



# Article CO<sub>2</sub> Methanation over Rare Earth Doped Ni-Based Mesoporous Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> with Enhanced Low-Temperature Activity

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Abstract: The Ni-based catalysts have a wide range of industrial applications due to its low cost, but its activity of CO<sub>2</sub> methanation is not comparable to that of precious metal catalysts. In order to solve this problem, Ni-based mesoporous Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> solid solution catalysts doped with rare earth were prepared by the incipient impregnation method and directly used as catalysts for the methanation of CO<sub>2</sub>. The catalysts were characterized systematically by X-ray powder diffraction (XRD), N<sub>2</sub> physisorption, transmission electron microscopy (TEM), energy-dispersed spectroscopy (EDS) mapping, X-ray photoelectron spectroscopy (XPS), H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR), CO<sub>2</sub> temperature programmed desorption (CO<sub>2</sub>-TPD), and so on. The results show that Ni is highly dispersed in the mesoporous skeleton, forming a strong metal-skeleton interaction. Therefore, under the condition of  $CO_2$  methanation, the hot sintering of metallic Ni nanoparticles can be effectively inhibited so that these mesoporous catalysts have good stability without obvious deactivation. The rare earth doping can significantly increase the surface alkalinity of catalyst and enhance the chemisorption of CO<sub>2</sub>. In addition, the rare earth elements also act as electron modifiers to help activate CO2 molecules. Therefore, the rare earth doped Ni-based mesoporous Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> solid solution catalysts are expected to be an efficient catalyst for the methanation of CO<sub>2</sub> at low-temperature.

**Keywords:** Ni-based catalyst; mesoporous  $Ce_{0.8}Zr_{0.2}O_2$  solid solution; rare earth doped; low-temperature catalytic activity;  $CO_2$  methanation

# 1. Introduction

In the past hundred years, with the growth of the world population and the development of the global economy,  $CO_2$  emissions from the burning of fossil fuels have been on the rise [1,2]. Therefore, the massive emissions of CO<sub>2</sub> have also led to many environmental problems such as global warming, sea level rise, polar ice melting and so on [3]. It is reported that  $CO_2$  in the atmosphere is threatening the Earth's atmospheric system [4,5]. However, CO<sub>2</sub> is also considered to be one of the largest and cheapest carbon sources in the world, and the treatment and disposal technology of CO<sub>2</sub> has attracted worldwide attention [6]. Paul Sabatier first proposed the methanation of the  $CO_2$  reaction ( $CO_2$  (g) + 4H<sub>2</sub>  $(g) \rightarrow CH_4 (g) + 2H_2O (g), \Delta H_{298K} = -165.4 \text{ kJ/mol}, \Delta G_{298K} = -130.8 \text{ kJ/mol}) \text{ in } 1897 [5].$ This reaction can not only realize the utilization of CO<sub>2</sub> resources, but also has potential economic and environmental value, which is a widely studied topic [7]. Hashimoto et al. [4] also proposed a global  $CO_2$  cycle strategy to solve the problem of global  $CO_2$  emissions. Due to the exothermic properties of carbon dioxide, methanation of  $CO_2$  can be carried out at low temperature. However, this process is a kinetic-controlled reaction due to the high activation energy of the stable  $CO_2$ , which will cause a slow reaction rate and poor catalytic activity in low-temperature regions [8]. Therefore, in order to achieve high activity of CO2



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). methanation at low temperature, it is very important to use a highly efficient catalyst. In addition, due to the strong exothermic properties of the  $CO_2$  methanation catalyst bed, hot spots often exist in the catalyst bed during the reaction process, which leads to the hot sintering of the metal active center [9,10].

In the catalysts for  $CO_2$  methanation, the supported metals of Group VIII have been proved to be active. The Ru, Rh, and Ni are the most studied active metals due to their excellent catalytic activity [11,12]. The Ru and Rh-based catalysts' activity at low temperature is far better than that of Ni-based catalysts, but the preparation cost is higher, thus limiting its large-scale application in industry. Thus, Ni-based catalysts are extensively studied and recognized as the most active non-noble metal catalysts because they usually perform comparable activities to the noble metal catalysts at high temperature [13,14]. However, the active site of Ni metal is prone to hot sintering and can quickly deactivate the catalyst [15,16]. In addition, the low temperature activity of Ni-based catalysts is not as good as noble metal catalysts because of distinguished d and s outer layer orbits. Therefore, it is of great significance to study and develop Ni-based  $CO_2$  methanation catalysts with high activity and high stability [17,18].

