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Mesoporous nickel catalyst supported on multi-walled carbon nanotubes for carbon dioxide methanation[☆]

Wei Wang^{a,b,c}, Wei Chu^{a,b,c,*}, Ning Wang^d, Wen Yang^a,
Chengfa Jiang^{a,**}

^a Department of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China

^b Institute of New Energy and Low-carbon Technology, Sichuan University, Chengdu 610225, Sichuan, China

^c Sichuan Provincial Engineering Technology Center for Environmental Protection Catalytic Materials, Chengdu 610064, Sichuan, China

^d Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

Nickel-based catalysts supported on multi-walled carbon nanotubes (CNTs) promoted with cerium were successfully synthesized by ultrasonic-assisted co-impregnation, using γ - Al_2O_3 as comparative support, and employed in the carbon dioxide methanation reaction. Results indicated that the exceptional properties of CNTs together with the accession of cerium effectively enhanced the dispersion of metallic nickel, promoted the reduction of metal oxides and accelerated the CO_2 activation. Meanwhile, the confinement effect of CNTs and the promotion effect of cerium could efficiently prevent the active species migration and sintering, and restricted the carbon deposition reaction. Catalytic performances exhibited that $12\text{Ni}4.5\text{Ce}/\text{CNT}$ catalyst possessed the highest activity with 83.8% conversion of CO_2 and almost 100% selectivity of CH_4 without obvious deactivation after 100 h stability test under reaction conditions.

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Introduction

The concentration of carbon dioxide in the atmosphere is continuously and dramatically increasing during the past

decades due to the burning of fossil fuels such as coal and oil, which inevitably poses a serious threat to human life and the global ecological environment, such as the increase of extreme weather, the raise of sea level and the growing global temperature [1–3]. Therefore, the feasible approaches to CO_2

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* Corresponding author. Department of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China. Tel.: +86 028 85403836; fax: +86 028 85461108.

** Corresponding author. Tel.: +86 028 85403836; fax: +86 028 85461108.

E-mail addresses: chuwei1965@scu.edu.cn (W. Chu), jiangcf@scu.edu.cn (C. Jiang).

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emission mitigation have received more and more attention [4,5]. Among viable solutions, great efforts have been made on two strategies: the CO₂ capture and storage [6,7] and the CO₂ chemical recycling [8,9]. It is obviously that recycling of CO₂ as a carbon source for value added chemical productions, such as methane [10], methanol [11] or polycarbonate [12], should be considered as a more sustainable use of global carbon resources, which can indeed lead to less consumption of fossil fuels [13,14].

Since the methanation of CO₂ was first discovered by Sabatier and Senderens in 1902s, it remains the most advantageous with respect to thermodynamics, because this reaction is considerably faster than the formation of other hydrocarbons or alcohols [15]. However, an eight-electron process is prerequisite to completely reduce the fully oxidized carbon to methane. Meanwhile, there are significant kinetic limitations, which require a catalyst to achieve acceptable rate and selectivity [16]. Group VIII metals such as Rh [17], Pd [18] and Ni [19] supported on various oxide supports like Al₂O₃ [20], SiO₂ [21], and CeO₂ [22] have been tested in this reaction. Among them, the nickel-based catalysts have been extensively investigated under various conditions for their comparative low price and relative high activity. However, they easily suffer from rapid deactivation due to carbon deposition and metal nickel sintering. Therefore, catalysts with preferable resistance to carbon deposition and excellent thermal stability properties are need for this reaction [23,24]. Recently, Rahmani et al. [25] reported that rare earth cerium promoter could improve the reducibility of the catalyst by changing the interaction between nickel and support due to the special electronic and structure effects, and the optimized catalyst with 2 wt.% of cerium promoter possessed the highest stability and activity with 80.3% conversion of CO₂ under the experimental conditions. Meanwhile, Ocampo and co-workers [26] revealed that the incorporation of nickel cations into the Ce_{0.72}Zr_{0.28}O₂ fluorite oxide improved the redox properties of the catalyst and restricted the metal sintering. Combined with the high oxygen storage capacity of the mixed oxide, the 10NiCe_{0.72}Zr_{0.28}O₂ catalyst achieved the best catalytic performance, ending up with 75.9% of CO₂ conversion and 99.1% of CH₄ selectivity after 150 h reaction test.

