensurate with decreasing agglomeration. The optimal conditions for maximum CO$_2$ conversion of 37.9% were determined as stainless steel mesh size of 140, coated titania nanoparticles on mesh of 4 g, calcination temperature of 600 °C, UV light power of 250 W and 10% of CO$_2$ in feed. Correspondingly, the selectivity of products were 4.7%, 4.3%, 3.9%, 41.4% and 45.7% for ethane, acetic acid, formic acid, methyl acetate and methyl formate, respectively. The kinetic model, based on Langmuir–Hinshelwood, incorporated photocatalytic adsorptive reduction and oxidation reactions over the catalyst surface, and fitted-well with the experimental data.

1. Introduction

The major causes of global warming are mainly attributed to greenhouse gases such as carbon dioxide, methane and chlorofluorocarbons. According to the literatures, CO$_2$ exceeds the natural carbon cycle by about 3.9% [1,2]. The carbon-flow between the oceans and atmosphere is considered natural and a yearly excess of CO$_2$ is added to the cycle by human activities [3,4]. There is an excess of 115 ppm of CO$_2$ in the atmosphere with respect to the pre-industrial value of 270 ppm that amounts to approximately 900 Gt CO$_2$ [2]. In order to bring the CO$_2$ level back to where it was, we need to develop techniques, processes and applications capable of handling CO$_2$ at high scale. Handling CO$_2$ at high scale implies significant challenges. C$_1$ chemistry addresses important subjects including utilization and conversion of CH$_4$ and CO$_2$, but it offers no practical conversion technique [5–9]. Usually, the direct CH$_4$ and CO$_2$ conversion to oxygenated mixtures is not promising from the thermodynamical aspect and there is no catalyst available for selective and efficient conversion [10]. CH$_4$ conversion is an
oxygenation reaction, while that of CO₂ is a reduction process. The simultaneous process of CO₂ and CH₄ conversion is considered as a perfect redox reaction.

Photocatalytic conversion represents one of the main studied areas of research related to energy with integrated applications stretching from energy production and storage to sustainability and medical uses. Furthermore, recent theoretical and experimental findings related to specific applications in the energy and environmental fields such as photo/electro-catalysts, organic photovoltaics and batteries are reported for various energy engineering applications.

All types of catalytic reductive conversion of CO₂, including photocatalysts, electrocatalysts, homogeneous, heterogeneous and biocatalysts are generally perceived to play a major role in such reduction reactions. The greatest challenge common to all the different types of catalytic systems is to develop highly efficient and selective catalysts. Limited number of compounds that have been synthesized from CO₂ through homogeneous and heterogeneous catalytic pathways as well as low selectivity of reactions in electrochemical CO₂ reduction provide the needs for other favorable reduction methods. Besides, there is yet an economically viable industrial process involving biocatalytic conversion of CO₂. Significant improvement of the efficiency of photocatalytic systems can be achieved by developing appropriate reductants, selecting semiconductors with suitable band gap energy and optimizing reaction conditions. Therefore, the most favorable CO₂ reduction method is by applying photocatalysts since visible light irradiation or UV can reduce it to useful compounds at certain conditions [11–14].

Semiconductor catalysts such as TiO₂, CdS, CeO₂, ZrO₂, NbO₅, ZnO are the excitation source for irradiation with distinct energy. The photo-excited electrons reduced CO₂ with another reductant compound such as CH₄, H₂ and H₂O on the catalyst surface and generate energy-bearing products such as methanol, carbon monoxide, formaldehyde and acetic acid [15–18].

Using catalysts for the direct conversion of CH₄ and CO₂ mixtures to valuable products is quite common. A two-step reaction sequence on catalysts of the Cu–Co base have been used by Huang et al. [10] to investigate the viability of the direct conversion of CH₄ and CO₂ to oxygenated mixtures at low temperature. They performed direct acetic acid synthesis using heterogeneous [19] and homogeneous [20] catalysts without irradiation. Kim et al. [21] used catalysts with different Ni amounts supported on γ-Al₂O₃ through the electron beam radiation to convert the mixture of CO₂:CH₄:He = 1:1:1 into synthetic gas under temperature of 500 °C. Dielectric barrier discharge plasma was used by Zhang et al. [22] to transform methane while carbon dioxide was present, and the final product comprised of syngas, oxygenated compounds and gaseous hydrocarbons. Guo et al. [23] prepared a series of catalysts Ni/SiO₂ holding different Gd₂O₃ amounts. It was used in fluidized bed reactor for CO₂ reforming of methane. Fidalgo et al. [24] studied the microwave-assisted carbon dioxide reforming of CH₄ assessed over mixtures of Ni/Al₂O₃ and carbonaceous materials (metallurgical coke and activated carbon). Yet, these reactions frequently necessitate high pressure and/or high temperature.

In contrast, photocatalytic reduction of photo-irradiation assisted CO₂ is possible even in mild conditions without pollution and the processing involves the use of low purity reactants and is very tolerant to many impurities that are toxic to chemical catalysts. The mild conditions used for these reactions make the partial hydrogenation of CO₂ to formic acid and derivatives highly feasible. Few researchers have applied photocatalysts to convert CH₄ and CO₂ mixtures into usable products. Zirconium oxide or ZrO₂ was used by Tanaka et al. [25] to photoreduce CO₂ to CO by methane and hydrogen. Increased irradiation time improved the amount of carbon monoxide formation, even though the CO formation rate was somewhat slowed. Teramura et al. [26] studied the photocatalytic reduction mechanism of the CO₂ to CO with CH₄ or H₂ over MgO. Yuliati et al. [27] reported the photocatalytic conversion of CH₄ and CO₂ over ZnO was studied by Mahmodi et al. [2], who reported a CO₂ conversion of 11.9%. Highly scalable and novel reactors designs are critical for converting CO₂ and CH₄ to viable hydrocarbon fuels efficiently and economically.

Titania (TiO₂) is the most commonly used and one of the most favored photocatalysts among several semiconductor metal oxides for the photocatalytic degradation of chemicals and organic dyes. It has multipurpose properties such as a wide band gap (3.2 eV) and large binding energy of excitation. Using TiO₂ photocatalysts in the reduction process is advantageous since the catalysts are nontoxic, highly stable toward photo-corrosion and can operate at low temperature. Moreover, TiO₂ is not costly and consume significantly low energy [29–32]. Merajin et al. [33] reported formation of acetic acid and formic acid as the main product in the photocatalytic reaction between methane and CO₂ over TiO₂, in which the CO₂ conversion was 27.9%.