Enhancing the activity of carbon dioxide at low temperatures and constructing strong metal-carrier interaction (SMSI) are potential solutions [19,20]. Therefore, the activation of  $CO_2$  can be enhanced by changing the surface alkalinity and metal-carrier interactions by doping rare earth elements (La, Pr, Yb, Sm, etc.) [21–23] as catalytic agents. Compared with other elements, rare earth elements, due to their unique d-orbital electronic structure, can not only be used as a basic modifier for the metal active site, but can also regulate the electronic properties of the metal active site [24]. Zhi et al. [25] successfully prepared Ni/SiC and La<sub>2</sub>O<sub>3</sub> modified Ni/SiC by the impregnation method, and used for the CO<sub>2</sub> methanation reaction. The results showed that La<sub>2</sub>O<sub>3</sub> modified Ni/SiC had better catalytic activity and stability than pure Ni/SiC. They found that La<sub>2</sub>O<sub>3</sub> could effectively inhibit the growth of nano-sized NiO, improve the dispersion of NiO, and enhance the interaction between NiO and SiC. The  $La_2O_3$  could also change the electronic environment around Ni atoms, so that CO<sub>2</sub>, the reactant on Ni atoms, was easier to activate. Takano et al. [26] found that compared with the Ni-Zr catalyst, the Ni-Zr-Sm catalyst showed higher CO2 methanation activity. The main reason is that the  $Zr^{4+}$  ion is replaced by the  $Sm^{3+}$  ion to form tetragonal ZrO<sub>2</sub>, and the oxygen vacancy may interact strongly with the oxygen atom in the CO<sub>2</sub> molecule, thus weakening the strength of the C=O bond, leading to the enhancement of the hydrogenation of CO<sub>2</sub> to form CH<sub>4</sub> and H<sub>2</sub>O. Therefore, rare earth doped Ni based catalysts are promising catalysts toward CO<sub>2</sub> methanation.

It is well known that the performance of the catalyst also depends on the characteristics of the carrier to a large extent as the catalytic carrier will also significantly affect the various properties of the catalyst such as metal-support interaction [27], acid-base performance [28], redox performance [29], etc. Oxides such as SiO<sub>2</sub> [30], Al<sub>2</sub>O<sub>3</sub> [31], ZrO<sub>2</sub> [32], and CeO<sub>2</sub> [33] have been widely used as carriers of Ni-based CO<sub>2</sub> methanation catalysts. Among them, CeO<sub>2</sub> shows a unique redox performance and high sample capacity [34–36], which is of great significance for the activation of carbon dioxide in the process of catalytic methane. However, due to the poor stability of pure CeO<sub>2</sub>, its redox effect will be lost with the increase in temperature. It has been reported that Zr atoms can greatly stabilize the CeO<sub>2</sub> matrix by combining the CeO<sub>2</sub> lattice with isomorphic substitution [37,38]. In addition, due to the difference in ionic radii between Ce<sup>4+</sup> (0.97 A) and Zr<sup>4+</sup> (0.84 A), the addition of ZrO<sub>2</sub> will cause serious deformation of the crystal structure and form defects in the crystal structure. Therefore, this can promote the activation of CO<sub>2</sub> in the methanation of CO<sub>2</sub>.

Herein, the rare earth (La, Sm, Pr, Yb) doped Ni-based bimetal catalysts supported on the mesoporous  $Ce_{0.8}Zr_{0.2}O_2$  solid solution (Ce/Zr = 80/20 molar ratio) were synthesized and utilized as the catalysts for CO<sub>2</sub> methanation to further improve the low-temperature catalytic performance. It can be found that the Ni species are highly dispersed in mesoporous skeleton and forming strong metal-skeleton interaction. Therefore, under the condition of CO<sub>2</sub> methanation, the hot sintering of metallic Ni nanoparticles can be effectively inhibited so that these mesoporous catalysts have good stability without obvious deactivation. Rare earth doping enhances the chemisorption of CO<sub>2</sub> by increasing the surface alkalinity of the catalyst. In addition, the addition of rare earth elements can help activate carbon dioxide molecules. A series of characterization methods (XRD, TEM, N<sub>2</sub> physical adsorption, XPS, CO<sub>2</sub>-TPD, H<sub>2</sub>-TPR) were used to characterize the catalyst in detail, which will be discussed in this paper.

