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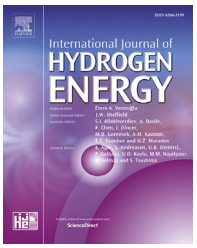

Enhanced low-temperature activity for CO_2 methanation over Ru doped the Ni/CexZr$_{(1-x)}O_2$ catalysts prepared by one-pot hydrolysis method

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ABSTRACT

A series of 30 wt%Ni/$Ce_xZr_{1-x}O_2$ catalysts doped with Ru ranging from 0 to 5 wt% were prepared by one-pot hydrolysis of metal nitrates with ammonium carbonate for carbon dioxide methanation at low temperature range of 150–310 °C. The influences of Ce/Zr molar ratios and Ru contents on the physicochemical properties and catalytic activities of prepared catalysts were systematically investigated. The addition Ru can improve the Ni dispersion and the basicity of the yRu-30Ni/$Ce_{0.9}Zr_{0.1}O_2$ catalysts surface. As a result, their low-temperature catalytic activity had been enhanced over these doped Ru promoted catalysts. The optimal catalyst was 3Ru-30Ni/$Ce_{0.9}Zr_{0.1}O_2$ on which the CO_2 conversion reached theoretical equilibrium value as high as 98.2% with the methane selectivity of 100% at a reaction temperature as low as 230 °C. Moreover, there was almost no deactivation for the 3Ru-30Ni/$Ce_{0.9}Zr_{0.1}O_2$ catalyst during 300 h at 230 °C indicating excellent catalytic stability and coke resistence ability. It was also found that the low-temperature activity of 3Ru-30Ni/$Ce_{0.9}Zr_{r0.1}O_2$ catalyst prepared by one-pot hydrolysis method was much higher than the one prepared by impregnation method.

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Introduction

The increase of carbon dioxide concentration in the atmosphere has resulted in severe effects on the environment and the global climate [1–3]. The catalytic hydrogenation of carbon dioxide to produce methane, introduced by Sabatier and Senderens in 1902, is considered as one of the efficient approaches to recycle CO_2 emissions to give a useful fuel, with potential commercial applications and environmental benefits [4–8]. Many researchers were devoted to the development of effective and stable catalysts for this particular reaction. A number of catalysts were reported to be active for CO_2 methanation reaction, such as noble metals Rh [9,10], Ru [11–14], Pd [15] and VIII metals Ni [16–21] and Fe [22] supported on various oxides like Al_2O_3 [23–25], SiO_2 [26,27], ZrO_2 [28], CeO_2 [29–32], $Ce_xZr_{1-x}O_2$ solid solution [33–40] and so on. Ni-based catalysts have been widely investigated because of their good compromise between high activity and low price [41]. However, these catalysts have low catalytic active so that

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CO_2 conversion cannot reach thermodynamic equilibrium value at temperatures below 300 °C.

$$H_2 + CO_2 \leftrightarrow CH_4 + H_2O \quad \Delta H^\circ = -165KJ/mol \tag{1}$$

Methanation of carbon dioxide, represented by Eq. (1), is a strong exothermal reaction, the challenge of the catalysts for CO_2 methanation is to improve the low-temperature activity, not only for the purpose of energy saving, but also for the reason that the low reaction temperature favors the high CO_2 conversion based on its thermodynamic characteristics [30]. In addition, the sintering of the active species during the reaction can be avoided at low temperature. Furthermore, if the operation temperature is higher than 320 °C, the reverse water gas shift reaction occurs during the reaction, which leads to formation of by-products, such as CO [42]. Therefore, a low temperature catalyst is urgently required for CO_2 methanation. Considerable work has been done to develop thermally stable Ni-based catalysts with high activities at low temperatures [43–48], but their low-temperature activity is still to be enhanced further.

In the last decade, $Ce_xZr_{1-x}O_2$ ($CeZrO_2$) supported Ni catalysts have attracted a lot of attention due to the high oxygen storage capacity of $CeZrO_2$ solid solution together with the presence of highly dispersed nickel which result in their excellent catalytic activity and stability [34]. The catalyst for CO_2 methanation is sensitive to the structure of the catalyst, the preparation method, preparation conditions, and the component of the catalyst significantly influence its performance [35]. Therefore, various methods including impregnation [36–38], precipitation [38,39], sol–gel method [34,40], plasma-enhanced chemical vapor deposition [49] and so forth have been widely applied in methanation catalysts synthesis.