Carbon nanotubes have raised much interest due to their exceptional properties in recent years. As a new type of novel nano-carbon catalyst support, they have large specific surface areas and unique tubular structure, which can efficiently improve the dispersion of the active components and enhance the adsorption of reactants. Their outstanding confinement effect can effectively restrict the particle size of the encapsulated materials down to the nanometer scale and prevent their migration and agglomeration, which can modify the reduction property of the catalyst and the catalytic activity meaningfully [27,28]. Meanwhile, they possess excellent electrical conductivity, which can facilitate the electron transfer from active species and the support to the reactants [29]. Together with their favorable property for adsorption and spillover of hydrogen [30,31], carbon nanotubes may exhibit preferable catalytic performance in the methanation reaction.

In this work, based on our previous theoretical calculation [32] and experimental researches [33,34], CNTs was utilized as support and γ -Al₂O₃ as comparative carrier, and cerium

promoted nickel-based catalysts were also systematically prepared by ultrasonic-assisted co-impregnation method. The confinement effect and special electronic distribution of carbon nanotubes in conjunction with the promotion effect of cerium promoter ultimately endowed the 12Ni4.5Ce/CNT catalyst with the highest activity and stability for the CO₂ methanation.

Experimental

Catalyst preparation

Pretreatment of catalyst supports. Gamma aluminum oxide with particle size 40–60 mesh was activated by thermal treatment in air for 4 h at 500 °C with a heating rate of 5 °C/min. The raw multi-walled carbon nanotubes (outer diameter of 10–20 nm, Chengdu Organic Chemicals Co., LTD) were opened and purified by refluxing in concentrated HNO₃ (65–68 wt.%) at 140 °C for 14 h. After that, the mixture was diluted with deionized water, filtered, washed and dried at 110 °C overnight [35,36].

For the preparation of the catalysts, quantitative catalyst support was impregnated in a mixed aqueous solution with 70 vol.% ethanol containing the metal nitrate precursors Ni(NO₃)₂·6H₂O and/or Ce(NO₃)₃·6H₂O, sonication for 2 h at a power output of 120 W. Then the mixture was heated up to 80 °C in water bath until the liquid was completely evaporated [35,36]. The obtained samples were dried at 100 °C overnight and calcined at 350 °C for 4 h. The nominal nickel loading in the catalyst was fixed at 12 wt.%, while cerium loading was varied from 0 to 6 wt.%, resulting in catalytic systems: 12Ni/Al₂O₃, 12Ni4.5Ce/Al₂O₃, 12NixCe/CNT, where x represents the nominal content of Ce in wt.% (x = 0, 1.5, 3, 4.5, 6).

Catalyst characterization

The N₂ adsorption–desorption isotherms were measured at –196 °C using an automated surface area & pore size analyzer (Quantachrome NOVA 1000e apparatus). The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation, and the pore size distribution and average pore diameter were determined from desorption branch of isotherms using the Barrett–Joyner–Halenda (BJH) model.

The power X-ray diffraction (XRD) patterns were recorded on a DX-2700 diffractometer (Haoyuan, China) using Cu K α radiation at 40 kV and 30 mA. The 2 θ scanning range was from 10° to 90° with a scan step 0.03°/s in a continuous mode. Reduced catalysts were cooled down to room temperature in Ar atmosphere and immediately carried out XRD characterization.

The hydrogen temperature-programmed reduction (H₂-TPR) measurement was performed in a fixed-bed reactor at atmospheric pressure. 50 mg sample was loaded in the middle of the reactor tube, and the reduction gas of 5% H₂/N₂ with a total gas flow rate of 30 mL/min was introduced. The system was kept at 100 °C for 1 h until the baseline was stable, and then the temperature of the reactor was raised linearly from 100 °C to 800 °C at a heating rate of 5 °C/min. The H₂ uptake amount during the reduction was analyzed on-line by a SC-

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