Full Length Article

Ni/Al$_2$O$_3$-ZrO$_2$ catalyst for CO$_2$ methanation: The role of γ-(Al, Zr)$_2$O$_3$ formation

Yingying Zhan[a], Yangyan Wang[a], Dongmei Gu[a], Chongqi Chen[a,*], Lilong Jiang[a,*], Katsuomi Takehira[b]

[a] National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Gongye Road 523, Fuzhou 350002, Fujian, China
[b] Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

ARTICLE INFO

ABSTRACT

CO$_2$ methanation could offer significant energy and environment benefits if efficient catalyst is developed. Ni-based catalyst is the most promising catalyst for this reaction. Herein, a series of ZrO$_2$ doped Ni/Al$_2$O$_3$ catalysts were fabricated by a co-precipitation method, and their reactivities with respect to the CO$_2$ methanation were evaluated. Catalytic activities of the ZrO$_2$-doped Ni/Al$_2$O$_3$ catalysts for CO$_2$ methanation are superior to the undoped one. Characterization results suggest that γ-(Al, Zr)$_2$O$_3$ solid solution is formed after the introduction of ZrO$_2$, which results in weakening the NiO-Al$_2$O$_3$ interaction and inhibits the formation of spinel NiAl$_2$O$_4$. After activated by hydrogen reduction, those ZrO$_2$-doped NiO/Al$_2$O$_3$ catalysts show smaller Ni nanoparticles sizes, and the one doped with 16 wt% ZrO$_2$ (Ni/AZ16) possesses the smallest sizes of Ni nanoparticles and shows the highest reactivity in the CO$_2$ methanation.

1. Introduction

Carbon dioxide (CO$_2$) is one of the main contributors to greenhouse effect with consequent climate change, therefore, growing efforts are put in to control the accumulation of atmospheric CO$_2$. The most commonly studied technology is Carbon Capture and Sequestration (CCS) that consists capture, transportation and underground storage [1]. However, because CO$_2$ turns out to be an attractive C1 building block, conversions of CO$_2$ to a variety of value added products, e.g. methanol [2] or methane [3], are considered to be more attractive routes.

CO$_2$ methanation (CO$_2$ + 4H$_2$ ↔ CH$_4$ + 2H$_2$O, ΔH$_{298}$ = −165 kJ/mol) is one such route where CO$_2$ is converted to value added CH$_4$, which is a promising building block for chemicals production or directly uses as fuels [4]. CO$_2$ methanation is a catalytic reaction based on supported VIII group metals (e.g., Ru, Rh, Co, Fe, Ni) on various oxide supports [5–7]. Ni-based catalysts are the most widely studied materials due to its low cost and good catalytic activity towards CO$_2$ methanation [8–10]. Both reducible and inert oxides can be used as catalyst supports. Ni catalysts supported on reducible supports CeO$_2$ or CeO$_2$-ZrO$_2$ with abundant oxygen vacancies are effective in CO$_2$ or oxygen species adsorption, showing highly catalytic activity [11,12]. Al$_2$O$_3$ and SiO$_2$ are inert supports for Ni-based catalysts [13,14], and the Ni/Al$_2$O$_3$

catalyst, either alone or with addition of promoters [13,15], is currently the most widely investigated systems for CO$_2$ methanation.

Metallic nickel (Ni^0) in Ni/Al$_2$O$_3$ catalyst is supposed to be active species for CO$_2$ methanation, and the Ni^0 with small particle size shows highly catalytic activity and selectivity [16]. NiAl$_2$O$_4$ can be formed during high temperature calcination of Ni/Al$_2$O$_3$ catalysts, and the amount of NiAl$_2$O$_4$ increased upon decreasing the Ni/Al ratio [17]. NiAl$_2$O$_4$ was proved to be effective in enhancing the stability of Ni nanoparticles, owning to its spinel structure, whereas the formation of NiAl$_2$O$_4$ results in decreasing the amount of active Ni^0 [17]. Therefore, in order to improve the catalytic performance of Ni/Al$_2$O$_3$ catalyst with low Ni/Al ratio, an optimized amount of NiAl$_2$O$_4$ formation is desirable. It was stressed by Aghayan et al. [16] that NiO with average particle size of 4 nm was formed on the surface of Al$_2$O$_3$; this Al$_2$O$_3$ is covered by a NiAl$_2$O$_4$ nanolayer, which prevented the NiO from reacting with Al$_2$O$_3$ to form more NiAl$_2$O$_4$; in this way, the catalyst stayed active and stable for CO$_2$ methanation.

