

Synergistic effect of catalyst basicity and reducibility on performance of ternary CeO₂-based catalyst for CO₂ OCM to C₂ 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 CeO₂-based catalysts in the CO₂ oxidative coupling of methane (CO₂ 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 CO₂-TPD and H₂-TPR studies indicate synergistic effect between the catalyst basicity and reducibility for the 12.8CaO–6.4MnO/CeO₂ ternary metal-oxide catalyst in enhancing the CO₂ OCM performance.

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1. Introduction

In chemical industries, C₂ 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 CO₂/CH₄ 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 CO₂ OCM offers an alternative route to produce useful chemicals, while utilizing carbon dioxide for environmentally benefit chemical process.

The conversion of methane to C₂ hydrocarbons using carbon dioxide as an oxidant has received considerable attention

[1–4]. Recently, He et al. [5] developed the nano-CeO₂/ZnO catalyst for the CO₂ OCM. In another development, the screening of CeO₂-based catalysts over binary and ternary metal oxides identified the CaO–MnO/CeO₂ as the probable catalyst for the CO₂ 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 CO₂ OCM reported maximum C₂ hydrocarbons selectivity and yield of 76.6% and 3.7%, respectively, over the 12.8% CaO–6.4% MnO/CeO₂ catalyst [7,8]. The optimal CO₂/CH₄ 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 CO₂ OCM process [9].

The CO₂ OCM process is a complex heterogeneous–homogeneous process involving [10]:

- oxygen-assisted breakage of a C–H bond in the CH₄ molecule on the solid surface;
- heterogeneous decomposition of CO₂ to CO and oxygen active species;
- homogeneous recombination of CH₃* radicals released from the surface;
- homogeneous oxidative or radical dehydrogenation of C₂H₆ to C₂H₄.

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