Photocatalytic conversion of carbon dioxide and methane over titania nanoparticles coated mesh: Optimization study

Saeed Delavari, Nor Aishah Saidina Amin*

Low Carbon Energy Group/Chemical Reaction Engineering Group (CREG), Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor, Malaysia

Abstract

Immobilized titania (TiO$_2$) nanoparticles semiconductor on stainless steel mesh was used for photocatalytic conversion of CO$_2$ and CH$_4$. This study utilized experimental design and process optimization tools to maximize the desired response using response surface methodology (RSM) with central composite rotatable design (CCRD). The experimental parameters were stainless steel mesh size, titania nanoparticles loading, calcination temperature, UV light power and initial ratios of CO$_2$:CH$_4$:N$_2$ in feed. The optimal conditions were determined as follows: stainless steel mesh size of 140, 4 g of coated titania nanoparticles on mesh, calcination temperature of 600 °C, UV light power of 250 W and 10% of CO$_2$ in feed to achieve a maximum CO$_2$ conversion of 37.87%. Correspondingly, the selectivity of products were 4.66%, 4.28%, 3.97% and 87.09%, for ethane, acetic acid, formic acid and methyl acetate, respectively.

© 2014 The Authors. Published by Elsevier Ltd.

Keywords: Photocatalytic; Optimization; Response Surface Methodology; Nanoparticles; Titania

1. Introduction

The major causes of global warming are mainly attributed to greenhouse gases such as carbon dioxide, methane and chlorofluorocarbons. Environmental and chemistry researchers always seek solutions to reduce pollutant effect of carbon dioxide, with the aim of addressing the global environmental problems as well as supporting vital carbon resources with a new approach. The most favorable CO$_2$ reduction method is by applying photocatalysts as noticeable light irradiation or UV reduces it to useful compounds on certain conditions [1-3]. Semiconductor catalysts such as titania (TiO$_2$) is the most commonly-used photocatalyst and one of the favorable photocatalysts among several semiconductor metal oxides for the...
photocatalytic degradation of chemicals and organic dyes. It has multipurpose properties such as wide, direct band gap and large binding energy of excitation [1, 4]. 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 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 response (i.e. CO₂ conversion) were studied concurrently in a rotatable central composite design (RCCD, a classical experimental design method) and an empirical mathematical model correlating the response to the variables was developed and presented as well.

2. Experimental

2.1. Preparation of photocatalyst

Titanium dioxide P-25 (Anatase/Rutile: 80/20) was supplied by Degussa. An efficient and simple method was used to immobilize titania nanoparticles on stainless steel meshes. Stainless steel was formerly used to support nanoparticles of TiO₂. In this study, we selected stainless steel due to its large surface area, good ventilation for passing gases and resistance to corrosion.

2.2. Photocatalytic reaction experiment

The gas phase stainless steel cubic reactor, which has a dimension of 20 cm × 20 cm × 10 cm was equipped with a quartz window. 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 9 hr. The conversion products were characterized using FTIR.

2.3. 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), titania nanoparticles loading (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 involved in this study.

3. Results and discussion

3.1. Coded empirical model equation for CO₂ conversion

The summary of the experimental runs indicated the carbon dioxide conversion ranged from 26.80% to 37.87%, depending on the conditions in the experiments. The adequacy of the model was further justified through analysis of variance (ANOVA).
The predicted values reasonably matched the experimental values with $R$-squared = 0.9548 for CO$_2$ conversion, meaning that 95.48% of the total variations for CO$_2$ in the results can be attributed to the independent variables that were investigated. Fig. 1(a) exhibits the comparison between the actual response values obtained from experimental work and the predicted response values based on the quadratic model. It also displays that the experimental range of studies is adequately covered by the model. From analysis of the ANOVA data and the statistical parameters, the final empirical model in terms of coded factors, after exclusion of the insignificant terms are given in Eq. (1).

$$CO_2 \text{ Conversion (\%)} = 34.98 + 3.70X_1 + 3.07X_2 + 0.77X_3 + 3.35X_4 - 0.45X_5 - 1.61X_1^2 - 1.52X_2^2 - 0.68X_4^2 + 3.20X_1X_2 - 0.48X_1X_3 + 2.69X_1X_4 + 3.78X_2X_4 + 0.37X_2X_5 - 0.87X_3X_4$$

(1)