A large number of experiments are required to find improved conditions covering all the actual factors with all the possible combinations of parameters, which is not practical. One approach is the design experiments that consider several variables to reduce the number of experiments. In order to optimize all of the parameters, statistical experimental design was applied by Response Surface Methodology (RSM). This methodology can effectively optimize complicated systems such as industrial processes and/ or chemical reactions, which allows the assessment of multiple parameter effects, alone or in combination with response variables [34]. This technique (RSM) quantifies the relationship between the manageable input parameters and the obtained response surfaces. RSM enables faster process optimization in comparison to the conventional, time consuming one-factor-at-a-time approach [35].

In this study, firstly, calcinated titania nanoparticles semiconductor was coated on stainless steel mesh, and used for photocatalytic conversion of CO₂ in the presence of CH₄ as the reductant. The large surface area was provided for TiO₂ film by the mesh structure, as well as for proper gas ventilation. The tests were conducted under UV irradiation in a gas phase reactor. Optimization of photocatalytic conversion of CO₂ and CH₄ over titania nanoparticles coated on stainless steel mesh by using RSM was performed with five important variables. The effects of these variables on the desired responses (i.e. conversion of CO₂ and CH₄) were studied concurrently in a central composite rotatable design (CCRD, a classical experimental design method) and empirical mathematical models correlating the response to the variables were developed and presented as well. Kinetic model based on Langmuir–Hinshelwood model was developed to determine the kinetic parameters and to provide fundamental insights on possible reactions.

2. Experimental

2.1. Preparation of photocatalysts

An efficient and simple method was used to immobilize titania nanoparticles on stainless steel meshes. This perfect method for industrial applications experts at the Energy Research Centre of the Netherlands (ECN) first introduced this technique for titania deposition on quartz slides for solar cell preparation [36].
Stainless steel was formerly used to support nanoparticles of TiO₂ [37,38]. In this study, we selected stainless steel due to its large surface area, good ventilation for gases passing and resistance to corrosions. TiO₂ powder in different amounts (2, 3 and 4 g) was added to ethanol (15 mL) for coating support with titanium dioxide and then the mixture was stirred for one hour. It can be seen that the powder disperses easily through the ethanol in a cloud-shape manner producing slurry. Afterwards, drops of dilute nitric acid (5 mL, pH of 3.5) were added to slurry with the purpose of providing an acidity media to make the slurry uniform and stable. The meshes were cleaned with acetone and distilled water to remove any organic and inorganic attached materials on surface and dried under atmospheric conditions. In order to coat meshes with titania nanoparticles, the meshes (mesh size set of experiments) were immersed in well dispersed slurry for one minute. Next, the stainless steel mesh was dried for 8 h at 120 °C. As a final point, titania nanoparticles coated meshes were calcined at 200 °C, 400 °C and 600 °C for 30 min.

2.2. Characterization of photocatalysts

In order to determine the absorbance spectra of titania nanoparticles, the compact UV-3101PC spectrophotometer was used. The recombination rate was measured by photoluminescence (PL) spectra employing PerkinElmer LS 55. The N₂ adsorption and desorption isotherms of the catalysts were carried out at 77.33 K using a Micromeritics ASAP 2020 Analyzer for the determination of Brunauer–Emmett–Teller (BET) surface area and pore size distribution. The Barrett–Joyner–Halenda (BJH) pore size distribution was obtained according to the desorption isotherm. The surface morphology of the photocatalyst samples was observed by using a field-emission scanning electron microscopy (FESEM). X-ray diffraction (XRD) was used to identify the structure of the photocatalysts. A Bruker D8 diffractometer, equipped with a Cu kα radiation source (λ = 1.542 Å) in continuous scanning mode at the rate of 5° min⁻¹ from 10° to 80°, was used to obtain the XRD patterns. Fourier-transform infrared spectroscopy (FTIR) was recorded using MB160 FTIR to characterize products.

2.3. Photocatalytic reaction experiment

The general view of the gas phase reactor is illustrated in Fig. 1. The gas phase stainless steel cubic reactor, which has a dimension of 20 cm x 20 cm x 10 cm was equipped with a quartz window.

![Fig. 1. General view of the gas phase reactor. (1) Gas mixer, (2) feed gas inlets, (3) covering cap, (4) plastic gasket, (5) quartz window, (6) stainless steel platform, (7) lab jack, (8) purge valve, (9) product gas outlets.](image)

The stainless steel mesh coated with titania was located in the center of the reactor, under direct irradiation by the UV lamp. The reaction using gaseous feed (CO₂, CH₄ and N₂) occurred in the photoreactor, continuously illuminated by UV lamp, for maximum of 6 h. An optical process monitor (ILT OPM-1D) was used to measure the light intensity. The conversion products were characterized using FTIR and GC. The photocatalytic efficiency was calculated based on CO₂ and CH₄ conversions, formulated in Eqs. (1) and (2):

\[
\text{CO}_2 \text{ Conversion (\%) } = \frac{\text{Moles of CO}_2^i - \text{Moles of CO}_2^f}{\text{Moles of CO}_2^i} \times 100 \tag{1}
\]

\[
\text{CH}_4 \text{ Conversion (\%) } = \frac{\text{Moles of CH}_4^i - \text{Moles of CH}_4^f}{\text{Moles of CH}_4^i} \times 100 \tag{2}
\]

where (CO₂ and CH₄) and (CO₂ and CH₄) are the initial and final concentrations of CO₂ and CH₄, respectively.

2.4. Design of experiments, analysis and model fitting

The purpose of this study was to determine the functional relationship between four numerical factors including stainless steel mesh size (X₁), amount of titania nanoparticles (X₂), calcination temperature (X₃), UV light power (X₄) and one categorical factor, CO₂:CH₄:N₂ ratios in feed (X₅) based on Response Surface Methodology (RSM) in conjunction with central composite rotatable design (CCRD). In order to generate design of experiments (DOE), perform statistical analysis, and create regression model, design expert software (Stat-Ease, Inc. Silicon Valley, CA, USA) was used. Table 1 exhibits the ranges of the independent variables and levels of experimental design that were used in this study.

