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# Highly efficient $Ni/ZrO_2$ catalysts prepared via combustion method for $CO_2$ methanation

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ABSTRACT

The 15 wt% $Ni/ZrO_2$ catalyst was firstly synthesized using urea as the combustion medium, which shows high catalytic performance for $CO_2$ methanation due to its high reducibility and Ni dispersion, small Ni particle size and excellent $CO_2$ adsorption capacity. The $CO_2$ conversion of $Ni/ZrO_2$ prepared by the urea combustion method achieves 60% while the conversion of $Ni/ZrO_2$ using n-propanol as the combustion medium is less than 13% at 300 °C, 0.1 MPa and a WHSV of 48,000 $mL\cdot g^{-1}\cdot h^{-1}$. A series of catalysts were synthesized using different combustion mediums including ethanol, n-propanol, urea, glycol and glycerol. The prepared catalysts were characterized by BET, ICP-OES, XRD, $H_2$-TPR, $H_2$-TPD and $CO_2$-TPD. The results illustrate that the combustion mediums significantly affect the catalytic pore structure, interaction between active metal and support, Ni dispersion, Ni particle size, the crystal structure of $ZrO_2$ and $CO_2$ adsorption capacity. In addition, the synergistic effect between nickel and mediums leads to a total phase transformation of zirconia from m-$ZrO_2$ to t-$ZrO_2$. The 15Ni/$ZrO_2$ catalyst prepared by urea combustion method exhibits not only higher activity but also better stability due to its smaller Ni particle size and better resistance to carbon deposition than the one prepared by impregnation method.

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## 1. Introduction

In the 21st century, two of the biggest challenges are environmentally sustainable development and sustainable supply of natural resources. The two issues have direct bearings on the sustainable development of human society [1,2]. Fossil fuel reserves have being decreasing year by year and the natural environment is getting worse and worse. The increasing emission of $CO_2$ not only affects the environment but also causes a waste of carbon resources [3,4]. Therefore, the utilization of $CO_2$ compared with capture, storage and separation has aroused considerable attention. $CO_2$ methanation is a hot topic because of the great commercial value of methane ($CH_4$, the product of methanation) [5–7]. Due to the kinetic limitation, converting $CO_2$ to methane needs high reaction temperature and pressure. However, high temperature has a negative impact on $CO_2$ methanation which is an exothermic reaction. Therefore, abundant research efforts have been directed towards the development of catalysts for $CO_2$ methanation to reduce the reaction temperature and pressure. Precious metals such as Ru [8–13], Rh [14–17] and Pd [18,19] and transition metals for example Ni [20–24] are applied to $CO_2$ methanation as active metals. There are various supports such as $SiO_2$ [25,26], $Al_2O_3$ [27], $ZrO_2$ [28], $TiO_2$ [29] and $CeO_2$ [30]. Although noble metal-based catalysts have good catalytic activities of $CO_2$ methanation, their low reserve and high cost significantly limit the application of noble metals. Among transition metals, Ni is often preferred to be used as the active metal due to its low price and highly catalytic activity toward $CO_2$ methanation [31]. $ZrO_2$ as one of the transition metal oxides is widely used as the support or promoter for methanation reactions [32–35]. The $Ni/ZrO_2$ catalyst has been investigated for $CO_2$ methanation [36] and efforts have been devoted to improving catalytic activity by adding promoters or using different preparation methods. Some researchers focus on adding promoters including La [37], Co, Ru, Pd [38], Sm [39], Ce [40] and Fe [41] to enhance the catalytic performance of $Ni/ZrO_2$ for methanation. Some report that the $Ni/ZrO_2$ catalyst has been synthesized by the ultrasound-assisted [40], hydrogel [42], co-precipitation [43] and impregnation methods [28]. The results demonstrated that the catalyst prepared by co-precipitation method was more active than the one synthesized by impregnation method due to its better resistance to carbon deposition while

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the hydrogel method made active metal distributed uniformly on the surface of $Ni/ZrO_2$ catalyst.

