



CO₂ methanation over Ca doped ordered mesoporous Ni-Al composite oxide catalysts: The promoting effect of basic modifier



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ABSTRACT

Ni is usually used as the catalyst for the CO₂ methanation to generate the substitute natural gas (SNG) due to the low cost. However, it often possesses relatively worse low-temperature catalytic activity than the noble metal counterparts. In order to solve this problem, a series of Ca doped Ni based ordered mesoporous materials had been facilely fabricated via the one-pot evaporation induced self-assembly (EISA) strategy and directly used as the catalysts for CO₂ methanation. These materials had been systematically characterized by XRD, N₂ adsorption-desorption, TEM, SAED, EDS, XPS, H₂-TPR, and CO₂-TPD measurements. It was discovered that the large specific surface areas (210.7–240.7 m²/g), big pore volumes (0.37–0.46 cm³/g), and narrow pore size distributions (8.3–9.5 nm) of these materials had been successfully retained after 700 °C calcination. In these materials, Ni species were homogenously dispersed among the Al₂O₃ matrix via the one-pot fabrication strategy and the strong interaction between Ni and mesoporous framework had been formed. Thus, the seriously thermal sintering of the metallic Ni nanoparticles could be successfully inhibited. Hence, they displayed no deactivation after 50 h stability test toward CO₂ methanation. More importantly, the doping of the Ca greatly enhanced the surface basicity, which could favor the chemisorption and activation of CO₂. As a result, the apparent activation energies of CO₂ could be remarkably decreased from 75.2 to 53.6 kJ/mol and the low-temperature catalytic activity had been significantly promoted. Therefore, these Ca doped Ni based ordered mesoporous materials promised potential catalysts for CO₂ methanation.

1. Introduction

In recent years, the anthropogenic emission of CO₂ drastically increases because of the combustion of the fossil fuels and subsequently causes the global climate change via its greenhouse effect [1,2]. Thus, it is of great urgency as well as significance to reduce the CO₂ concentration in the atmosphere. The transformation of CO₂ into value-added fuels and chemicals is of great importance from the perspectives of recycling the CO₂ resource and processing the environmental issues [1,3,4]. The hydrogenation of CO₂ by sustainable hydrogen source to generate methane (CO₂ methanation), also known as Sabatier reaction, has been considered as one of the most promising CO₂ recycling utilization routes [5–8]. By means of this approach, CH₄ can be theoretically generated under mild conditions due to its thermodynamically favorable feature ((CO₂(g) + 4H₂(g) = CH₄(g) + 2H₂O(g),

$\Delta G = -173.1 + 0.1983T$ kJ/mol)) [5,7]. Nevertheless, the full reduction of the CO₂ (+4) into CH₄ (-4) is an eight-electron process with greatly kinetic barrier, which requires an efficient catalyst to achieve an acceptable CO₂ conversion, especially at low reaction temperature [5]. Therefore, the development of effective and stable catalysts is an important concern. Although the noble metal catalysts, such as Ru [9–12], Rh [13,14], and Pd [15,16], possess outstanding low-temperature catalytic activity as well as stability toward CO₂ methanation, their large-scale industrial application will be restricted due to the high cost. Therefore, it is more practical to design and develop Ni based non-noble transition catalysts with outstanding low-temperature activity [17–20], which has gradually attracted increasing attention for their comparable catalytic activity and availability.