DOE is the first requirement for RSM to determine the number of runs that are required to give a reliable measurement of the desired response [39]. The optimization was performed for methane and carbon dioxide conversion responses. Therefore, in this study, the number of experimental runs, determined from CCRD, was 44, corresponding to 12 center points, 16 axial points and 16 factor points replications. The 2 axial points on the axis of each design variable were located at a distance, α, of 1.25. Table 2 shows the complete design matrix, carbon dioxide and methane conversion responses of the experiments employed in this study. The data were then fit to the following second order polynomial equation.

\[
Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j + \epsilon_0
\]

where the response variable of conversion is shown by Y, Xᵢ and Xⱼ are decoded independent process variables, β₀ is the interception coefficient; βᵢ, βⱼ and βᵢⱼ the interaction coefficients of linear, quadratic and the second-order terms, respectively, and \(\epsilon_0\) is the standard error. The quality of the fit of polynomial model was expressed by the coefficient of determination \(R^2\) and \(R^2_{adj}\) in following equations.

\[
R^2 = 1 - \frac{SS_{residual}}{SS_{residual} + SS_{model}}
\]

\[
R^2_{adj} = 1 - \frac{SS_{residual}/DF_{residual}}{(SS_{residual} + SS_{model})/(DF_{residual} + DF_{model})}
\]

The terms SS and DF corresponds to sum of squares and degrees of freedom, respectively. After ensuring the model validity, the equation was used to plot the two dimensional interaction plot, contour and three dimensional response surface plots. These plots are useful to examine the influence of each variable on the desired responses.
3. Results and discussion

3.1. Characterization of calcinated titania nanoparticles catalyst

A low-cost method was used to coat the titania nanoparticles on mesh. After coating, particles were calcinated for proper immobilization and improving titania durability on the support. The calcination temperatures were 200 °C, 400 °C and 600 °C based on the references from the literatures. Calcination method was reported to reduce particles size and thus surface area of catalyst was increased [40–42]. Agglomeration is reduced and particles are distributed uniformly through calcination, and consequently the active surface is increased [43]. Mechanical stability of mesh coated with catalyst was very good. The ranges of UV–vis absorption of the commercial and calcinated titania at room temperature is shown in Fig. 2. The evolution of photocatalyst properties is very much dependent on the absorption of UV–vis light [33]. The findings show that UV–vis absorption concentration was improved by calcination. Moreover, minor shift is seen to visible area in absorption peak due to calcinations, which, the shift of the onset
absorption edges toward longer wavelength with the increase in calcination temperature to 600 °C can be observed. This shift toward longer wavelength normally originates from narrowing of the band gap energy, which result in lower energy required for the excitation of electrons from the valence band to the conduction band. Meanwhile, the commercial titania exhibited weaker absorption in the whole wavelength before calcinations. As the catalyst is irradiated by UV-light of suitable wavelength and sufficient light intensity photo-excited electron–hole pairs and the charge transfer excited state species are produced. Higher desired product yield rates were observed due to efficient production and separation of photogenerated electron–hole pairs (e⁻/h⁺), resulting in higher reduction efficiency.

Fig. 3(a) exhibits the N₂ adsorption and desorption isotherms of titania nanoparticles at 77.33 K. The sample (calcinated titania nanoparticles at 600 °C) shows the type IV isotherms with H₃ hysteresis loops according to Brunauer–Deming–Deming–Teller (BDDT) classification which can be attributed to the mesoporous structures of the material [44]. The BET surface area of titania nanoparticles was 251.3957 m²/g. At higher relative pressure (P/P₀ between 0.8 and 1.0), a notable increase of adsorbed nitrogen was observed, suggesting an important external surface area contribution. At lower relative pressure (P/P₀ < 0.2), gradual and rounded transitions indicated the presence of a small number of non-slit-like micropores [45]. Fig. 3(b) shows the BJH pore size distribution of titania nanoparticles, which displays the narrow pore distribution in the catalyst structure. The broad peak with the pore width ranged from 2 to 50 nm was derived from the hysteresis loop ascribed to the aggregation of titania nanoparticles [46].

Field-emission scanning electron microscopy (FESEM) was used to determine morphology of the catalyst. Fig. 4 represents the FESEM images of commercial and calcinated titania surface structure. Particle size and agglomeration by calcination technique did not show any significant difference when comparing structure of commercial titania (Fig. 4(a)) with calcinated titania (Fig. 4(b)). Based on the shift toward longer wavelength (390 nm) normally originates from narrowing of the band gap energy, 3.18 eV band gap was found for the prepared calcinated titania photocatalyst (Eq. (6)), where E₉₈ is the photocatalyst band-gap energy and λ is the peak wavelength (nm) [30].

\[
E_{bg} (\text{eV}) = \frac{1240}{\lambda}
\]

X-ray diffraction (XRD) configurations of the coated samples were used to evaluate the coating quality from the structural aspect to know if noticeable changes were resulted in crystallite size and structural properties of titania nanoparticles crystals during the calcination process. Before the analysis with X-ray diffraction analyzer, the coated samples were detached from mesh surface and converted to fine powder through grinding. Patterns of X-ray diffraction of titania nanoparticles photocatalysts pre and post calcination are shown in Fig. 5. No significant changes in the titania structure was seen due to the coating and calcination processes. Thus, probably calcination process had no significant
effect on crystalline morphology of particles. The graphs demonstrate no noticeable impurity, which is important for the mesh coating using stainless steel as impurities of iron due to heating could affect the catalyst photocatalytic efficiency negatively. No new impurity peak was seen, demonstrating that 600 °C as calcination temperature had no effect on the crystal phase of titania nanoparticles.

3.2. Coded empirical model equations for CO₂ and CH₄ conversion

The results of the experimental runs are summarized in Table 2. The carbon dioxide and methane conversion ranged from 26.8% to 48.7%, respectively, depending on the conditions in the experiments. The adequacy of the models was further justified through analysis of variance (ANOVA) [47], and the ANOVA for the quadratic model of carbon dioxide and methane conversion are summarized in Tables 3a and 3b, respectively. As shown in Tables 3a and 3b, the predicted values matched the experimental values reasonably well with R-squared = 0.9603 and R-squared = 0.9716 for CO₂ and CH₄ conversion, respectively, meaning that 96.03% and 97.16% of the total variations for CO₂ and CH₄ in the results can be attributed to the independent variables that were investigated.

The p-value and F-value were used to determine the significance of each term at a specified level of confidence. The smallest level of significance that could be used to reject the null hypothesis, H₀, is called p-value. Therefore, the smaller the value is, the more significant its corresponding coefficient and the contribution toward the response variable [48].

From the ANOVA in Tables 3a and 3b, it was observed that some of the variables were highly significant to the regression model as indicated by the high F-value. As can be seen in Table 3a, based on the F-value, five linear factor terms (X₁, X₂, X₃, X₄, X₅), four quadratic terms (Xᵡ₁, Xᵡ₂, Xᵡ₃, Xᵡ₄) and ten interaction factors (X₁X₂, X₁X₃, X₁X₄, X₁X₅, X₂X₃, X₂X₄, X₂X₅, X₃X₄, X₃X₅, X₄X₅, X₅X₁) had the largest effect on CO₂ conversion at 95% confidence level, as indicated by the low p-value (<0.05) and high F-value. Moreover, according to Table 3b, the largest effect on CH₄ conversion at 95% level of confidence was related to five, four and ten terms of linear, quadratic and interaction factors, respectively.

