



# Improved activity and coke resistance by promoters of nanosized trimetallic catalysts for autothermal carbon dioxide reforming of methane

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## ABSTRACT

Autothermal carbon dioxide reforming of methane was studied over trimetallic NiCoMn/ZrO<sub>2</sub> catalyst promoted with different promoters (Ce, La, Ca, K) aiming to improve the performance of the catalyst and increase their resistance to coking. The promoted catalysts prepared by a coprecipitation method showed metal sizes less than 10 nm and were studied with a CH<sub>4</sub>:CO<sub>2</sub>:O<sub>2</sub> mole ratio of 1:0.8:0.2 at 800 °C under atmospheric pressure. The addition of promoters to NiCoMn/ZrO<sub>2</sub> catalyst markedly improved CH<sub>4</sub> and CO<sub>2</sub> conversions as well as selectivities to H<sub>2</sub> and CO relative to the unpromoted catalyst. Rare earths Ce and La were more effective promoters than alkaline earth (Ca) and alkali metal (K), showing high and stable CO<sub>2</sub> conversions of 95.5% and 89.9%, respectively. The promoted catalysts exhibited higher activity and improved stability with no severe coke deposition and the Ce-promoted NiCoMn/ZrO<sub>2</sub> catalyst displayed the highest activity with no apparent activity loss. The roles of the promoters were discussed based on the results of various physicochemical characterization techniques.

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## 1. Introduction

Catalytic autothermal reforming (ATR) of methane with carbon dioxide has received significant attention in recent years, as the process converts two greenhouse gases (CH<sub>4</sub> and CO<sub>2</sub>) to valuable synthesis gas (syngas), a mixture of CO and H<sub>2</sub> [1]. The reforming processes are generally classified into three groups; partial oxidation (exothermic reaction), carbon dioxide and/or steam reforming (endothermic reaction) and autothermal reforming (combined exothermic and endothermic reactions) of methane. The autothermal reforming of methane was designed to save energy, because the required thermal energy is generated *in situ* by the partial oxidation of methane. As this process consumes the thermal energy that it produces, it is called ‘autothermal’ [2]. The ATR has been identified as a preferred option for large-scale, economic synthesis gas production.

The ATR reaction proceeds well over noble metal based catalysts (Pt and Ru) that can provide high activity with little carbon deposition [3]. Yet noble metals are unsuitable for practical applications due to their easy sintering and high cost. Therefore base metal-based catalysts (like Fe, Ni, Co, Mn) are more practical options. The Ni-based catalysts have been investigated most widely because of their excellent catalytic activity and low price. However, the

Ni-based catalysts have their own shortcomings, such as Ni particle sintering and coke deposition, which result in catalyst deactivation. The deactivation can be suppressed significantly when ZrO<sub>2</sub> is used as a catalyst support because the tetragonal phase of ZrO<sub>2</sub> enhances the thermal stability of the Ni catalysts by helping them endure the increased temperature at hot spots, which are approximately 100 °C higher than operating temperature of the system [4]. Promoters are commonly introduced to methane reforming catalysts [5–7] to enhance the activity and metal dispersion such as CeO<sub>2</sub> [8] and La [9] on Ni/Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> on Ni/ZrO<sub>2</sub> [10,11]. In carbon dioxide dry reforming of methane to produce synthesis gas over Ni/Al<sub>2</sub>O<sub>3</sub> modified with La<sub>2</sub>O<sub>3</sub>, MgO and CaO, Roh and Jun [12] found that La<sub>2</sub>O<sub>3</sub> increased better the activity and stability compared with MgO or CaO. It was suggested that carbon deposition was suppressed when Ni was supported on a metal oxide with a strong Lewis basicity [13]. The nature of the support was reported to significantly influence the performance of the catalyst due to a metal–support interaction and acid–base properties of the catalyst [14,15]. Additional metals loaded to Ni-based catalysts can improve their activity and stability in CO<sub>2</sub> reforming of methane. We earlier reported high activity and stability of Mn-containing Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for CO<sub>2</sub> reforming that showed negligible amounts of coke formation [16]. Cobalt has attracted interest as an active metal for the CO<sub>2</sub> reforming of methane [17]. A transition metal oxide like Co<sub>3</sub>O<sub>4</sub> is active for ATR reaction because of its high redox property [18]. The cobalt catalyst when combined with other oxides showed different activities. The Co–Mn mixed oxides were found to be the

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