#### 2. Results and Discussion

#### 2.1. Characterizations of the Catalysts

# 2.1.1. X-ray Diffraction (XRD) Analysis

The XRD analyses were carried out to determine the crystalline phases of the catalysts. The XRD patterns of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts are shown in Figure 1. It was noteworthy that all the catalysts displayed six different diffraction peaks at 28.5°, 33.0°, 47.7°, 56.6°, 69.8°, and 77.6°, which were ascribed to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (4 0 0), and (3 3 1) crystalline planes, respectively. This indicated that M-Ce80Zr20 support (Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>) was a cubic crystalline structure (PDF-#-34-0394). Moreover, the absence of the ZrO<sub>2</sub> diffraction peak indicated that ZrO<sub>2</sub> was successfully integrated into the CeO<sub>2</sub> lattice to form a solid solution while maintaining the crystal structure of fluorite [39]. As for the NiO (PDF-#-78-0429), it was interesting to observe that the NiO peak strength of the 15Ni2R/M-Ce80Zr20 catalysts were much weaker than that of 15Ni/M-Ce80Zr20, demonstrating better NiO dispersion over the 15Ni2R/M-Ce80Zr20 catalysts. Among them, the NiO diffraction peak of the 15Ni2La/M-Ce80Zr20 catalyst was the weakest, which also indicated that the doping of rare earth La was most conducive to the dispersion of NiO. Therefore, the characteristic peaks of the rare earth were not observed over these doped 15Ni2R/M-Ce80Zr20 catalysts because of the high dispersion and low loading amount.



Figure 1. X-ray diffraction (XRD) patterns of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts.

#### 2.1.2. N<sub>2</sub> Physisorption Analysis

The structural properties of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts were investigated by N<sub>2</sub> physisorption. The N<sub>2</sub> adsorption-desorption isotherms and pore size distributions of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts are displayed in Figure 2. As can be observed in Figure 2a, all the catalysts displayed the type IV H2-shaped isotherms based on the IUPAC classification [40]. Therefore, the catalysts still maintained the mesoporous structure after loading the metal and calcination. Furthermore, the mesoporous catalysts in Figure 2b showed the pore diameter distribution with the peaks in the 9.9 nm range. Compared with the 15Ni/M-Ce80Zr20 catalyst, the 15Ni2R/M-Ce80Zr20 catalysts displayed slightly bigger pore diameters. This indicated that the shrinkage of the mesoporous framework was effectively inhibited after the preparation and calcination of the catalysts [40].



**Figure 2.**  $N_2$  adsorption-desorption isotherms (**a**) and pore size distributions (**b**) of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts.

Furthermore, the values of the specific surface areas, pore volumes, and average pore diameters of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts are summed up in Table 1. It was noted that the specific surface area of the 15Ni2R/M-Ce80Zr20 catalyst was larger than that of the 15Ni/M-Ce80Zr20 catalyst. This suggested that the loading of the Ni and the rare earth caused the partial blockage of the mesoporous channels of the catalysts. However, the average pore diameters of these catalysts did not suffer any decrease. This demonstrated that the catalyst successfully retained the mesoporous skeleton and provided sufficient thermal stability.

Samples	Specific Surface Area (m²/g)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Diameter (nm)	Isotherm Type
15Ni2La/M-Ce80Zr20	51.91	0.13	9.93	IV H2
15Ni2Pr/M-Ce80Zr20	45.54	0.13	9.99	IV H2
15Ni2Sm/M-Ce80Zr20	50.46	0.16	9.98	IV H2
15Ni2Yb/M-Ce80Zr20	55.04	0.15	9.97	IV H2
15Ni/M-Ce80Zr20	45.27	0.12	9.26	IV H2

Table 1. Structural properties of the catalysts based on the N<sub>2</sub> physisorption.

# 2.1.3. TEM, STEM and EDS-Mapping Analyses

The TEM characterization of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts were performed to determine the dispersions of surface NiO. The TEM images are displayed in Figure 3. As can be observed in Figure 3, the NiO nanoparticles of around 10.0 nm were highly dispersed among the M-Ce80Zr20 with wormlike mesoporous channels. As for the high-resolution TEM images of these catalysts, the lattice fringe spacing around 0.24 nm, 0.21 nm, and 0.15 nm could be observed over all the catalyst surfaces, which were ascribed to the (1 1 1), (2 0 0), and (2 2 0) planes of NiO, respectively.