The effect of terms on the response model was not statistically significant at the 95% confidence level as the p-value of each of these terms was more than 0.05. It means that only the model terms with p < 0.05 were determined to be significant to the model equation. In order to improve the model, the insignificant model terms were removed. Model reduction involves this type of backward elimination procedure of all those insignificant terms to ultimately produce a new and improved experimental model. The ANOVA analysis of the reduced model (new model) equation after removing the insignificant terms for CO₂ and CH₄ conversion are shown in Tables 4a and 4b, respectively. The R-squared values for CO₂ and CH₄ conversion were 0.9548 and 0.9643, respectively, indicating an excellent agreement between the experimental and predicted CO₂ and CH₄ conversion.

The R-squared value in the reduced model was less than that obtained in the unreduced model. Although the value of R-squared decreases when variables are eliminated from a regression model, the adjusted R-squared value considers the number of variables that was taken into account in this study. It means that the R-squared expressed the quality of the polynomial model, which

![Fig. 5. XRD patterns of commercial and calcinated titania nanoparticles (600 °C).](image-url)

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**Table 3a**

ANOVA for the CO₂ conversion as the desired response (unreduced models).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>DF</th>
<th>Mean square</th>
<th>F value</th>
<th>Prob &gt; F</th>
<th>Comments</th>
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<td>19</td>
<td>19.06</td>
<td>29.31</td>
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<td>Significant</td>
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<td>X₁</td>
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<td>1</td>
<td>85.58</td>
<td>131.65</td>
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</tr>
<tr>
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<td>1</td>
<td>59.06</td>
<td>90.85</td>
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</tr>
<tr>
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<td>13.02</td>
<td>20.04</td>
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</tr>
<tr>
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<td>70.24</td>
<td>108.06</td>
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</tr>
<tr>
<td>X₅</td>
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<td>8.89</td>
<td>13.68</td>
<td>0.0012</td>
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</tr>
<tr>
<td>Xᵡ₁</td>
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<td>46.66</td>
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<tr>
<td>Xᵡ₄</td>
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<td>0.64</td>
<td>0.94</td>
<td>0.5660</td>
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</tr>
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<td>5.42</td>
<td>8</td>
<td>0.68</td>
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</table>

| R-squared   | 0.9603         | Adj R-Squared | 0.9276   |
signifies the proportion of variability in the experimental results that is considered by the statistical model. Certainly, R-squared increases as the number of variables in the model increases. For that reason, it is more suitable to use the adjusted R-squared value, which modifies the R-squared value as extra variables are included in the model. In fact, the adjusted R-squared value increases if unnecessary terms are deleted [49]. The adjusted R-squared values of the unreduced model equations for CO₂ and CH₄ conversion were 0.9276 and 0.9481, respectively (Tables 3a and 3b), while, the adjusted R-squared values of the reduced model equations for CO₂ and CH₄ conversion were 0.9323 and 0.9501, respectively (Tables 4a and 4b), representing an improvement in the models after elimination of the non-significant model terms. Moreover, as shown in Tables 4a and 4b, the models resulted in an F-value of 42.30 and 67.62 with an extremely low p-value (<0.0001) for CO₂ and CH₄ conversion, respectively, implying that the models are highly significant and are acceptable for the response variables that were tested.

Comparison between the actual response values obtained from experimental work and the predicted response values based on the quadratic model, demonstrates that the experimental range of studies is adequately covered by the model (see Supplementary Fig. S1 and Fig. S2). There are adequate correlation to the linear regression fit, with R-squared values of 0.9548 and 0.9643 for CO₂ and CH₄ conversion, respectively. Additionally, the central composite design provides relatively precise predictions over a broad area around the center point. In fact, the standard error plot shows how the variance associated with prediction changes over the design space (see Supplementary Fig. S3 and Fig. S4) [50]. From analysis of the ANOVA data and the statistical parameters, the final empirical models in terms of coded factors (parameters), after exclusion of the insignificant terms are given in Eqs. (7) and (8).

$$Y_{CO_2} = 34.98 + 3.70X_1 + 3.07X_2 + 0.77X_3 + 3.35X_4 - 0.45X_5$$

$$- 1.61X_1^2 - 1.52X_2^2 - 0.68X_3^2 + 3.20X_1X_2 - 0.48X_1X_3$$

$$+ 2.69X_1X_4 + 3.78X_2X_4 + 0.37X_2X_5 - 0.87X_3X_4$$

(7)
Table 4b
ANOVA for the CH\textsubscript{4} conversion as the desired response (reduced models).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>DF</th>
<th>Mean square</th>
<th>F value</th>
<th>Prob &gt; F</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadratic</td>
<td>760.96</td>
<td>12</td>
<td>63.41</td>
<td>67.62</td>
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</tr>
<tr>
<td>X\textsubscript{1}</td>
<td>262.74</td>
<td>1</td>
<td>262.74</td>
<td>280.19</td>
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<tr>
<td>X\textsubscript{2}</td>
<td>79.43</td>
<td>1</td>
<td>79.43</td>
<td>84.71</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>X\textsubscript{3}</td>
<td>43.25</td>
<td>1</td>
<td>43.25</td>
<td>46.13</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>X\textsubscript{4}</td>
<td>114.79</td>
<td>1</td>
<td>114.79</td>
<td>122.41</td>
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<td>Significant</td>
</tr>
<tr>
<td>X\textsubscript{5}</td>
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<td>1</td>
<td>24.84</td>
<td>26.49</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>X\textsubscript{2}\textsuperscript{2}</td>
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<td>1</td>
<td>82.53</td>
<td>88.01</td>
<td>&lt;0.0001</td>
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<tr>
<td>X\textsubscript{3}\textsuperscript{2}</td>
<td>9.92</td>
<td>1</td>
<td>9.92</td>
<td>10.58</td>
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</tr>
<tr>
<td>X\textsubscript{3}\textsuperscript{2}</td>
<td>25.43</td>
<td>1</td>
<td>25.43</td>
<td>27.12</td>
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<td>Significant</td>
</tr>
<tr>
<td>X\textsubscript{4}\textsuperscript{2}</td>
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<td>39.08</td>
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<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>X\textsubscript{1}\textsuperscript{2}</td>
<td>77.51</td>
<td>1</td>
<td>77.51</td>
<td>82.66</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>X\textsubscript{1}\textsuperscript{2}</td>
<td>141.04</td>
<td>1</td>
<td>141.04</td>
<td>150.41</td>
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</tr>
<tr>
<td>X\textsubscript{1}\textsuperscript{2}</td>
<td>5.71</td>
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<td>5.71</td>
<td>6.09</td>
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</tr>
<tr>
<td>Residual</td>
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<td>30</td>
<td>0.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>24.80</td>
<td>22</td>
<td>1.13</td>
<td>2.70</td>
<td>0.0746</td>
<td>Not significant</td>
</tr>
<tr>
<td>Pure error</td>
<td>3.34</td>
<td>8</td>
<td>0.42</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-squared 0.9643  Adj R-Squared 0.9501

