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Optimization of process parameters and catalyst compositions in carbon dioxide oxidative coupling of methane over CaO–MnO/CeO_2 catalyst using response surface methodology

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Abstract

The optimization of process parameters and catalyst compositions for the CO_2 oxidative coupling of methane (CO_2-OCM) reaction over CaO–MnO/CeO_2 catalyst was developed using Response Surface Methodology (RSM). The relationship between the responses, i.e. CH_4 conversion, C_2 hydrocarbons selectivity or yield, with four independent variables, i.e. CO_2/CH_4 ratio, reactor temperature, wt.% CaO and wt.% MnO in the catalyst, were presented as empirical mathematical models. The maximum C_2 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 CH_4 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 C_2 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 CO_2-OCM process.

Keywords: CO_2-OCM; CaO–MnO/CeO_2 catalyst; Catalysts optimization; Process parameters optimization; Response surface methodology; Central composite design

1. Introduction

The direct conversion of methane to ethane, ethylene and acetylene (C_2 hydrocarbons) has a large implication towards the utilization of natural gas in the gas-based petrochemical and liquid fuels industries. The high CO_2/CH_4 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 CO_2-OCM to produce C_2 hydrocarbons with carbon monoxide and water as the by-products.

$$2CH_4 + CO_2 \rightleftharpoons C_2H_6 + CO + H_2O \quad (1)$$

$$\Delta H^\circ_{1073\ K} = 108.0\ kJ/mol;\ \Delta G^\circ_{1073\ K} = 72.9\ kJ/\ mol.$$

$$2CH_4 + 2CO_2 \rightleftharpoons C_2H_4 + 2CO + 2H_2O \quad (2)$$

$$\Delta H^\circ_{1073\ K} = 285.7\ kJ/mol;\ \Delta G^\circ_{1073\ K} = 71.9\ kJ/\ mol.$$

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