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CO₂ methanation over Co–Ni bimetal-doped ordered mesoporous Al₂O₃ catalysts with enhanced low-temperature activities

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ABSTRACT

The Ni based catalysts have been considered as potential candidates for the CO₂ methanation owing to the low cost. However, the poor low-temperature catalytic activities limit their large-scale industrial application. In order to address this challenge, a series of Co–Ni bimetal doped ordered mesoporous Al₂O₃ materials have been designed and fabricated via the one-pot evaporation induced self-assembly strategy and employed as the catalysts for CO₂ methanation. It is found that the large specific surface areas (up to 260.0 m²/g), big pore volumes (up to 0.59 cm³/g), and narrow pore size distributions of these catalysts have been successfully retained after 700 °C calcination. The Co and Ni species are homogeneously distributed among the Al₂O₃ matrix due to the unique advantage of the one-pot synthesis strategy. The strong interaction between metal and mesoporous framework have been formed and the severely thermal sintering of the metallic Co–Ni active centers can be successfully inhibited during the processes of catalyst reduction and 50 h CO₂ methanation reaction. More importantly, the synergistic effect between Co and Ni can greatly enhance the low-temperature catalytic activity by coordinating the activation of H₂ and CO₂, prominently decreasing the activation energy toward CO₂ methanation. As a result, their low-temperature activities are evidently promoted. Furthermore, the effect of the Co/(Co + Ni) molar percentage ratio on the catalytic property has been also systematically investigated over these catalysts. It is found that only the catalyst with appropriate ratio (20.0%) behaves the optimum catalytic performances. Therefore, the current Co–Ni based ordered mesoporous materials promise potential catalysts for CO₂ methanation.

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Introduction

With the prosperous development of the CO₂ activation and resource utilization researches, the CO₂ methanation process has become a rather attractive topic. In 1902, Sabatier et al. firstly reported the CO₂ methanation reaction (also known as the Sabatier reaction, CO₂(g) + 4H₂(g) → CH₄(g) + 2H₂O(g), ΔH_{298K} = −165.4 kJ/mol, ΔG_{298K} = −130.8 kJ/mol) [1]. This process can convert renewable hydrogen energy from biomass, solar energy, etc. to methane and transport the methane through the existing natural gas transporting pipeline network, which is one of the most promising approaches for large-scale chemical utilization of CO₂ [2–6]. Besides, this reaction is a thermodynamically favorable process with a negative Gibbs free energy change in a fairly wide temperature range. Compared with the processes of hydrogenation of CO₂ to lower alcohols, dimethyl ether, etc., CO₂ methanation can theoretically achieve high CO₂ conversion and high catalytic selectivity to methane under milder reaction conditions with lower energy consumption [7–9]. However, the reduction of the CO₂ (+4) to the CH₄ (−4) is an eight-electron process with high kinetic energy barrier [7,10]. Therefore, efficient catalysts are usually required to achieve high conversion of CO₂ in the low reaction temperature range. Furthermore, this process is also a strongly exothermic process and the hot spot is often present in the catalyst bed, which can easily lead to thermal sintering of the metallic active center and result in rapid deactivation of the catalyst [10,11]. Previous studies have shown that almost all of the Group VIII transition metal elements are active toward this catalytic process [7,12]. Although noble metal series (Rh, Ru, Pt, etc.) catalysts have superior low-temperature catalytic activity and selectivity, their high price and rarity have greatly limited their scaled application. Cobalt based catalysts usually perform superior low-temperature catalytic activity; however, the selectivity of CH₄ over them is usually low [13]. As a contrast, Ni-based non-precious metal-based catalysts have attracted increasing attention because of excellent high-temperature catalytic activity and low cost [12]. However, their low-temperature catalytic activity and selectivity are expected to be further improved. Besides, the Tammann temperature of metallic Ni-based catalysts is relatively low (590 °C) and the sintering of metallic active centers is liable to cause rapid deactivation of the catalyst during the reaction process [14,15]. Therefore, the development of a sort of Ni-based non-precious metal based CO₂ methanation catalysts with excellent catalytic activity, selectivity and stability under low reaction temperature conditions is of great significance and is also a research spotlight as well as challenge in this research field.

Based on the challenges confronted by Ni-based catalysts for CO₂ methanation, the developing trend of this type of catalyst can be summarized as the following two aspects: the improvement of the low-temperature catalytic activity and the enhancement of the anti-sintering property of the Ni based catalysts. In order to improve the low-temperature catalytic activity of Ni-based catalysts, the researchers have carried out lots of work through the expansion of catalytic carrier types [16,17], the addition of dopants [18–20], the preparation of bimetallic catalysts [21–25], the improvement

of preparation methods [6,26], etc. As a result, the low-temperature catalytic activity of the catalysts can be markedly promoted by improving the dispersion of metallic Ni active centers and the activation ability of the reactants. Among these strategies, the addition of the secondary metal to Ni based catalysts has been recognized as a simple and promising method to improve the low-temperature catalytic activity and stability. For example, Ren et al. designed a series Ni-M/ZrO₂ (M = Fe, Co, Cu) bimetallic catalysts for the CO₂ methanation reaction [21]. It is found that the catalyst doped by 3 wt% of Fe performs the best low-temperature catalytic activity by facilitating the adsorption and activation of hydrogen molecules. The reason for this can be attributed to the synergistic effect between Ni and Fe, which evidently enhances the electron-donating ability of the catalyst and promote the reducibility of active centers and supports. Zhen et al. developed a sort of Ni–Ru/Al₂O₃ bimetallic catalysts for the CO₂ methanation reaction [23]. It is found that the segregation phenomenon of Ru occurred on the catalyst surface in the co-impregnation preparation process, by which more active Ni and Ru species (metallic Ru) could be exposed over the surface of Ni–Ru catalyst. As a result, the catalysts exhibited superior low temperature catalytic activity and no deactivation after 100 h stability test. Besides, Zhu et al. found that the addition of Co as the second metal to Ni/Ce_xZr_{1-x}O₂ catalysts could improve the low-temperature catalytic activity toward CO₂ methanation due to the Co–Ni synergistic effect [27]. However, the sintering of the metallic active centers at high reaction temperatures cannot be effectively avoided over the catalysts fabricated by conventional methods, such as impregnation and precipitation methods. In order to overcome the inherent limitations of traditional CO₂ methanation catalysts, designing and constructing a new catalyst system that can provide sufficient active centers for gaseous reactants as well as can firmly confine the metallic active centers is the key measure to solving the problem. Inspired by this guideline, a series of Ni based ordered mesoporous catalysts with large specific surface areas and big pore volumes have been synthesized and utilized as the catalysts for CO₂ methanation [28–30]. For these mesoporous catalysts, more accessible Ni active centers are exposed to the gaseous reactants. At the same time, metallic Ni active centers can also be stabilized by ordered mesoporous framework during the processes of reduction and methanation reaction. As a result, they perform higher catalytic activities than the traditional supported catalysts and the serious thermal sintering of the metallic Ni active centers could be successfully inhibited by the confinement effect of the mesostructure. However, their low-temperature catalytic activities were far away from the thermodynamic equilibrium values, which demanded further improvement.

In order to further promote the low-temperature catalytic activity, a series of Co–Ni bimetal-doped ordered mesoporous Al₂O₃ composite oxides with different Co/(Co + Ni) molar percentage ratios are designed and fabricated by one-pot evaporation-induced self-assembly (EISA) method. The obtained materials with outstanding structural properties are employed as catalysts for CO₂ methanation, which can provide sufficient accessible metallic active sites for gaseous feedstock. Besides, the Co and Ni active centers are

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