Fig. 6. Response surface plots representing the interaction effect of (a) UV light power and amount of titania nanoparticles; (b) amount of titania nanoparticles and stainless steel meshsize; (c) UV light power and calcination temperature and (d) UV light power and stainless steel mesh size on CO\textsubscript{2} conversion.
\[ Y_{\text{CH}_4} = 44.89 + 6.48X_1 + 3.56X_2 + 1.39X_3 + 4.29X_4 + 0.75X_5 \\
- 2.65X_1^2 - 0.92X_2^2 - 1.47X_3^2 + 2.95X_1X_2 + 4.15X_1X_4 \\
+ 5.60X_2X_4 - 0.60X_1X_4 \]

where \( Y_{\text{CO}_2} = \text{CO}_2 \) conversion (%); \( Y_{\text{CH}_4} = \text{CH}_4 \) conversion (%); \( X_1 = \text{Stainless steel mesh size} \); \( X_2 = \text{Amount of titania nanoparticles (g)} \); \( X_3 = \text{Calcination temperature (°C)} \); \( X_4 = \text{UV light power (W)} \); \( X_5 = \text{CO}_2:\text{CH}_4:N_2 \) ratios in feed (%).

3.3. Interactions between process variables

It is important to check the interactions between the model terms because of their significance to the model equation. Stainless steel mesh size \( (X_1) \) is the most significant parameter of \( \text{CO}_2 \) and \( \text{CH}_4 \) conversions, followed by UV light power \( (X_4) \). The amount of titania nanoparticles \( (X_2) \), calcination temperature \( (X_3) \) and \( \text{CO}_2:\text{CH}_4:N_2 \) ratios in feed \( (X_5) \) are less important among the five parameters.

Alternatively, the efficiency of \( \text{CO}_2 \) conversion is affected by quadratic of \( X_1^2 \), \( X_2^2 \) and \( X_3^2 \), and two way interactions of \( X_1X_2 \), \( X_1X_3 \), \( X_1X_4 \), \( X_2X_4 \), \( X_3X_4 \) and \( X_1X_4 \). Meanwhile, \( \text{CH}_4 \) conversion is affected by quadratic of \( X_1^2 \), \( X_2^2 \) and \( X_3^2 \), and two way interactions of \( X_1X_2 \), \( X_1X_3 \), \( X_2X_4 \) and \( X_3X_4 \). These interactions are depicted clearly by plotting two variables at a time on a contour and three-dimensional surface plots. Since the model has more than two variables, several of these plots were created, each with two targeted variables and the remainder of the variables held constant.

In Fig. 6, the effects of the manipulated variables on maximum \( \text{CO}_2 \) conversion are described. Fig. 6(a) shows the effects of different UV light power and amount of titania nanoparticles coated mesh on the \( \text{CO}_2 \) conversion in three dimensional surface response. From the figure, it is obvious that at any designated quantity of titania nanoparticles from 2 to 4 g, the photocatalytic conversion of \( \text{CO}_2 \) increases proportionally with UV light power. Also, the photocatalytic conversion of \( \text{CO}_2 \) augmented when the amount of titania nanoparticles was increased from 2 to 4 g at any constant UV light power within the range of 50–250 W. The observed phenomenon occurred as increasing the UV light power enhanced the reaction rate and eventually the photocatalytic conversion of \( \text{CO}_2 \) [33]. As shown in Fig. 6(b), the photocatalytic \( \text{CO}_2 \) conversion increases significantly with larger stainless steel mesh size and increasing amount of titania nanoparticles coated mesh, due to increase in active surface of photocatalyst. However, the \( \text{CO}_2 \) conversion is not affected by increasing titania nanoparticles coating above 4 g as a result of constant photocatalyst surface and overlapping of catalyst layer formed. The photocatalytic \( \text{CO}_2 \) conversion increases with increasing UV light power and calcination temperature of commercial titania nanoparticles (Fig. 6(c)). The higher light power provides higher energy for more titania particles to generate electron hole pairs [51]. As shown in Fig. 2, related to UV–visible spectra of calcinated titania, band gap of TiO\(_2\) is large and required high light power for excitation of electrons. As illustrated in Fig. 6(d), the photocatalytic \( \text{CO}_2 \) conversion increased significantly with increasing the UV light power and stainless steel mesh size. The photogenerated radicals were not able to convert all gasses to new products, due to reduction of effective strike and interaction among photogenerated radicals and components. Increasing the UV light power and stainless steel mesh size improved \( \text{CO}_2 \) conversion due to increasing photogenerated radicals and active surfaces. According to the final empirical model, the \( \text{CO}_2 \) conversion was inversely affected by the \( \text{CO}_2 \) ratio in feed. The photocatalytic \( \text{CO}_2 \) conversion decreased slightly with increasing \( \text{CO}_2/\text{CH}_4 \) ratio. Higher \( \text{CO}_2 \) stability relative to \( \text{CH}_4 \) can be considered as the reason for the decline in \( \text{CO}_2 \) active radicals [33].

Fig. 7 illustrates the response surface plot of photocatalytic conversion of \( \text{CH}_4 \). The maximum conversion of methane was achieved in stainless steel mesh size of 140, UV light power of 250 W, calcination temperature of 600 °C, 80% of \( \text{CO}_2 \) in feed and 4 g titania coated on mesh. As shown in Fig. 7(a), the photocatalytic methane conversion increased significantly with increasing stainless steel mesh size and amount of titania nanoparticles coated mesh, due larger active surface of photocatalyst. However, the methane conversion is not affected by increasing titania nanoparticles coating above 4 g as a result of constant photocatalyst surface and overlapping of catalyst layer formed. Fig. 7(b) shows the photocatalytic methane conversion increases dramatically with increasing UV light power and amount of titania nanoparticles. The higher light power provides higher energy for more titania particles to generate electron hole pairs [51].

