



## Full Length Article

# CeO<sub>2</sub>-assisted Ni nanocatalysts supported on mesoporous $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the production of synthetic natural gas



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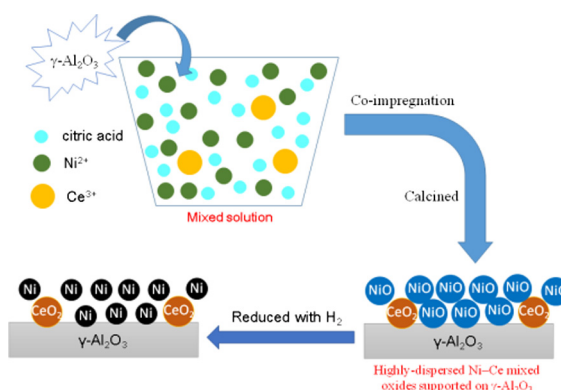
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## HIGHLIGHTS

- NiO-*x*CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by co-impregnation with citric acid.
- CeO<sub>2</sub> addition could lower metallic Ni particle sizes and generate oxygen vacancies.
- NiO-*x*CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts showed 100% CH<sub>4</sub> selectivity for CO<sub>2</sub> methanation.
- Equilibrium conversion of CO<sub>2</sub> was achieved at a low temperature of 300 °C.

## GRAPHICAL ABSTRACT

Mesoporous  $\gamma$ -alumina-supported highly dispersed Ni-Ce oxides were prepared for CO<sub>2</sub> methanation under lower reaction temperature.



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## ABSTRACT

Ni-Ce oxides (NiO-*x*CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) supported on mesoporous  $\gamma$ -alumina with various mass percentage contents of CeO<sub>2</sub> (*x* = 0, 1, 2, 3, 4 and 5) were prepared through co-impregnation with citric acid. The influences of CeO<sub>2</sub> content on the catalyst structure, surface characteristics, interaction between Ni species and the support, reducibility of Ni<sup>2+</sup> ions and Ni particle dispersion were investigated in detail. The Ni-Ce oxides were highly dispersed on mesoporous  $\gamma$ -alumina and producing uniform Ni nanoparticles throughout  $\gamma$ -alumina frameworks after H<sub>2</sub> reduction. The addition of CeO<sub>2</sub> could lower metallic Ni particle sizes and generate oxygen vacancies. The reduced Ni-*x*CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were investigated for their catalytic behaviors in CO<sub>2</sub> methanation and exhibited excellent catalytic performance at low temperature in the range of 150–350 °C. Equilibrium conversion of CO<sub>2</sub> was achieved at a low temperature of 300 °C over the optimal CeO<sub>2</sub> content of 3 wt%.

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## 1. Introduction

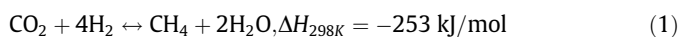
Natural gas, mainly of methane, is preferred potential fossil fuels due to its ready availability, high energy density and conversion efficiency, well-established distribution infrastructures, and smoke- and slag-free composition. In recent years, the consump-

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tion of natural gas is the world's fastest growing energy. Production of synthetic natural gas has attracted more and more attention due to exhaustion of natural gas and rising price [1]. The synthetic natural gas production *via* CO<sub>2</sub> methanation process can not only produce fuels and chemicals, but also enhance the reduction of greenhouse gas emissions to the atmosphere [2–4]. Furthermore, this reaction has a wide range of applications, such as the application in the future with respect to manned space exploration on Mars by converting the Martian CO<sub>2</sub> atmosphere into methane and water for astronaut life-support systems, the purification of synthesis gas for the synthesis of ammonia, etc [5,6].

CO<sub>2</sub> methanation, also called the Sabatier reaction, is the most advantageous reaction with respect to thermodynamics ( $\Delta G_{298K} = -130.8 \text{ kJ mol}^{-1}$ ) among CO<sub>2</sub> conversion reactions [7–8]. However, this process is an eight-electron process with significant kinetic limitations. It remains a great challenge to develop a catalyst with acceptable CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity under lower reaction temperature.



In recent years, a considerable amount of studies have been conducted on the hydrogenation of CO<sub>2</sub> to methane. It has been widely believed that noble- and transition-metal supported catalysts were active catalysts for CO<sub>2</sub> methanation [9–18]. Compared to noble-metal (such as Pd, Ru, Rh, etc.) and other transition-metals (such as Co, Fe, etc.), Ni/Al<sub>2</sub>O<sub>3</sub> catalysts remained the most widely investigated catalysts due to their higher activity and selectivity to methane, lower cost, chemical and physical stability, and high mechanical resistance [19–27]. However, the sintering of Ni nanoparticles and carbon deposition has easily appeared on the surface of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, which resulted in rapid deactivation. It has been shown that the structure and surface properties of the catalysts depend strongly on chemical composition and synthesis procedures, resulting in significant change in catalytic performance. Therefore, a great deal of effort has been made to improve the activity, stability, and resistance to coke formation of nickel-based catalysts through adding promoters, modifying catalyst supports, improving catalyst preparation routes, etc [6–10,28–33]. Generally, CeO<sub>2</sub> was often employed as the structural and electronic promoter in heterogeneous catalysts to improve the dispersion of Ni and change the properties of metal Ni through strong metal to support interactions [24–31].