Compared with the noble catalysts, the Ni based catalysts usually perform poorer low-temperature catalytic activity. Great efforts have

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been devoted to exploring the effective and stable Ni catalysts. For CO₂ methanation, it has been widely believed that the activation of the stable carbon dioxide molecule could finally determine the reaction rate of the whole reaction [1,5]. Therefore, the catalytic activity at low temperature was desirable to be improved through enhancing the process of CO₂ activation. Thus, the basic species, such as alkaline-earth and rare earth elements, have been doped into the catalysts by intensifying the chemisorption of the CO₂, which will further decrease the activation energy of CO₂ [21–23]. The influences of the basic categories and quantities have been extensively investigated. It has been found that the promoting effect of the basic modifier on the catalytic performance is greatly determined by its surface properties, such as intensity, type, etc [23–26]. Pioneering literatures confirmed that the basic modifier could initiate the methanation reaction by binding a CO₂ molecule to form the carbonate species by ambient-pressure XPS, in situ DRIFT characterizations, and DFT calculations, which would be followed by hydrogenation with dissociated hydrogen to generate methane [9,23,27]. For example, Liu et al. reported that the Ni_x/Mg_{2-x}Al-MMO (mixed metal oxides, MMO) catalysts with hydrotalcite structure exhibited enhanced low-temperature catalytic activities toward CO₂ methanation [23]. They found that the incorporation of Mg alkaline promoter could remarkably intensify the medium-strong basic sites, which served as the active sites for converting CO₂ into carbonate/hydrocarbonate intermediates. This could decrease the energy barrier for CO₂ activation, finally accounting for enhanced low-temperature activity.

The activation of the H₂ molecule is also another important concern for enhancing the catalytic activity and CH₄ selectivity toward CO₂ methanation. It is widely believed that the H₂ molecule is dissociated over the surface of metallic Ni active sites [19,28], which is greatly influenced by the metal dispersion. The high dispersion of the metallic Ni is beneficial to the facile dissociation of the H₂ by exposing sufficient active sites [19]. In order to improve the dispersion of Ni based catalysts, the porous materials are commonly selected as the candidates of catalytic supports. For instance, Du et al. reported that the excellent catalytic performance (96.0% CH₄ selectivity, 91.4 g/(kg h) space-time yield) comparable to Ru/SiO₂ catalyst could be achieved over 1%Ni/MCM-41 catalyst (1140 m²/g) at a space velocity of 5760/(kg h) owing to the high dispersion metallic Ni up to 100% [29]. Zhen et al. reported the CO₂ methanation over Ni/MOF-5 (2961 m²/g) and Ni/MIL-101 (3297 m²/g), on which 41.8% and 42.3% metal dispersion could be achieved [30,31]. As a result, the highly dispersed Ni nanoparticles confined in metal-organic frameworks of MOF-5 and MIL-101 endowed these catalysts with enhanced low-temperature catalytic activities (e.g. 47.2% CO₂ conversion at 280 °C over Ni/MOF-5) and excellent stabilities as long as 100 h. Therefore, the high dispersion of Ni can be facilely obtained by employing porous materials as supports, which will subsequently contribute to the promotion of the catalytic performances. Based on this viewpoint, the ordered mesoporous Ni-Al composite oxide catalyst for CO₂ methanation has already been designed and synthesized via one-pot evaporation induced self-assembly (EISA) strategy in our previous study [32], where the Ni active sites were homogeneously embedded among the Al₂O₃ matrix. The tiny metallic Ni nanoparticles could be obtained by the *in-situ* reduction and stabilized by the confinement effect of the mesoporous framework. Therefore, compared with the conventional Ni/γ-Al₂O₃ supported catalyst, the NiO-Al₂O₃ mesoporous catalysts displayed much better catalytic activity and stability.

In this work, so as to further improve the low-temperature catalytic activity of ordered mesoporous Ni-Al catalyst, the Ca basic promoter has been successfully doped into the mesoporous framework via the one-pot EISA strategy. The final Ca doped ordered mesoporous Ni-Al composite oxides with different Ca/Al molar ratios (0–10%) were carefully characterized by various techniques and directly used as the catalysts for CO₂ methanation. The introduction of Ca could dramatically increase the surface basicity based on CO₂-TPD analysis, which

would intensify the capacity of CO₂ chemisorption. As a result, compared with the pristine Ni-Al reference catalyst, the low-temperature catalytic activities of the Ca modified catalysts had been noticeably promoted. Furthermore, the kinetic investigation indicated that the doping of Ca could greatly decrease the apparent activation energies. Besides, these ordered mesoporous catalysts displayed excellent stability up to 50 h without deactivation due to the outstanding anti-sintering property of the metallic Ni via the confinement effect of mesoporous framework. Generally, the cooperative effect between the Ni active site and Ca basic promoter synergistically contributed to the enhanced catalytic performance.