ZrO$_2$ is soluble in γ-Al$_2$O$_3$ to form amorphous polymer-like structure γ-(Al, Zr)$_2$O$_3$ solid solution on the surface of Al$_2$O$_3$ [19,20]. ZrO$_2$ along with TiO$_2$ and CeO$_2$ were introduced into γ-Al$_2$O$_3$ as support for Ni-based CO$_2$ methanation catalyst [21], and it was found that the reducibility nature of the catalyst was improved, consequently better catalytic performance was achieved. However, to the best of our

knowledge, the effect of γ-(Al, Zr)$_2$O$_3$ on γ-Al$_2$O$_3$ supported Ni-based catalyst is still not unraveled. In this contribution, a series of Ni/Al$_2$O$_3$ catalysts modified by different amount of ZrO$_2$ utilizing co-precipitation method were prepared. Their catalytic performances with respect to CO$_2$ methanation were investigated. The physicochemical properties of those catalysts were characterized by XRD, N$_2$-physisorption, H$_2$-TPR, TEM, DRS and XPS techniques. The effect of the doping amount of ZrO$_2$ on the catalyst structures and their catalytic performances for CO$_2$ methanation was discussed in detail. It is reported for the first time that the formation of γ-(Al, Zr)$_2$O$_3$ solid solution weakens the interaction between NiO and Al$_2$O$_3$ and inhibits the formation of NiAl$_2$O$_4$. The ZrO$_2$ modified Ni/Al$_2$O$_3$ catalysts show higher catalytic activities towards CO$_2$ methanation than the undoped one.

2. Experimental

2.1. Catalyst preparation

Materials: Analytical grade nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O), zirconium nitrate (Zr(NO$_3$)$_4$·5H$_2$O), polyethylene glycol (PEG), and sodium carbonate (Na$_2$CO$_3$) were purchased from Shanghai Chemical Reagent Ltd. and used without further purification.

Synthesis: ZrO$_2$-doped Ni/Al$_2$O$_3$ catalysts were prepared by a co-precipitation method: Ni(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and Zr(NO$_3$)$_4$·5H$_2$O were dissolved in 200 mL of deionized (DI) water together with an appropriate amount of PEG. The mixed aqueous solution was co-precipitated with an aqueous solution of 1 mol/L Na$_2$CO$_3$ at pH = 8.0 ± 0.2 at 60 °C under vigorous stirring. The resulting precipitates were aged at the same temperature for 16 h, filtered and washed with DI water, dried at 90 °C for 12 h. The powders were calcined at 800 °C for 4 h in static air. The as-prepared samples were denoted as NiO/AZX, where X represents the nominal content (wt.%) of ZrO$_2$ in ZrO$_2$-Al$_2$O$_3$, X = 0, 8, 12, 16, and 20. The samples reduced by 75 vol% H$_2$/N$_2$ (50 mL min^{-1}) at 750 °C for 1.5 h were denoted as Ni/AZX. The nominal Ni loading of the Ni/AZX catalysts was fixed at 15 wt%. Those samples calcined at 800 °C for 4 h followed by calcined at 1000 °C for 2 h were named as NiO/AZX-1000.

2.2. Catalyst characterizations

Powder X-ray diffraction (XRD) measurements were performed on a PANalytical X'pert Pro diffractometer using Co Kα radiation (λ = 0.1789 nm) at 40 kV and 40 mA for 2θ angles ranging from 20 to 100°.

N$_2$-physisoption was carried out on a Micrometeritics ASAP 2020 apparatus at liquid nitrogen temperature. Prior to analysis, samples were degassed at 300 °C for 3 h to a residual pressure of less than 10^{-5} Torr. The specific surface area was calculated by BET method and the pore size distribution was calculated by BJH method. Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai G2 F30 microscope at 300 kV. A few droplets of sample suspended in ethanol were placed on a carbon-coated copper grid followed by evaporation at ambient conditions.

