

# Synergistic effect of catalyst basicity and reducibility on performance of ternary CeO<sub>2</sub>-based catalyst for CO<sub>2</sub> OCM to C<sub>2</sub> hydrocarbons

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## Abstract

The present investigation focuses on the synergistic effect of catalyst basicity and reducibility on the catalytic activity of binary and ternary CeO<sub>2</sub>-based catalysts in the CO<sub>2</sub> oxidative coupling of methane (CO<sub>2</sub> OCM). Proper amount of medium and strong basic sites together with lower amount of very strong basic sites are identified as pertinent factors in increasing the catalytic performance. The CO<sub>2</sub>-TPD and H<sub>2</sub>-TPR studies indicate synergistic effect between the catalyst basicity and reducibility for the 12.8CaO–6.4MnO/CeO<sub>2</sub> ternary metal-oxide catalyst in enhancing the CO<sub>2</sub> OCM performance.

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**Keywords:** CO<sub>2</sub> OCM; CaO–MnO/CeO<sub>2</sub> catalyst; Catalyst basicity; Catalyst reducibility

## 1. Introduction

In chemical industries, C<sub>2</sub> hydrocarbons (ethylene, ethane, and acetylene) are important basic chemicals in producing higher value-added chemicals. Meanwhile, utilization of both methane and carbon dioxide, known as greenhouse gas contributors, is desirable in our efforts to suppress the trend of global warming. Furthermore, methane and carbon dioxide are components of natural gas which compositions vary with locations. The compositions of natural gas in Natuna's fields are unique with the CO<sub>2</sub>/CH<sub>4</sub> ratio being 71/28 making it a highly acidic natural gas. Therefore, the conversions of both gases have significant implication towards the utilization of natural gas in the gas-based petrochemical and liquid fuels industries. The CO<sub>2</sub> OCM offers an alternative route to produce useful chemicals, while utilizing carbon dioxide for environmentally benefit chemical process.

The conversion of methane to C<sub>2</sub> hydrocarbons using carbon dioxide as an oxidant has received considerable attention

[1–4]. Recently, He et al. [5] developed the nano-CeO<sub>2</sub>/ZnO catalyst for the CO<sub>2</sub> OCM. In another development, the screening of CeO<sub>2</sub>-based catalysts over binary and ternary metal oxides identified the CaO–MnO/CeO<sub>2</sub> as the probable catalyst for the CO<sub>2</sub> OCM process [6] since it displayed notable stability with no obvious coking during 20 h of reaction time on stream. Furthermore, the single- and multi-responses optimizations of CO<sub>2</sub> OCM reported maximum C<sub>2</sub> hydrocarbons selectivity and yield of 76.6% and 3.7%, respectively, over the 12.8% CaO–6.4% MnO/CeO<sub>2</sub> catalyst [7,8]. The optimal CO<sub>2</sub>/CH<sub>4</sub> ratio of 2 corresponding to the optimal reactor temperature being 1127 K is relevant for the utilization of Natuna's field natural gas in the CO<sub>2</sub> OCM process [9].

The CO<sub>2</sub> OCM process is a complex heterogeneous–homogeneous process involving [10]:

- oxygen-assisted breakage of a C–H bond in the CH<sub>4</sub> molecule on the solid surface;
- heterogeneous decomposition of CO<sub>2</sub> to CO and oxygen active species;
- homogeneous recombination of CH<sub>3</sub><sup>\*</sup> radicals released from the surface;
- homogeneous oxidative or radical dehydrogenation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub>.

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