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CO₂ methanation over ordered mesoporous NiRu-doped CaO-Al₂O₃ nanocomposites with enhanced catalytic performance

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ABSTRACT

The ordered mesoporous NiRu-doped CaO-Al₂O₃ nanocomposites were synthesized via a facile evaporation-induced self-assembly method for CO₂ methanation. Metallic Ni and Ru species retained the single-component heterostructure rather than NiRu alloy over the 600 °C-reduced catalysts. Owing to the synergistic effect of bimetallic Ni–Ru as well as the improved H₂ and CO₂ chemisorption capacities after the addition of Ru and CaO promoters, the ordered mesoporous 10N1R2C-OMA catalyst exhibited enhanced catalytic activity and selectivity, which achieved the maximum CO₂ conversion of 83.8% and CH₄ selectivity of 100% at 380 °C, 0.1 MPa, 30000 mL g⁻¹ h⁻¹. In a 550 °C-109 h-lifetime test, the ordered mesoporous 10N1R2C-OMA catalyst showed high stability and superior anti-sintering property due to the confinement effect of the ordered mesostructure.

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Introduction

The carbon-rich fossil fuels consumption has always occupied large proportion in the energy consumption in the world. As a

result, a large amount of CO₂ has been discharged into the atmosphere, which causes a series of environmental problems, e.g. the global warming and climate change due to its greenhouse effect [1]. Hence, reducing emission of CO₂ is of utmost importance for sustainable development, and various

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strategies, such as CO₂ capture [2,3], storage [4], separation [5], recycling utilization [6–8], and the controlled photobiosynthesis [9–13], have been used to achieve this goal. Among them, chemical conversion and utilization of CO₂ to a variety of value added products is a more attractive and promising solution [14].

CO₂ hydrogenation can produce a wide range of chemicals including hydrocarbon, higher alcohols and liquid fuels. Among these reactions, CO₂ methanation (CO₂ + 4H₂ → CH₄ + 2H₂O, ΔH_{298 K} = −165.0 kJ mol^{−1}) is an important catalytic process with both fundamental academic interest and viable commercial application [6,15–18]. In this reaction, the eight-electron reduction of CO₂ to CH₄ by hydrogen is difficult due to its significant kinetic limitation, which requires the CO₂ methanation catalyst to possess acceptable catalytic activity and selectivity [19]. The Ni-based catalysts have been widely investigated due to the low cost and relatively high catalytic activity [20], while the more active and selective materials for this reaction are supported noble metal-based catalysts [21–23]. For example, Ru/RuO_x/TiO₂ [19], and Rh/γ-Al₂O₃ [24] can be active for CO₂ methanation at ambient temperature and pressure. However, the high cost of noble metal has restricted their use as the methanation catalysts. Lately, the functionalized iron tetraphenylporphyrin has been reported to be the highly active catalyst for CO₂ methanation under mild conditions, while there are also some shortcomings for these metal complexes such as harsh preparation processes and poor thermal stability at high temperatures [18].

Recently, the addition of Ru as the doped metal to Ni-based catalyst forming bimetallic catalyst has been proposed as an effective strategy to improve the catalytic activity and stability for some reactions [25–27]. The dispersion of active Ni and Ru species over the Ni–Ru bimetallic catalyst is crucial for the activity and selectivity for CO₂ methanation [26]. The bimetallic Ni–Ru dispersion is relevant to their real state which may be very complicated. Lange et al. observed that bimetallic Ni–Ru/ZrO₂ catalysts with low Ni–Ru loadings were in the form of highly dispersed alloys but higher Ni–Ru loadings led to segregation and agglomeration of Ni particles [27]. In addition, the surface composition as well as geometric factor of NiRu bimetal also played important part in the improvement of the catalytic performance [25,28]. Polanski et al. reported that the catalyst with an oxide passivation layer on the surface of nano-Ru/Ni catalyst appeared to be highly productive and efficient at low temperature for CO₂ methanation [25]. Moreover, the addition of Ru could improve the sulfur tolerance of the supported Ni catalyst when the S species binded with both Ni and Ru atoms simultaneously [28]. In short, the enhanced activity by the bimetallic/alloy catalysts over their monometallic counterpart was argued to occur due to the synergistic effect between two metals. However, the sintering of metal nanoparticles at high temperatures could be severe especially over the bimetallic catalysts prepared by the conventional method such as impregnation or precipitation method. Besides, how the synergistic effect alters the structural and chemical property of the bimetallic catalysts, and the key factors of the bimetallic catalysts that improve the catalytic activity need to be understood. Hence, the catalytic activity and stability of the bimetallic catalyst should be further improved.

As we know, the presence of basic centers in catalysts can promote CO₂ chemisorption, which is beneficial to accelerate the reaction rate of CO₂, resulting in their enhanced catalytic activities [29–34]. CaO, a typical alkaline earth metal oxide, has been widely used as an excellent promoter for various catalysts owing to its large CO₂ chemisorption capacity [35–39]. Thus, the simultaneous addition of Ru and CaO species to Ni-based catalyst may further enhance its catalytic activity for CO₂ methanation.

Confinement effect of the ordered mesostructure is an efficient strategy to improve the stability of the metal catalyst. The ordered mesoporous catalysts can not only confine active metal nanoparticles in a fixed space to inhibit their sintering, but also offer high surface areas for the high dispersion of active metals, thus promising to enhance both the activity and stability of the catalysts [40–43]. The ordered mesoporous Ni-based catalysts have exhibited high anti-sintering property for high-temperature reactions, such as CO methanation [44–46] and CH₄ dry reforming [38,47–50], while its application for CO₂ methanation has been few reported [51].

Continuing our research work on catalysis [52–57], especially to simultaneously improve both the catalytic activity and stability of the Ni catalyst for CO₂ methanation, the ordered mesoporous NiRu-doped CaO–Al₂O₃ nanocomposites were synthesized. In order to know how the Ru–Ni synergistic effect and CaO promoter impact the catalytic activity and stability as well as the intercorrelation of structure and performance of the catalysts, a series of characterizations and activity evaluations were carried out in this work.

Experimental

Synthesis

The ordered mesoporous NiRu-doping CaO–Al₂O₃ nanocomposites were prepared by the one-pot evaporation induced self-assembly (EISA) method reported in our previous works [41,42]. Typically, 2.5 g P123 was dissolved in 40.0 mL of anhydrous ethanol, followed with addition of 3.3 mL 67 wt% nitric acid, 4.08 g Al(OPr)₃ and stoichiometric quantities of Ni(NO₃)₂·6H₂O, Ru(acac)₃ and Ca(NO₃)₂·4H₂O in sequence under vigorous stirring at room temperature. After 5 h, the mixture was transferred to a Petri dish to undergo the slow EISA process at 60 °C for 48 h in an oven. Finally, the obtained gel was calcined at 550 °C for 4 h with a heating rate of 1 °C min^{−1}. The samples were denoted as 10N-OMA, 10N1R-OMA, and 10N1R2C-OMA with the NiO, RuO₂, and CaO contents fixed at 10, 1 and 2 wt%, respectively. In addition, 1R-OMA doped with 1 wt% RuO₂ was also prepared as the reference sample using the same process above. Moreover, the complex of NiO and RuO₂ (10N1R) with the weight ratio of 10: 1 was prepared by the calcination of the milled Ni(NO₃)₂·6H₂O and Ru(acac)₃ mixture at 550 °C for 4 h.

Characterization

The morphology of the samples was observed by TEM and HAADF-STEM (Tecnai G2 F20 U-TWIN, FEI, USA) under a working voltage of 200 kV equipped with EDS. BET

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