2. Experimental

2.1. Materials

The anhydrous C₂H₅OH (Sinopharm Chemical Reagent Co. Ltd.), (EO)₂₀(PO)₇₀(EO)₂₀ triblock copolymer (Pluronic P123, Mn = 5800, Sigma-Aldrich), 67% HNO₃ (Sinopharm Chemical Reagent Co. Ltd.), aluminum isopropoxide (C₉H₂₁AlO₃, 98 + %, Sigma-Aldrich), Ni(NO₃)₂·6H₂O (Sigma-Aldrich), Ca(NO₃)₂·4H₂O (Sigma-Aldrich) were employed as the solvent, structure directing agent (SDA), acid modifier, and precursors, respectively. All of the chemicals were directly employed without further purification.

2.2. The synthesis of the Ca doped ordered mesoporous Ni-Al composite metal oxides

The Ca doped ordered mesoporous Ni-Al composite oxides with various Ca/Al molar ratios were fabricated by improved one-pot EISA strategy reported elsewhere [33–35]. In these materials, the Ni/Al molar ratios were fixed at 10% and the Ca/Al molar ratios were controlled at x% (x = 0, 1, 3, 5, 8, and 10), respectively. These mesoporous materials were denoted as OMA-10Ni_xCa, where the “OMA”, “10”, and “x” referred to the “mesoporous alumina matrix”, “Ni/Al molar ratio”, “Ca/Al molar ratio”, respectively. In a specific synthesis procedure, 1.0 g P123 was completely dissolved in 20.0 mL anhydrous ethanol with vigorous agitation. 1.6 mL 67% HNO₃, 10 mmol Al(iso-OPr)₃, 1 mmol Ni(NO₃)₂·6H₂O, and certain amounts of Ca(NO₃)₂·4H₂O were sequentially added into the above P123-ethanol solution and vigorously stirred for 5 h. The obtained transparent solution was transferred into a 60 °C convection oven with low relative humidity (< 50%) to conduct the EISA process for 48 h. The obtained xerogels were further calcined at 700 °C for 5 h with 1 °C/min ramping rate in Muffle furnace under static air atmosphere. Finally, these OMA-10Ni_xCa materials would be directly investigated as the catalysts for CO₂ methanation.

2.3. Catalysts characterization

Small-angle (0.5–5.0°) and wide-angle (20–80°) powder X-ray diffraction (XRD) patterns of the samples were obtained on a PANalytical X'pert Pro multipurpose diffractometer, using Ni-filtered Cu Kα radiation (λ = 0.15046 nm) at 40 kV voltage, 40 mA current, and a step size of 0.02°/s. N₂ adsorption-desorption analyses were carried out using a Quantachrome NOVA 2200e instrument with two analysis stations. Prior to N₂ adsorption, the samples were outgassed at 200 °C for 4 h to desorb moisture and impurity on the surface of the sample. Metal elements analysis was carried out using an Optima 7300DV (Perkin Elmer) inductively coupled plasma-atomic emission spectrometer (ICP – AES). Transmission electron microscopy (TEM) observation, selected area electron diffraction (SAED), and energy-dispersive spectroscopy (EDS) were carried out on a JEOL 2010F transmission electron microscope under a working voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analyses of the catalysts were carried out on a VG ESCALAB 210 (Thermo Scientific) spectrometer. The fresh catalyst powder was loaded on sample holder with the conductive adhesive tape. The binding

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