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Effect of the addition of Ce and Zr over a flower-like NiO-MgO (111) solid solution for CO_2 reforming of methane

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ABSTRACT

Ni-based catalysts have been extensively employed in the CO_2 reforming of methane because of its superior activity, low cost, and exhaustive availability. The Ce, Zr or co-doped flower-like NiO-MgO solid solution catalysts, covered by (111) facets, were prepared by applying the solvothermal synthesis method in the CO_2 reforming of methane. The high surface energy of (111) facets in the NiO-MgO solid solution contributed to the prominent reactivity. The addition of Ce and Zr into $Ni_{0.1}Mg_{0.9}O$ (111) resulted in enhanced activity and coke resistance. It did this by providing a smaller nickel particle size due to stronger interactions, and an increase in surface oxygen species which improves the CO_2 adsorption capacity. The Ce/Zr co-doped catalyst, possessing a molar ratio of 0.01:0.01, exhibited the highest catalytic activity and long-term stability.

1. Introduction

In recent decades, the mitigation of greenhouse gases has become a crucial component in the management of global warming [1]. Dry (CO_2) reforming of methane (DRM), not only provides a pathway to consume two major greenhouse gases, carbon dioxide and methane, but fulfills a requirement of the Fischer-Tropsch synthesis for producing syngas with a H_2/CO ratio ≤ 1 [2,3], which also holds significance for industry. From the point of thermodynamic analysis, DRM is a strongly endothermic reaction and therefore, elevated temperatures are needed to attain high syngas yields [4]. Noble metal catalysts like Rh, Pt, Pd or Ru, possess excellent performance on coke resistance even with an operating temperature as high as 900 ºC [5]. Nonetheless, owing to the limited availability of noble metal catalysts, nickel-based catalysts would be a suitable substitute in the industrial process of methane reforming, because of its outstanding activity, low cost and abundant supplies [6–8]. Unfortunately, Ni-based catalysts undergo severe deactivation at elevated temperatures due to carbon deposition and sintering [9–12].

There is no doubt that the small metal particle size can improve the coke resistance of the catalyst. In addition, a basic support possessing a strong adsorption and activation for CO_2 would also play a key role in anti-carbon deposition [13–15]. Therefore, greater interest has been directed towards reduced NiO-MgO solid solutions with small Ni particles [16]. The feasibility with respect to the formation of a NiO-MgO solid-solution was due to the approximate lattice parameters (4.17 Å for NiO, 4.21 Å for MgO) [17]. Ruckenstein, et al. investigated and reported the characteristics of catalysts for DRM in the presence of NiO-MgO solid solution [18–20]. It was further demonstrated that NiO was isolated by MgO, which presented some difficulties regarding the reduction of NiO. As a result, small nickel particles could be obtained on the surface [21]. After taking the surface basicity and the small metal particle size into consideration, a NiO-MgO solid-solution shows an excellent stability against metal sintering, as well as a strong resistance to coking.

Additionally, the capacity of MgO as a support is not limited by its function as a strong Lewis base, but it also participates in the chemisorption of CO_2, followed by hydrogenation and dissociation in the production of CO and OH [22]. As confirmed by Guo, et al. [23], who employed the DFT modelling method, CO_2 could hydrogenate and dissociate on MgO (111) with a minimum energy barrier of 0.37 eV, followed by MgO (110). In other words, higher Miller index surfaces, such as (111), are favored for the adsorption of CO_2 [24]. Furthermore, MgO (111) is characterized as a polar Tasker III type surface with an appreciable amount of basic sites. It is made up of alternating polar monolayers of Mg^{2+} and O^{2-} atoms, which promotes CO_2 adsorption [25,26].

A comprehensive investigation has been reported on redox promoters, which could facilitate both the activity and the stability of Ni-based catalysts [27–29]. It was demonstrated that ceria-based materials significantly increase the redox and oxygen transfer properties of catalysts. Furthermore, there are substantial amounts of oxygen species on

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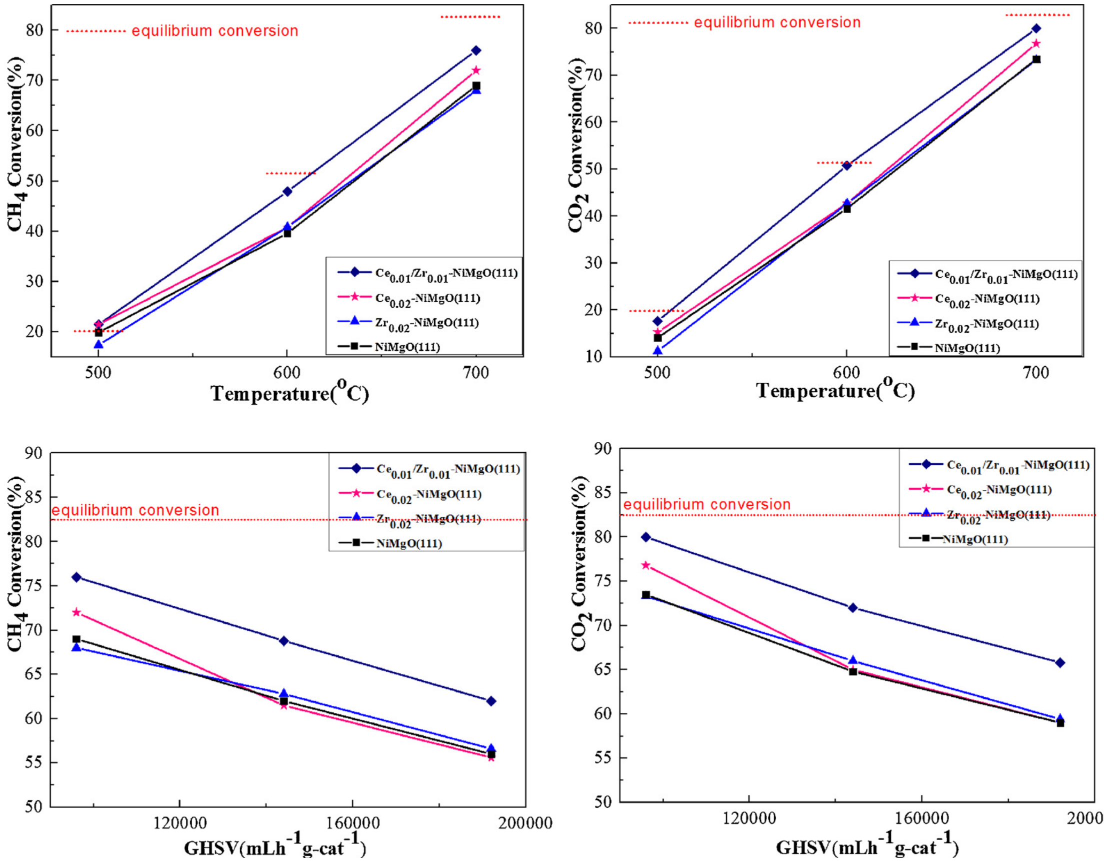