3.4. Process optimization

Design expert software program provides numerical optimization function to search for the combinations of all variables that
simultaneously satisfy the desired requirements. In this process, the lower and upper limit of each variable (stainless steel mesh size, amount of titania nanoparticles, calcination temperature, UV light power and CO₂:CH₄:N₂ ratios in feed) and desired responses (i.e. CO₂ and CH₄ conversion), as predicted by the models, were provided based on the contour and surface plots. The ultimate goal of the optimization process was to obtain the maximal responses that simultaneously satisfied all of the variable properties. Table 5a lists the constraints of each variable. As presented in Table 5b, the model predicted the optimum conditions as 4 g TiO₂, 10% CO₂ in feed, 140 mesh, calcination temperature of 600 °C and UV light power of 250 W for maximum CO₂ conversion. In addition, the optimum values of the process variables for the maximum CH₄ conversion were the same except for 80% of CO₂ in feed. The observed and predicted maximum conversions were 37.9% and 38.1%, for CO₂, and 48.7% and 49.4% for CH₄, respectively. It is apparent that the optimization exercise is more efficient with response surface methodology method.

3.5. Characterization of conversion products and photoreaction mechanism

3.5.1. FTIR spectra of titania catalyst products

Direct conversion of CH₄ and CO₂ to oxygenated compounds was conducted over immobilized titania nanoparticles coated on stainless steel meshes. The conversion products were characterized using FTIR to identify photocatalysis products. These spectra were detected after photoirradiation of coated titania in the presence of CH₄ and CO₂ (see Supplementary Fig. S5). The peaks at 1303 and 3016 cm⁻¹ correspond to the C–H stretch in methane and the C=O stretch in CO₂ was observed at the regions of 2138 and 1667 cm⁻¹ [10]. The bands were observed in the regions of 3550–2500 cm⁻¹ and 2000–1200 cm⁻¹ indicating the presence of strong hydrogen bonding due to the existence of carboxylic groups in the catalyst structure. The strong hydrogen bonding resulted in the interaction between acidic hydrogen of hydroxyl groups of an acid molecule with oxygen atom of carbonyl group of another molecule generated a wide peak in the 3550–2500 cm⁻¹. In addition, a very strong peak at 1667 cm⁻¹ is enough evidence for the presence of acidic/esteric group in the structure of the product [26].

These vibrational bands can be attributed to characteristic absorption band of methyl asymmetric C–H stretching (2853 cm⁻¹), methyl symmetric C–H stretching (2958 cm⁻¹). Moreover, the vibration bands between 1200 and 1500 cm⁻¹ showed several peaks at the region of 1297 and 1014 cm⁻¹. These peaks can be attributed to the C–O bands for the carboxylic and ester functional groups. These peaks assigned to the various functional groups such as ester and carboxylic acid. However, according to the mechanism of CH₄ and CO₂ conversion on the semiconductor photocatalysts presented in previous research [8,25–27] the peaks are attributed to produce of formic and acetic acid and also formate and acetate ester compounds. Teramura et al. [26] reported similar results in CO₂ photocatalytic reduction in the presence of CH₄ over MgO. The observed peaks at the areas of 1666 cm⁻¹ was assigned to a bidentate carbonate. In agreement with the obtained FTIR results, Huang et al. [10] reported the adsorption of CO₂ over the Cu/Co based catalyst. They observed the strong band of C–H stretching at 2853, 2922 cm⁻¹.

3.5.2. Mechanism of photocatalytic reduction over titania catalyst

Photocatalytic synthesis of formate and acetate derivatives over TiO₂ catalyst from CH₄ and CO₂ may take place with the reaction mechanism as given by the following reactions shown in Eqs. (9)–(18).

\[
\text{TiO}_2 \xrightarrow{hv} h^+ + e^- \quad (9)
\]

\[
\text{CH}_4 + h^+ \rightarrow \text{CH}_3 + \text{H}^+ \quad (10)
\]

\[
\text{CO}_2 + e^- \rightarrow \text{CO}^-_2 \quad (11)
\]

\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3 \quad (12)
\]

\[
\text{CH}_4 + \text{CO}_2^- \rightarrow \text{CH}_3\text{COO}^- + \cdot\text{H} \quad (13)
\]

\[
\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} \quad (14)
\]

\[
\text{CO}_2 + \cdot\text{H} \rightarrow \text{HCOO}^- \quad (15)
\]

\[
\text{HCOO}^- + \cdot\text{H} \rightarrow \text{HCOOH} \quad (16)
\]

\[
\text{CH}_3\text{COOH} + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{COOCH}_3 + \cdot\text{H} \quad (17)
\]

\[
\text{HCOOH} + \cdot\text{CH}_3 \rightarrow \text{HCOOCH}_3 + \cdot\text{H} \quad (18)
\]

The TiO₂ is excited by absorbing UV irradiation and generated valence band hole (h⁺) and conduction band electron (e⁻) (Eq. (9)). The holes and electrons play major role in the catalyzed oxidation and reduction reactions, respectively. Methyl radical (\(\cdot\text{CH}_3\)) is produced through oxidation of CH₄ by the valence band holes and H⁺ are simultaneously released (Eq. (10)). The conduction band electrons reduce CO₂ to the CO₂ radicals (Eq. (11)). Then, two \(\cdot\text{CH}_3\) coupled to produce ethane (Eq. (12)). If CO₂ are attacked by CH₄, acetate is formed (Eq. (13)) [8]. The acetate reacts with H⁺ to produce acetic acid (Eq. (14)). If the CO₂ are attacked by H⁺, formate is formed (Eq. (15)) and the formate product reacts with H⁺ to produce formic acid (Eq. (16)) [33]. CH₃ is attacked by acetic acid and formic acid to produce methyl acetate and methyl formate, respectively (Eqs. (17) and (18)). Consequently, at optimized conditions the selectivities of ethane, acetic acid, formic acid, methyl acetate and methyl formate could reach up to 4.7%, 4.3%, 3.9%, 41.4% and 45.7%, respectively.
3.6. Effect of individual parameters on CO₂ and CH₄ conversion with time

3.6.1. Effect of stainless steel mesh size applied as a support

In this study, stainless steel mesh was selected as a base for titania nanoparticles because of its advantages, including the possibility to obtain a large surface area for titania films, as well as better absorption of UV light, and the absence of toxicity. Furthermore, catalyst coating on mesh has very good mechanical stability. In mesh size set of experiments, the influence of stainless steel mesh size, based on main levels of RSM (i.e. -1.25, 0, +1.25) varying from 60 to 140, on the degradation rate of CO₂ and CH₄ was investigated. The obtained results are given in Fig. 8 (a) and (b). The increases in mesh size lead to significant effects. The surface area of TiO₂ and total active sites increased with increasing mesh size. Therefore, according to empirical results and mentioned reasons, mesh by size 140 produced the highest efficiency under our experimental conditions.