### Table 1. Experimental range and levels of the respective independent variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbols</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel mesh size</td>
<td>$X_1$</td>
<td>50 60 100 140 150</td>
</tr>
<tr>
<td>Titania nanoparticles loading (g)</td>
<td>$X_2$</td>
<td>1.75 2 3 4 4.25</td>
</tr>
<tr>
<td>Calcination temperature (°C)</td>
<td>$X_3$</td>
<td>150 200 400 600 650</td>
</tr>
<tr>
<td>UV light power (W)</td>
<td>$X_4$</td>
<td>25 50 150 250 275</td>
</tr>
<tr>
<td>CO$_2$:CH$_4$:N$_2$ ratios in feed (%)</td>
<td>$X_5$</td>
<td>10:80:10 - 80:10:10 -</td>
</tr>
</tbody>
</table>

3.2. Interactions between process variables

Stainless steel mesh size is the most significant parameter, followed by UV light power whereas the titania nanoparticles loading, calcination temperature and CO$_2$:CH$_4$:N$_2$ ratios in feed are less important among the five parameters. Fig 1(b), illustrates the response surface plot of CO$_2$ conversion. The maximum conversion was achieved for stainless steel mesh size of 140, UV light power of 250 W, calcination temperature of 600 °C, 10% of CO$_2$ in feed and 4 g titania coated on mesh. As shown in Fig. 1(b), the photocatalytic CO$_2$ conversion increases significantly with increasing stainless steel mesh size, due to enlarged active surface for photocatalytic activity. Similarly, the photocatalytic CO$_2$ conversion increases dramatically with increasing UV light power. The higher light power provides higher energy for more titania particles to generate electron hole pairs [4].

3.3. Process optimization and products

The ultimate goal of the optimization was to obtain maximum response that simultaneously satisfies all of the variable properties. The model predicted an optimum condition of 4 g TiO$_2$, 10% CO$_2$ in feed, stainless steel mesh size of 140, calcination temperature of 600 °C and UV light power of 250 W for CO$_2$ conversion. The observed and predicted maximum conversions were 37.87% and 38.15% for CO$_2$, and 48.65% and 49.45% for CH$_4$, respectively. Thus, the objective to optimize the conversion by response surface methodology for photocatalytic conversion of CH$_4$ and CO$_2$ was achieved. The conversion products were characterized to be formate and acetate derivatives, where the selectivities of ethane, acetic acid, formic acid, and methyl acetate reached up to 4.66%, 4.28%, 3.97% and 87.09%, respectively at the optimized conditions.
In particular, CO₂ conversion can be significantly improved by lowering the gas hourly space velocity (GHSV) and thus increasing the residence time of the reagents in contact with the active sites of catalyst. Therefore, at optimum conditions, the maximum CO₂ conversion obtained by selecting 550 h⁻¹ of GHSV.

Fig. 1. (a) Comparison between predicted and actual response values; (b) response surface plot representing the effect of the interaction of stainless steel mesh size and UV light power on CO₂ conversion

4. Conclusions

The application of experimental design and response surface methodology was shown in this study to determine the optimum process variables in CO₂ and CH₄ photocatalytic conversion by calcinated immobilized titania nanoparticles coated on stainless steel meshes. Model evaluation and statistical analysis revealed that response surface methodology can efficiently improve process variables and the predicted values were in accordance with the experimental ones. The optimal photocatalytic efficiency is obtained using anatase with a small admixture of rutile. The anatase/rutile ratio begins to decrease as a result of treatment at temperature between 600 °C and 800 °C. Optimum experimental conditions indicated that the maximum CO₂ conversion can reach up to 37.87%. The conversion products were characterized to be ethane, acetic acid, formic acid and methyl acetate.

Acknowledgements

The authors would like to extend their deepest appreciation to the Ministry of Higher Education (MOHE), Malaysia and Universiti Teknologi Malaysia for the financial support of this research under LRGS (Long-term Research Grant Scheme, Vot 4L800) and RUG (Research University Grant, Vot 00H49). SD is also a UTM fellowship recipient (Ref. No.: UTM.J10.02.00/13.14/1/125-073).

References


Biography

Professor Dr. Nor Aishah Saidina Amin has been with the Faculty of Chemical Engineering since 1986. Her main research interests are in catalytic reaction engineering and modeling of chemical reaction systems. She obtained her Ph.D from the Illinois Institute of Technology, Chicago, Illinois, USA in 1996.