Recently, Nizio et al. [50,51] evaluated CO_2 methanation activity of $CeZrO_2$ supported Ni catalyst under hybrid plasma-catalytic conditions and the results revealed that $CeZrO_2$ supported Ni catalysts exhibited excellent catalytic activity and stability at very low temperature around 100 °C. On the contrary in the absence of plasma, the same catalytic activity only achieved at much higher temperatures around 300 °C for the same catalyst. Therefore, there is still a great deal of interest in developing a novel approach to prepare CO_2 methanation catalysts with high catalytic activity and stability at low temperature. On the other hand, the improvement of the long-term stability of Ni-based catalysts in CO_2 methanation requires more efforts. The deactivation of catalysts by coke formation and sintering of metal particles is accelerated when a large amount of heat is released as the exothermal reaction further proceeds [26,52]. In the last decade, bimetallic catalysts have also attracted a lot of attention due to their higher activity. Ru can be combined with Ni to form a bimetallic methanation catalyst, which showed much enhanced catalytic performances [33,53–55]. Adding small amount of Ru in Ni catalyst is a promising way to promote methanation reaction long time stability, high activity because Ru exhibited better resistant properties to sintering and carbon deposition than Ni [56,57].

In the present study, a series of 30 wt%Ni/$CeZrO_2$ catalysts doped with Ru ranging from 0 to 5 wt% were prepared by one-pot hydrolysis of metal nitrates with ammonium carbonate. The effects of Ce/Zr molar ratio and Ru content on the physicochemical properties and the catalytic performance of catalysts in CO_2 methanation were investigated in a fixed-bed reactor at temperatures ranging from 150 °C to 310 °C at atmospheric pressure. Long-term experiments were performed during 300 h on stream at low temperature of 230 °C to investigate the stability and the deactivation of the 3Ru-30Ni/$Ce_{0.9}Zr_{0.1}O_2$ catalyst prepared from one-pot hydrolysis method and the conventional impregnation method.

Experimental

Preparation of the catalysts

All the reagents were analytical-grade, purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without purification. A series of 30 wt%Ni/$CeZrO_2$ catalysts doped with Ru ranging from 0 to 5 wt% were prepared by one-pot hydrolysis of metal nitrates with $(NH_4)_2CO_3$ as hydrolyzer. In a typical synthesis, 5 g $Ni(NO_3)_2 \cdot 6H_2O$ along with required amounts of different molar ratio of $Zr(NO_3)_4 \cdot 5H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ and $Ru(NO)(NO_3)_3$ were dissolved in 50 mL deionized water at 80 °C. The 100 mL $(NH_4)_2CO_3$ aqueous solution (2 mol/L) was poured into the above aqueous solution of metal salts with vigorous magnetic stirring until the water was evaporated out. The obtained solide was dried at 100 °C for 12 h and calcined at 500 °C for 5 h in air with a heating ramp of 2 °C/min. The prepared samples were denoted as yRu-30 wt% Ni/$Ce_xZr_{1-x}O_2$ (x = 0.95, 0.9, 0.8, 0.7; y = 0, 0.5, 1, 3 and 5 wt%), where x/(1-x) represented Ce/Zr molar ratio; y represented Ru content (wt%). For instance, 3Ru-30Ni/$Ce_{0.9}Zr_{0.1}O_2$ referred to a $CeZrO_2$ solid solution with the Ce/Zr molar ratio of 90/10, Ru content of 3 wt% and Ni content of 30 wt%. For comparison, we also prepared 3Ru-30Ni/$Ce_{0.9}Zr_{0.1}O_2$ by impregnation method according to the document [36], denoted as 3Ru-30Ni/$Ce_{0.9}Zr_{0.1}O_2$-imp.

Catalyst characterization

The powder X-ray diffraction analysis of catalyst was conducted on a Bruker D8 Advance diffractometer with a Cu Kα radition ($\lambda = 0.15418$ Å) at 3 kw. The 2θ angles that were scanned range from 10 to 90. The crystallite sizes of NiO and $CeZrO_2$ were estimated using the full width at half maximum (FWHM) of the of NiO (200) and $CeZrO_2$ (111) peaks respectively though the Scherrer equation: $d = 0.94\lambda/(\beta\cos\theta)$, where λ is the half of the wavelength of radiation, β is FWHM, and θ is the half of diffraction angle [58].

Temperature programmed reduction with H_2 (H_2-TPR) measurements were carried out on a homemade fixed-bed reactor to observe the reducibility of the catalysts. Prior to the measurement, 0.1 g of sample placed in a quartz reactor was first pretreated in an Ar stream (30 mL/min) at 100 °C for 0.5 h to remove moisture and other absorbed impurities and then cooled to room temperature. After this pretreatment, H_2-TPR was conducted with a gas mixture of 5 vol% H_2 in Ar at 30 mL/min. The temperature was raised to 800 °C at a heating

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