3.6.2. Effect of UV light power

Polychromic light sources, such as Hg lamps, high pressure mercury lamps have been used in most of the photolysis experiments in the presence of a semiconductor photocatalyst. In this study, The UV illumination sources used for these experiments were three mercury lamps (50 W, 150 W and 250 W). In set of UV light power experiments, the influence of UV light power varying from 50 to 250 W, on the degradation rate of CO₂ and CH₄ was investigated. The conversions of CO₂ and CH₄ increased dramatically with increasing reaction time in the presence of 250 W light power because of desorption of CO₂ and CH₄. UV light power of 250 W was found be the highest efficiency under our experimental conditions. Similar observations are reported in literature during photocatalytic CO₂ reduction over ZnO [2]. Tahir et al. [29] reported that the rate of the photon of energy increased linearly as the UV intensity increased. It means that electron–hole generation process was positively affected by rate of photon irradiation. Consequently, the rate of reaction closer to the semiconductor surface improves; thus with increasing of light power from 50 W to 250 W, CO₂ and CH₄ conversion were increased.

3.6.3. Effect of amount of titania nanoparticles

The amount of titania nanoparticles used in photocatalytic studies play a crucial role in increasing product yield. Higher amount of catalyst may be useful due to possible aggregation resulting in larger surface area available for light-harvesting. The optimum catalyst mass has to be chosen in order to avoid excessive catalyst and to ensure total absorption of efficient photons. In amount of titania nanoparticles set of experiments, the influence of titania varied from 2 g to 4 g on the degradation rate of CO₂ and CH₄ was investigated. From the obtained results, it was obvious that larger amount of catalyst led to significant effect (see Supplementary Fig. S6 and Fig. S7). The total active sites increased with increasing catalyst amount. Moreover, surface area available for light-harvesting increased due to aggregation of TiO₂ particles at 4 g of coated TiO₂ mass.

---

![Fig. 8. Effect of stainless steel mesh size on (a) CO₂ conversion and (b) CH₄ conversion (UV light power: 250 W; amount of titania nanoparticles: 4 g; calcination temperature: 600 °C; CO₂:CH₄:N₂ ratios in feed: 10:80:10).](image1)

![Fig. 9. Effect of UV light power on (a) CO₂ conversion and (b) CH₄ conversion (stainless steel mesh size: 140; amount of titania nanoparticles: 4 g; calcination temperature: 600 °C, CO₂:CH₄:N₂ ratios in feed: 10:80:10).](image2)
3.6.4 Effect of calcination temperature

In calcination temperature set of experiments, the influence of calcination temperature varying from 200 °C to 600 °C on the degradation rate of CO₂ and CH₄ was investigated. The catalysts were calcinated at temperature from 200 °C to 600 °C with the same amount of TiO₂. It is clear that the photocatalytic activity of titania nanoparticles catalyst increased with increasing calcination temperature from 200 °C to 600 °C. The maximum calcination temperature used for samples preparation in this study was 600 °C, and at this temperature, the conversions of both CO₂ and CH₄ increased due to increasing anatase/rutile ratio in TiO₂ and surface area due to decreasing mean crystallite (see Supplementary Fig. S8 and Fig. S9). However, due to low mechanical strength of the TiO₂ coated stainless steel mesh, the catalysts must be calcinated at high temperature. Therefore, there exists an optimum temperature for the calcination process. It is evident that the TiO₂ film treated at 600 °C exhibited the highest photo-activity for CO₂ and CH₄ degradation.

3.6.5 Effect of CO₂:CH₄:N₂ ratios in feed

In feed set of experiments, the influence of CO₂:CH₄:N₂ ratios in the feed varying from (10:80:10) to (80:10:10), on the degradation rate of CO₂ and CH₄ was investigated. As expected from the results, in both cases of initial ratios in feed, there were similar trends in conversions of CH₄ and CO₂ with reaction time. Which, conversions in case of 10% CO₂: 80% CH₄: 10% N₂ were more than the case of 80% CO₂: 10% CH₄: 10% N₂ due to higher CO₂ stability relative to CH₄ can be considered as the reason for the decline in CO₂ active radicals (see Supplementary Fig. S10 and Fig. S11) [33].

3.7 Effect of irradiation time on product selectivity

Fig. 10 depicts the effect of irradiation time on product selectivity in photocatalytic CO₂ conversion with CH₄ over titania nanoparticles coated on stainless steel mesh at optimum conditions. From the GC analysis, five products, namely ethane, acetic acid, formic acid, methyl acetate and methyl formate were identified. The product selectivity increased proportionally with increasing irradiation time. As can be seen in Fig. 10, the product selectivity increased dramatically as the same trend when irradiation time increased to 3 h. Beyond that, the selectivity of methyl acetate and methyl formate increased slowly, with increasing irradiation time up to 6 h while the selectivities of ethane, acetic acid, formic acid remained almost constant. It is apparent that CH₃ plays an intermediate role between hydrocarbon products and ‘C=H is attacked by acetic acid and formic acid to produce methyl acetate and methyl formate, respectively [33].

3.8 Quantum efficiency analysis

The product compositions of photoreactors are usually quantified based on quantum efficiency. Table 6 highlights the operating parameters used to calculate quantum efficiency, calculated for each experiment, as the ratio of product rate (mole per sec) with photonic flux (mole per sec) [52]. The light intensity was measured with an online optical process monitor ILT OPM-1D and a SED008/W sensor. The quantum efficiency of the photoreactor with immobilized titania nanoparticles coated on stainless steel meshes for methyl formate and methyl acetate as valuable products were 0.163% and 0.147%, respectively. The quantum efficiency of photoreduction of CO₂ and CH₄ by using titania have not been reported so far. Liu et al. [53] reported quantum efficiency of internally illuminated photoreactor for methanol production during CO₂ reduction with water vapors which was 0.012%. The significant improvement in the performance of the immobilized titania nanoparticles coated on stainless mesh is due to more catalyst being exposed to incoming irradiation flux. A summary of some important work involving photocatalytic conversion of CO₂ and CH₄ in order to explain and compare the concept presented in this study with other similar processes are presented in Table 7.

