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Studies on stability and coking resistance of Ni/BaTiO₃–Al₂O₃ catalysts for lower temperature dry reforming of methane (LTDRM)

Xiancai Li^{a,*}, Quanhong Hu^a, Yifeng Yang^a, Yan Wang^a, Fei He^b

^a Department of Chemistry, Nanchang University, Nanchang, Jiangxi 330031, China

^b Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

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ABSTRACT

Wt.%BaTiO₃-Al₂O₃ (wt.%BaTiO₃ = 0-100%) composite supports were synthesized through varying the BaTiO₃ content by the "sol-(xero)gel" method. Ni/wt.%BaTiO₃-Al₂O₃ nickel-based catalysts prepared by incipient wetness method were evaluated for dry reforming of methane carried out between 690 °C and 800 °C. Characterizations using XRD, IR, N2 adsorption-desorption, H2-TPR, SEM, and XPS were conducted to investigate the structure or properties of the wt.%BaTiO₃-Al₂O₃ composite supports as well as the Ni/wt.%BaTiO₃-Al₂O₃ catalysts. The results demonstrate that BaTiO₃ particles are discontinuously dispersed on the surface of γ -Al₂O₃ in the form of individual isolated particles for the wt.%BaTiO₃-Al₂O₃ composite supports. Meanwhile, it is probably that the coexistence of BaAl₂O₄ spinel phase with the BaTiO₃ phase on the surface of γ -Al₂O₃ inhibits the Ni/wt.%BaTiO₃-Al₂O₃ catalysts from the formation of NiAl₂O₄ spinel phase, improving the catalytic performance of the catalysts. The Ni/BaTiO₃ catalyst showed poor stability and severe coke formation in the dry reforming of methane tested at 690 °C, which was thought to be mainly originated from the excessive strong electronic donor intensity of Ni/BaTiO₃ catalyst as well as the resulted CO disproportionation reaction. Compared with the Ni/BaTiO₃ catalyst, the Ni/wt.%BaTiO₃-Al₂O₃ catalysts with the addition of BaTiO₃ had a higher dispersion of active nickel and a weakened electronic donor intensity of the NiO_x species. As a result, the synthesized Ni/32.4%BaTiO₃-Al₂O₃ catalyst exhibited a high catalytic activity, excellent stability as well as coking resistance for lower temperature dry reforming of methane.

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1. Introduction

Much attention has been paid to the methane reforming with carbon dioxide as this reaction is attractive in providing a preferable lower H_2/CO ratio (synthesis gas) for Fischer–Tropsch process. Therefore, the two low-cost greenhouse gases, CH_4 and CO_2 , can be indirectly converted to hydrocarbon or methanol, the liquid fuels, and thereby offering an environmental benefit [1,2].

Compared to noble metals, the metal nickel is the suitable catalysts for the CH_4/CO_2 reforming industrially due to its lower cost, high activity, and good product selectivity [3,4]. However, the reaction of CO_2 reforming of methane remains a significant challenge since the coke formation leading to premature catalyst deactivation and poor stability, especially when the metal nickel is used as catalyst active component. The coke formation is caused mainly by either methane decomposition or CO disproportionation (reactions (1) and (2)).

 $CH_4 \rightarrow C + 2H_2 \tag{1}$

 $2CO \rightarrow C + CO_2 \tag{2}$

Nevertheless, it has been shown that the deactivation of nickel catalysts can be attenuated when the metal nickel is supported on a metal oxide with a strong Lewis base as for example alkaline earth oxides, such as MgO, CaO, SrO or BaO [5,6].

In our previous preliminary studies [7,8], the perovskite BaTiO₃ supported Ni/BaTiO₃ and 5.0 wt.%Ni-0.75 wt.%La-BaTiO₃ nickelbased catalysts showed higher initial activity in CO₂ reforming of methane, which is likely attributing to more oxygen vacancies of perovskite-type oxide in the catalysts. The extensive use of perovskite-type oxides as catalyst support is due to their ability in providing high (lattice) oxygen mobility and also high structural stability [9]. However, one of the main drawbacks of the perovskitetype oxide as catalyst support is their very low specific surface area, usually with a few tens (m^2/g) [10–13]. Meanwhile, it is well known that the γ -Al₂O₃ is a kind of common commercial catalyst support with well pore size dispersion, high specific surface area and high mechanic strength (good crushing strength and attrition resistance). On the other hand, for the CO₂ reforming of methane reaction, calculations [14,15] suggest operation at high CO₂/CH₄ ratios above 1 and high temperatures, above 827 °C to avoid regions where there is a thermodynamic potential for carbon formation;



^{*} Corresponding author. Tel.: +86 791 83969251; fax: +86 791 83969251. *E-mail address:* xcli@ncu.edu.cn (X. Li).

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