Screening of MgO- and CeO\textsubscript{2}-Based Catalysts for Carbon Dioxide Oxidative Coupling of Methane to C\textsubscript{2+} Hydrocarbons

Istadi*, 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 catalyst screening tests for carbon dioxide oxidative coupling of methane (CO\textsubscript{2}-OCM) have been investigated over ternary and binary metal oxide catalysts. The catalysts are prepared by doping MgO- and CeO\textsubscript{2}-based solids with oxides from alkali (Li\textsubscript{2}O), alkaline earth (CaO), and transition metal groups (WO\textsubscript{3} or MnO). The presence of the peroxide (O\textsuperscript{2-}) active sites on the Li\textsubscript{2}O\textsubscript{2}, revealed by Raman spectroscopy, may be the key factor in the enhanced performance of some of the Li\textsubscript{2}O/MgO catalysts. The high reducibility of the CeO\textsubscript{2} catalyst, an important factor in the CO\textsubscript{2}-OCM catalyst activity, may be enhanced by the presence of manganese oxide species. The manganese oxide species increases oxygen mobility and oxygen vacancies in the CeO\textsubscript{2} catalyst. Raman and Fourier Transform Infra Red (FT-IR) spectroscopies revealed the presence of lattice vibrations of metal-oxygen bondings and active sites in which the peaks corresponding to the bulk crystalline structures of Li\textsubscript{2}O, CaO, WO\textsubscript{3} and MnO are detected. The performance of 5%MnO/15%CaO/CeO\textsubscript{2} catalyst is the most potential among the CeO\textsubscript{2}-based catalysts, although lower than the 2%Li\textsubscript{2}O/MgO catalyst. The 2%Li\textsubscript{2}O/MgO catalyst showed the most promising C\textsubscript{2+} hydrocarbons selectivity and yield at 98.0% and 5.7%, respectively.

Key words: catalyst screening, carbon dioxide, oxidative coupling, methane, ternary metal oxide, binary metal oxide, MgO, CeO\textsubscript{2}, C\textsubscript{2+} hydrocarbons

1. Introduction

The direct conversion of methane to ethane, ethylene and acetylene (C\textsubscript{2+} hydrocarbons) is considered to be one of the most effective uses of natural gas as a chemical resource. The compositions of natural gas from the Natuna’s fields contains up to 71% carbon dioxide and 28% methane [1]. The high CO\textsubscript{2}/CH\textsubscript{4} ratio in Natuna’s natural gas compositions should be strategically utilized for the production of higher hydrocarbons and other important chemicals. It is highly desirable from the environmental point of view to utilize and convert both methane and carbon dioxide from natural gas into higher value-added chemicals without having to separate the carbon dioxide first.

Carbon dioxide rather than oxygen may be the alternative oxidant for the catalytic reaction of methane to produce C\textsubscript{2+} hydrocarbons due to the fact that in the gas phase the methyl radicals are induced by the presence of oxygen and not by carbon dioxide [2,3]. Recently, the conversion of natural gas using carbon dioxide as the oxidant has received considerable attention [2-8]. Among 30 metal oxides studied, praseodymium and terbium oxides showed potential [2,3,5] for catalyzing the CO\textsubscript{2}-OCM reaction to produce C\textsubscript{2+} hydrocarbons. Carbon dioxide showed a positive role in the formation of C\textsubscript{2+} hydro-