Solution combustion method (SCM) as a simple, high efficient and economical method has been extensively adopted for the preparation of nanocrystalline materials and catalysts [44–49]. However, to the best of our knowledge, few studies have been reported using the combustion method to prepare $Ni/ZrO_2$ catalyst. In this paper, we successfully synthesized a series of $Ni/ZrO_2$ catalysts by combustion method using different mediums employed in $CO_2$ methanation reaction. The catalysts were characterized by $N_2$ physisorption, inductively coupled plasma optical emission spectroscopy (ICP-OES), hydrogen temperature-programmed reduction ($H_2$-TPR), hydrogen temperature-programmed desorption ($H_2$-TPD), carbon dioxide temperature-programmed desorption ($CO_2$-TPD) and X-ray diffraction (XRD) to elucidate the effect of combustion mediums on catalytic performance of the $Ni/ZrO_2$ catalyst.

## 2. Experimental

### 2.1. Preparation of the catalysts

All the reagents purchased from Guangfu Fine Chemical Research Institute (Tianjin, China) were analytic grade and used without further purification.

A series of $Ni/ZrO_2$ catalysts with Ni loading of 15 wt% were prepared by combustion method using different combustion mediums such as urea (U), glycerol (G2), glycol (G1), ethanol (E) and n-propanol (P). $Ni(NO_3)_2 \cdot 6H_2O$, $ZrO(NO_3)_2 \cdot 2H_2O$ ($n(Ni^{2+})/nZr^{4+}) = 0.31$), 4 mL deionized water and the combustion medium ($n(\text{combustion medium})/n(NO_3^-) = 0.7/1$) was mixed and stirred at room temperature for 0.5 h, then placed in a quartz tank. The mixture was heated to 550 °C under a 100 mL/min air flow in a tube furnace with a heating rate of 4 °C/min, kept at 550 °C for 4 h and then cooled to ambient temperature. The as-synthesized Ni-based catalysts were denoted as $Ni/ZrO_2$-M, where M represented the combustion mediums (M = U, G2, G1, E, P). In order to investigate the effect of combustion mediums on the $ZrO_2$ support, a support sample was prepared under the same condition of $Ni/ZrO_2$-U except the absence of Ni. The support was denoted as $ZrO_2$-U.

Another $ZrO_2$ support was obtained by calcining $ZrO(NO_3)_2 \cdot 2H_2O$ in air at 550 °C for 4 h and denoted as $ZrO_2$. To prepared $Ni/ZrO_2$ catalyst by impregnation method, a certain amount of $ZrO_2$ support (4 g) was put into nickel nitrate with six hydrate solution of deionized water (4.5 mL). The solution was kept at room temperature for 12 h and then dried at 110 °C for 12 h. The sample was heated to 550 °C with a heating rate of 4 °C/min and calcined at 550 °C for 4 h. The obtained sample was denoted as $Ni/ZrO_2$-imp.

### 2.2. Catalytic activity tests

The evaluation of Ni-based catalysts for $CO_2$ methanation was carried out in a 8 mm I.D. fix-bed quartz tubular reactor at atmospheric pressure. The quartz tube reactor was heated in a tube furnace equipped with a temperature controller. The pre-treatment and reaction temperature were measured by a K-type thermocouple which was inserted into the middle of the catalyst bed. The calibrated mass flow controller was used to monitor the flow rate of all gases. 0.3 g catalyst (20–40 mesh) was placed in the reactor and pre-reduced in situ at 500 °C for 2 h in a 50% $H_2/N_2$ stream with a total gas flow of 60 mL/min, then cooled to a certain temperature before catalytic performance tests. $H_2$, $CO_2$ and $N_2$ were introduced into the reactor at a molar ratio of $H_2:CO_2:N_2 = 36:9:5$, in which $N_2$ was the internal standard for GC analysis. The total flow rate was set to 240 mL/min, corresponding to a weight hourly space velocity (WHSV) of $48000\,mL \cdot g^{-1} \cdot h^{-1}$. Ultimately, the catalytic activity of all catalysts was studied over a temperature range of 250–500 °C. The outlet gases cooled by a cold trap were analyzed on-line by Agilent 4890D GC (fitted with a TDX-01 column) equipped with TCD. $H_2$ was the carrier gas of GC. Besides the main product $CH_4$, the byproduct CO is produced by the reverse water gas shift reaction. $CO_2$ conversion, $CH_4$ selectivity and carbon balance were defined as follows:

$$X_{CO_2}(\%) = \frac{F(CO_2)_{in} - F(CO_2)_{out}}{F(CO_2)_{in}} \times 100 \quad (1)$$

$$S_{CH_4}(\%) = \frac{F(CH_4)_{out}}{F(CO_2)_{in} - F(CO_2)_{out}} \times 100 \quad (2)$$

$$C_B(\%) = \left[1 - \frac{F(CO_2)_{out} + F(CH_4)_{out} + F(CO)_{out}}{F(CO_2)_{in}}\right] \times 100 \quad (3)$$

where $X$ is the conversion, $S$ is the selectivity, $F$ is the molar flow rate and $C_B$ is the carbon element balance. Footnotes "in" and "out" refer to the inlet gas and the outlet gas respectively. For all of tests in this work, $C_B$ is in the range of ±2%, proving that the experimental results are credible.

### 2.3. Characterization of the catalysts

$N_2$ adsorption-desorption isotherms were obtained with the Micromeritics Tristar-3000 instrument at −198 °C. Prior to the measurement, samples were purged with a $N_2$ gas at 90 °C for 1 h and then at 300 °C for 4 h. Specific surface area was measured by Brunauer-Emmett-Teller (BET) method. Pore volume and pore size were calculated using the Barrett-Joyner-Halenda (BJH) treatment.

The elemental analysis of nickel in all samples was performed on an inductively coupled plasma optical emission spectrometer (ICP-OES) (VISTA-MPX, Varian). About 50 mg sample was digested in the mixed solution (4 mL $H_2O$, 4 mL HCl, 2 mL HF and 4 mL $H_2SO_4$) assisted by microwave irradiation (Multiwave 3000, Anton Paar). Then, the resulted solution was diluted with distilled water to 100 mL before measurement.

The powder X-ray diffraction patterns of samples were recorded using a RigakuD/max-2500 X-ray diffractometer operated at 40 kV and 200 mA with a Cu Kα radiation over a 2 theta angle range of 10–80° and a position sensitive detector using a step size of 5°/min.

Hydrogen temperature programmed reduction ($H_2$-TPR) and temperature programmed desorption ($CO_2$-TPD and $H_2$-TPD) were carried out on Micromeritics 2910 TPR/TPD instrument. For $H_2$-TPR measurement, 0.1 g catalyst was placed in a quartz U-tube reactor and outgassed in argon stream at 200 °C for 1 h, then cooled to 50 °C. $H_2$-TPR was performed under a 10% $H_2$/Ar (30 mL/min) within a temperature range from 50 to 900 °C. For $CO_2$-TPD, 50 mg sample was pretreated in Ar at 200 °C for 1 h and then cooled down to 50 °C. The carrier gas was switched to He and the sample was pulsed $CO_2$ 8 times. To remove the physically adsorbed $CO_2$, the catalyst was degassed with a 30 mL/min He flow for 30 min before $CO_2$-TPD measurement. Then the sample was heated to 550 °C with a heating rate of 10 °C/min. For $H_2$-TPD, the catalyst (50 mg) was reduced by $H_2$ at 400 °C for 2 h and cooled to 100 °C. After that, the sample was flushed with Ar flow to get rid of the weakly adsorbed $H_2$. Then the temperature was raised to 400 °C at 10 °C/min. The Ni dispersion (D), Ni specific metal surface area ($S_{Ni}$) and the average size of Ni (d) were obtained from the $H_2$-TPD results by the

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