UV–Vis Diffuse reflectance spectra (DRS) of the samples were measured on a Perkin-Elmer Lambda 950 UV–Vis-NIR spectrometer using BaSO$_4$ as a reference material within a range of 300–800 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific ESCALAB 250 spectrometer using Al Kα radiation (1486.6 eV). In order to compare all spectra recorded, the C 1s core level attributed to adventitious carbon present in the samples was used as a reference, whose binding energy was fixed at 284.6 eV. Peaks areas of Ni^{2+} including satellites were fitted using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley.

Temperature-programmed reduction (TPR) measurements were carried out on an AutoChem II 2920 instrument. The H$_2$-TPR was performed by passing 10 vol% H$_2$/Ar (30 mL min^{-1}) on 50 mg catalyst at a heating rate of 10 °C min^{-1}. Firstly, samples were pretreated under O$_2$ atmosphere at 300 °C for 30 min and purged with Ar atmosphere at 300 °C for 30 min. Then the system was cooled down to ambient temperature under Ar atmosphere. The effluents were monitored by a thermal conductivity detector (TCD).

2.3. Catalytic activity test

CO$_2$ methanation catalytic activity tests were carried out in a continuous fixed-bed flow reactor under atmospheric pressure from 300 to 550 °C. The reaction was started by using 0.1 g catalyst mixed with 0.5 g quartz with similar sizes (40–60 mesh) in a space velocity of 40,000 mL h^{-1} g$_{cat}^{-1}$, and the gas composition is as follows: 72 vol% H$_2$, 18 vol% CO$_2$ and 10 vol% N$_2$, with a flow rate of 67.0 mL min^{-1}. Prior to activity test, catalysts were pre-reduced at 750 °C in 75 vol% H$_2$/N$_2$ (50 mL min^{-1}) for 1.5 h, and then cooled down to 300 °C purging with N$_2$. The effluents were analyzed online by gas chromatograph (Shimadzu GC-2014C) equipped with FID and TCD.

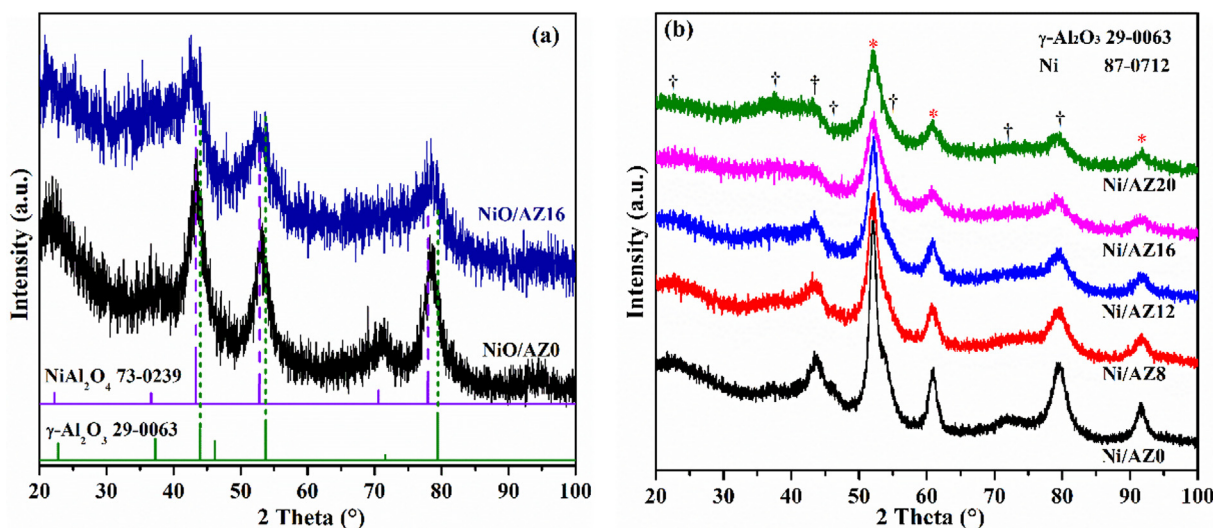**Fig. 1.** XRD patterns of the as-prepared NiO/Al$_2$O$_3$-ZrO$_2$ catalysts calcined at 800 °C (a) and followed by reduction at 750 °C for 1.5 h (b).