Fig. 1. Conversion of the pristine and promoted catalysts (a, b) with respect to temperature with a GHSV valued at 96,000 mL g-cat^{-1} h^{-1}, and (c, d) with respect to the GHSV with a temperature of 700 ºC after 10 h under reaction conditions.

the catalyst surface, which would favor the oxidation of carbon [30]. Moreover, according to Yao, et al. [31], the introduction of promoter Zr had a significant effect on both the activation of CH_4, as well as the formation of CO_{ads} and O_{ads} species. Rezaei, et al.[32] modified Ni-Al_2O_3 catalyst by promoting CeO_2, La_2O_3 and ZrO_2 and found out that the accumulated carbon in Ce and Zr-promoted catalysts were decreased. Although much attention has focused on Ce- and Zr-based catalysts due to their excellent redox property, to the best of our knowledge, the combination of the unique MgO (111) surface properties with the aforementioned redox promoters in Ni-based catalysts, particularly in a NiO-MgO solid-solution, has been scarce.

In the current work, the catalysts of a $Ni_xMg_{1-x}O$ (111) solid solutions, which employ redox promoters (Ce, Zr and Ce/Zr) were successfully synthesized via a facile solvothermal method. The catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 physisorption, CO_2 temperature-programmed desorption (CO_2-TPD), and X-ray photoelectron spectroscopy (XPS). The effect of redox promoters (Ce, Zr and Ce/Zr) on the catalytic performance of the prepared catalysts for CO_2 reforming of methane was also systematically investigated. It was indeed found that Ce/Zr co-doped catalysts showed a higher activity and stability, even under harsh reaction conditions.

2. Experimental

2.1. Catalyst preparation

All the chemicals were provided by the Sinopharm Chemical Reagent Corporation and were employed directly without further purification. M (M = Ce, Zr, Ce/Zr)-$Ni_{0.1}Mg_{0.9}O$ (111) were synthesized by a solvothermal method. In a typical synthesis, Mg, Ni, Ce and Zr acetates with molar compositions of 0.90:0.10:0.01:0.01 were dissolved in 100 mL of anhydrous methanol. The mixture was stirred continuously for 8 h to form a homogeneous solution. Then, the clear solution with 0.1 M of metal ions (Mg + Ni + Ce + Zr) was transferred into a 150 mL Teflon-lined steel autoclave and heated at 180 ºC for 48 h. Prior to calcination at 800 °C for 6 h with a ramp of 2 ºC min^{-1} under static air conditions, the prepared sample was filtered with methanol, followed by drying at 60 ºC for 24 h. The conventional NiMgO-con sample was synthesized by normal incipient impregnation method.

2.2. Catalyst characterization

The structures and crystal phases of the prepared catalysts were examined by X-ray diffraction (XRD) patterns by employing a Rigaku D/max-2500 X-ray diffractometer from 10° to 90°, with a scanning rate of 5°/min. The detailed structure of samples was observed by transmission electron microscopy (TEM) with a Tecnai G2 F20 instrument. The scanning electron microscopy (SEM, S-4800) technique was used to determine the morphology of the catalysts. The measured specific surface areas and pore-sized distributions were based on a N_2 physisorption isotherm. In addition, X-ray photoelectron spectroscopy (XPS) was employed to determine the surface composition of catalysts. Note that the XPS results were calibrated by C1s at 285.0 eV. CO_2 temperature programmed desorption (CO_2-TPD) was carried out to investigate surface properties of samples. For each measurement recorded, a 50 mg sample was first heated from room temperature (RT) to 780 ºC via a ramp of 10 ºC /min in a 10 vol. % H_2/Ar mixture, with a flow rate of 30 mL /min, followed by a reduction at 780 ºC for 2 h. The sample was purged with Ar (20 mL min^{-1}) for an additional 0.5 h, then cooled to room temperature. A flow of CO_2 (30 mL min^{-1}) was introduced for 0.5 h, then purged with Ar and heated steadily with a rate