

Optimization of process parameters and catalyst compositions in carbon dioxide oxidative coupling of methane over CaO–MnO/CeO₂ catalyst using response surface methodology

Istadi¹, Nor Aishah Saidina Amin^{*}

Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, UTM Skudai, Johor Bahru, 81310 Malaysia

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Abstract

The optimization of process parameters and catalyst compositions for the CO₂ oxidative coupling of methane (CO₂-OCM) reaction over CaO–MnO/CeO₂ catalyst was developed using Response Surface Methodology (RSM). The relationship between the responses, i.e. CH₄ conversion, C₂ hydrocarbons selectivity or yield, with four independent variables, i.e. CO₂/CH₄ ratio, reactor temperature, wt.% CaO and wt.% MnO in the catalyst, were presented as empirical mathematical models. The maximum C₂ hydrocarbons selectivity and yields of 82.62% and 3.93%, respectively, were achieved by the individual-response optimization at the corresponding optimal process parameters and catalyst compositions. However, the CH₄ conversion was a saddle function and did not show a unique optimum as revealed by the canonical analysis. Moreover pertaining to simultaneous multi-responses optimization, the maximum C₂ selectivity and yield of 76.56% and 3.74%, respectively, were obtained at a unique optimal process parameters and catalyst compositions. It may be deduced that both individual- and multi-responses optimizations are useful for the recommendation of optimal process parameters and catalyst compositions for the CO₂-OCM process.

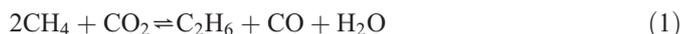
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Keywords: CO₂-OCM; CaO–MnO/CeO₂ catalyst; Catalysts optimization; Process parameters optimization; Response surface methodology; Central composite design

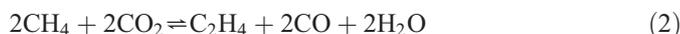
1. Introduction

The direct conversion of methane to ethane, ethylene and acetylene (C₂ hydrocarbons) has a large implication towards the utilization of natural gas in the gas-based petrochemical and liquid fuels industries. The high CO₂/CH₄ ratio in Natuna's natural gas compositions, comprising up to 71% carbon dioxide and 28% methane [1], should be strategically utilized for the production of higher hydrocarbons, liquid fuels and other important chemicals. It is highly desirable from the environmental point of view to utilize and convert both methane and carbon dioxide, greenhouse gas contributors, from natural gas

into higher value-added chemicals and liquid fuels without having to separate the carbon dioxide first. Oxidative coupling of methane is a promising route for the conversion of natural gas to ethane and ethylene for the production of petrochemicals or fuels [2]. The basic oxides, i.e. oxides of alkali, alkaline earth and rare earth metals, singly or in combination, constitute good catalysts for OCM reaction [2,3]. Further enhancement of the catalytic performance via simultaneous optimization of process parameters and catalyst compositions are necessary for the process to be commercialized. Eqs. (1) and (2) are the two main reaction schemes for CO₂-OCM to produce C₂ hydrocarbons with carbon monoxide and water as the by-products.



$$\Delta H_{1073\text{ K}}^\circ = 108.0 \text{ kJ/mol}; \Delta G_{1073\text{ K}}^\circ = 72.9 \text{ kJ/mol.}$$



$$\Delta H_{1073\text{ K}}^\circ = 285.7 \text{ kJ/mol}; \Delta G_{1073\text{ K}}^\circ = 71.9 \text{ kJ/mol.}$$

^{*} Corresponding author. Tel.: +60 7 5535588; fax: +60 7 5581463.

E-mail addresses: istadi@tekim.ft.undip.ac.id (Istadi), noraishah@fkkksa.utm.my (N.A.S. Amin).

¹ Present address: Department of Chemical Engineering, Diponegoro University, Jl. Prof. H. Sudharto, SH., Semarang, 50239, Indonesia.