3.9 Development of kinetic model using Langmuir–Hinshelwood model

In heterogeneous catalysis, the kinetic expression can be developed for the stable reactants and products in terms of surface concentrations of reactant and product. The surface reactions are usually assumed to be the slowest step and eventually the rate controlling step. If the reactants are competitively adsorbed on the same adsorption sites with different rate constants, then such reactions can be postulated by a Langmuir–Hinshelwood (L–H) mechanism [29]. For photocatalytic type reactions, when CO₂ and CH₄ were assumed to be adsorbed on the same active sites on

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>UV light power</td>
<td>250 W Hg</td>
</tr>
<tr>
<td>Calcination temperature</td>
<td>600 °C</td>
</tr>
<tr>
<td>Initial ratios in feed CO₂:CH₄:N₂</td>
<td>10:80:10</td>
</tr>
<tr>
<td>Stainless steel mesh size</td>
<td>140</td>
</tr>
<tr>
<td>Titania nanoparticles loading</td>
<td>4 g</td>
</tr>
<tr>
<td>Yield of products (μmole g-catal.⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Methyformate</td>
<td>571.1</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>517.5</td>
</tr>
<tr>
<td>Formic acid</td>
<td>49.7</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>53.5</td>
</tr>
<tr>
<td>Ethane</td>
<td>56.2</td>
</tr>
<tr>
<td>Yield rate of products (μmole g-catal.⁻¹ h⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Methyl formate</td>
<td>63.5</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>57.5</td>
</tr>
<tr>
<td>Formic acid</td>
<td>5.5</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>5.9</td>
</tr>
<tr>
<td>Ethane</td>
<td>6.5</td>
</tr>
<tr>
<td>Quantum efficiency of methyl formate</td>
<td>0.163%</td>
</tr>
<tr>
<td>Quantum efficiency of methyl acetate</td>
<td>0.147%</td>
</tr>
<tr>
<td>Quantum efficiency of formic acid</td>
<td>0.0141%</td>
</tr>
<tr>
<td>Quantum efficiency of acetic acid</td>
<td>0.0151%</td>
</tr>
<tr>
<td>Quantum efficiency of ethane</td>
<td>0.0167%</td>
</tr>
</tbody>
</table>

a Yield rates were calculated at 6 h irradiation basis.

b Quantum efficiency = (number of electrons × moles of production rate)/(moles of UV photons flux).
molecules have to compete with $K$ and value of intensity factor over titania and CH$_4$ and conversion can reach up to 37.9% and 48.7%, respectively over the entire catalyst surface.

are the ratios of rate constants for adsorption and desorption in feed. It was also revealed through the is the rate constant of any particular product, $k$ is the rate constant of any particular product, $I$ is UV flux intensity in which kinetic constants are evaluated. In general, the photocatalytic reaction rate is proportional to $I^2$, where $x$ is the reaction order of light intensity, having value one or less depending on light intensity. $K_{CH4}$, $K_{CO2}$, $K_{CO}$, $K_{CH4COOH}$, $K_{CH4COOH}$, $K_{CH4H2}$ and $K_{HCOOH}$ are the ratios of rate constants for adsorption and desorption of methane, carbon dioxide, ethane, acetic acid, formic acid, methyl acetate and methyl formate, respectively. Eq. (19) can be simplified assuming only reactants are adsorbed on the catalyst surface while all products desorbed immediately after chemical reaction. Thus, CO$_2$ and CH$_4$ were adsorbed on surface of the catalyst and the modified form of L–H model becomes Eq. (21).

$$\text{Rate} = \frac{k_1 I^2}{N}$$  \hspace{1cm} (19)

$$N = \left( 1 + K_{CH4}P_{CH4} + K_{CO2}P_{CO2} + P_{CH4}P_{CH3H5} + K_{CH4COOH}P_{CH4COOH} + K_{CH4H2}P_{CH4H2} + K_{HCOOH}P_{HCOOH} \right)^2$$  \hspace{1cm} (20)

where $k_1$ is the rate constant of any particular product, $I$ is UV flux intensity in which kinetic constants are evaluated. In general, the photocatalytic reaction rate is proportional to $I^2$, where $x$ is the reaction order of light intensity, having value one or less depending on light intensity. $K_{CH4}$, $K_{CO2}$, $K_{CO}$, $K_{CH4COOH}$, $K_{CH4COOH}$, $K_{CH4H2}$ and $K_{HCOOH}$ are the ratios of rate constants for adsorption and desorption of methane, carbon dioxide, ethane, acetic acid, formic acid, methyl acetate and methyl formate, respectively. Eq. (19) can be simplified assuming only reactants are adsorbed on the catalyst surface while all products desorbed immediately after chemical reaction. Thus, CO$_2$ and CH$_4$ were adsorbed on surface of the catalyst and the modified form of L–H model becomes Eq. (21).

$$\text{Rate} = \frac{k_1 I^2 K_{CH4}K_{CO2}}{\left( 1 + K_{CH4}P_{CH4} + K_{CO2}P_{CO2} \right)^2}$$  \hspace{1cm} (21)

The constants of the L–H model were determined by correlating it with experimental data. L–H model profile for photocatalytic CO$_2$ reduction over titania nanoparticles coated on stainless steel meshes is depicted in Fig. 11. It has been observed that the reaction rate is proportional to $P_{CO2}$ at a lower partial pressure when only a small fraction of the sites are occupied. However, as $P_{CO2}$ increases, the rate becomes less dependent on it and gradually slows down possibly due to adsorption of CO$_2$ over the entire catalyst surface. Under such circumstances, CH$_3$ molecules have to compete with CO$_2$ molecules for chemical reactions, resulting in lower rate of reaction. The best fitted rate constants $k_1$ adsorption equilibrium constants $K_{CH4}$ and $K_{CO2}$ and value of intensity factor over titania nanoparticles as a catalyst are listed in Table 8. The CO$_2$ and CH$_4$ adsorption constants (i.e. $K_{CO2}$ and $K_{CH4}$) over titania catalyst was 15 bar$^{-1}$ and 50 bar$^{-1}$, respectively.

### 4. Conclusions

Photocatalytic conversion of CO$_2$ and CH$_4$ over titania nanoparticles coated on stainless steel meshes were conducted in this study. The application of experimental design and Response Surface Methodology was shown in this study to determine the optimum process variables. Model evaluation and statistical analysis revealed that the RSM can efficiently improve process variables and the predicted values were in accordance with the experimental ones. The actual parameters on the efficiency of conversion were investigated such as stainless steel mesh size, amount of titania nanoparticles, calcination temperature, UV light power and initial ratios of CO$_2$:CH$_4$:N$_2$ in feed. It was also revealed through the comparison of commercial titania with calcinated titania structure that calcination technique reduced particles agglomeration. Optimum experimental conditions indicated that the maximum CO$_2$ and CH$_4$ conversion can reach up to 37.9% and 48.7%, respectively. Correspondingly, the photo-reduction products in gas medium were assigned to be ethane, acetic acid, formic acid, methyl acetate and methyl formate. The Langmuir–Hinshelwood model
revealed that yield rates of products were dependent on efficient adsorption of the reactants and desorption of products over the catalyst surface. The kinetic model confirmed photocatalytic adsorptive reduction and oxidation reaction over the catalyst surface. It also revealed higher mobility of electron on the catalyst surface and efficient desorption of products, resulting in higher product yield rates.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2015.03.125.

References