Recently, we have successfully synthesized mesoporous  $\gamma$ -alumina with high surface area, pore volume, and narrow pore size distributions (PSD) through simple partial hydrolysis of Al(NO<sub>3</sub>)<sub>3</sub> aqueous solution with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> without organic surfactants [34]. In this work, CeO<sub>2</sub>-assisted Ni nanocatalysts with a high dispersion supported on mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared via co-impregnation with citric acid, which exhibited excellent catalytic activity, CH<sub>4</sub> selectivity and stability for CO<sub>2</sub> methanation. The effects of Ce content on the catalyst properties and catalytic behavior were intensively investigated. A comprehensive understanding was provided to optimally design an effective catalyst for CO<sub>2</sub> methanation.

## 2. Experimental

### 2.1. Catalyst preparation

All reagents were analytical-grade, purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without purification.

Mesoporous  $\gamma$ -alumina was prepared via one-pot template-free partial hydrolysis route, as proposed in our previous study [34]. Typically, 0.1 mol of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was dissolved in 50 mL of

deionized water at 70 °C, and was dropped slowly with 1 mol L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> aqueous solution under vigorous magnetic stirring until a formation of transparent gel, and then the gel beaker was covered with plastic film and aged at 30 °C for 48 h. After this, the crude gel was dispersed in an open glass dish at 100 °C for 24 h. The as-prepared solid was treated at 200 °C in air for 10 h to remove ammonium nitrate, and further calcined at 500 °C for 10 h in air at a heating rate of 1 °C min<sup>-1</sup>.

Mesoporous  $\gamma$ -alumina supported Ni–Ce oxides were prepared via co-impregnation with citric acid. In a typical synthesis, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, and required amounts of citric acid (CA), where the molar ratio of CA/(Ni + Ce) was fixed at 1, were dissolved in 10 mL of deionized water at room temperature. 5 g  $\gamma$ -alumina was added in the above solution and stirred at room temperature for 2 h, and then continuously stirred at 80 °C until the water was evaporated out. The obtained solid was dried at 100 °C for 24 h and calcined at 500 °C for 5 h. The preliminary investigation indicated that  $\gamma$ -alumina-supported Ni–Ce catalysts containing 20wt% Ni loading showed the optimum catalytic performance for CO<sub>2</sub> methanation. Therefore, the loading of Ni in all the catalysts was fixed at 20 wt% in the present work. The  $\gamma$ -alumina supported Ni–Ce oxides with different Ce contents were denoted as NiO–*x*CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and read as Ni–*x*CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after H<sub>2</sub> reduction, where *x* represented the content of CeO<sub>2</sub> in wt%.

For comparison, the sample denoted NiO–3CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-imp, containing 20 wt% Ni, was prepared by an incipient impregnation method without citric acid.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder calcined at 500 °C was added into an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O under stirring and kept at ambient temperature for 2 h. The mixture was evaporated out at 80 °C and then dried at 100 °C overnight, and finally the solid was calcined at 500 °C for 5 h in air.

The other sample containing 20 wt% Ni, denoted NiO–3CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>\*</sup>, was usual  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Ni–Ce oxide, which was prepared via co-impregnation with citric acid. The usual  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was obtained by calcining SB pseudoboehmite powder (Condea) at 800 °C for 20 h with a heating rate of 1 °C min<sup>-1</sup>.

### 2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Rigaku D/Max-2550 diffractometer using Cu K $\alpha$  radiation at 40 kV and 200 mA. The crystallite sizes of metallic Ni were estimated using the full-widths at half maximum (FWHM) of the Ni (200) peak through the Scherrer equation [28,32].

N<sub>2</sub> adsorption and desorption isotherms were measured using a Micromeritics ASAP 2020 Sorptometer at liquid nitrogen temperature (–196 °C). Before the measurement, each sample was degassed at 250 °C for 6 h. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method in the P/P<sub>0</sub> range from 0.05 to 0.25. Pore size distribution curves were calculated using the desorption branch of the isotherms and the Barrett–Joyner–Halenda (BJH) method. The pore sizes were obtained from the peak positions of the distribution curves, and the average pore sizes were calculated by the BJH method. The pore volumes were taken at the P/P<sub>0</sub> = 0.990 single point.

TEM micrographs were obtained with a JEOL JEM-2010F field emission microscope operating at 200 kV. The sample was prepared by placing a drop of the ethanol solution of a well-ground catalyst powder on a carbon-coated copper grid (300 mesh), followed by evaporation of the ethanol. Size distributions of the Ni particles were obtained by counting ca. 200–250 particles in TEM images.

X-ray photoelectron spectra (XPS) of the samples were measured using an ESCALAB 250Xi spectrometer equipped with

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