The spatial distribution of elements in the mesoporous structure of the catalyst was studied by using scanning transmission electron microscopy (STEM) and EDS-mapping spectra. Figure 4 presents the STEM-EDS element mapping images. It could be seen that Ce, Ni, Zr, and the rare earths (La, Sm, Pr, Yb) were evenly dispersed in the catalyst, which indicated that the Ni and rare earth doping had been evenly dispersed on the surface of M-Ce80Zr20.

#### 2.1.4. H<sub>2</sub>-TPR Analysis

The H<sub>2</sub>-TPR analyses were conducted to investigate the metal-support interactions of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts by comparing the reduction peak positions and the shapes of the profiles in Figure 5. As can see from the figure, the main reduction peak appeared in the range of 447.0 °C to 480.0 °C, which should be attributed to NiO and rare earth with strong metal-support interaction. There was only one reduction peak in the H<sub>2</sub>-TPR profile, indicating the homogeneity of Ni species in the entire

mesoporous skeleton. In addition, compared with the original 15Ni/M-Ce80Zr20, the reduction peak of the rare earth doped 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts moved to the low temperature region, suggesting that the existence of rare earth enhanced the reducibility of Ni<sup>2+</sup> in 15Ni2R/M-Ce80Zr20.



**Figure 3.** Transmission electron microscopy (TEM) images of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts: (**a**,**b**) 15Ni2La/M-Ce80Zr20, (**c**,**d**) 15Ni2Sm/M-Ce80Zr20, (**e**,**f**) 15Ni2Yb/M-Ce80Zr20, (**g**,**h**) 15Ni2Pr/M-Ce80Zr20.



**Figure 4.** STEM-EDS element mapping images showing the spatial distribution of Ce, Zr, Ni, and R (R = La, Sm, Pr, Yb) elements: (a) 15Ni2Pr/M-Ce80Zr20, (b) 15Ni2Yb/M-Ce80Zr20, (c) 15Ni2Sm/M-Ce80Zr20, (d) 15Ni2La/M-Ce80Zr20.



Figure 5. H<sub>2</sub>-TPR profiles of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts.

# 2.1.5. CO<sub>2</sub>-TPD Analysis

The CO<sub>2</sub>-TPD analyses of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts were conducted to characterize the surface alkalinity of the catalysts. It is universally accepted that the CO<sub>2</sub> chemisorbed over the strong alkaline sites could be desorbed at high temperature because the strength of the catalyst basicity could be closely related to the desorption temperature [41]. As can be seen from Figure 6, the CO<sub>2</sub>-TPD profile shapes of all these catalysts were similar. Specifically, they found two groups of CO<sub>2</sub> desorption peaks around 155.0 °C and 350.0 °C, suggesting that both weak (155 °C) and strong (350.0 °C) alkaline sites with different intensities existed in these catalysts [42,43]. In addition, compared with 15Ni/M-Ce80Zr20, the rare earth doped 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts of the CO<sub>2</sub> desorption peak was stronger, demonstrating that the rare earth greatly increased the number of surface basic sites. This proved that rare earth (La, Sm, Pr, Yb) could promote the improvement of surface basic sites [44–48]. The surface basic sites enhanced by rare earth contributed to the low temperature activation of CO<sub>2</sub> methanation.



Figure 6. CO<sub>2</sub>-TPD profiles of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts.

2.1.6. X-ray Photoelectron Spectroscopy (XPS) Analysis

The XPS measurement of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts were applied to obtain the detailed coordination states and more detailed information about the surface elements. The Ce 3d, Zr 3d, Ni 2p, and O 1s XPS profiles of 15Ni2R/M-Ce80Zr20

are shown in Figure 7. The Ce 3d spectrum in Figure 7a was divided into eight overlapping peaks. According to previous reports, these peaks could be divided into Ce 3d<sub>5/2</sub> (V, V', V", V"') and Ce 3d<sub>3/2</sub> (U, U', U", U") [49]. The U (901.0 eV), U" (908.0 eV), U"' (917.0 eV) and V (882.0 eV), V'' (889.0 eV), V''' (901.0 eV) peaks were derived from the Ce<sup>4+</sup> cation in +4 valence. These were caused by electrons moving from a complete O 2p orbital to an empty Ce 4f orbital. The presence of U' and V' in the Ce 3d spectrum indicated that  $Ce^{3+}$ exists in the +3 valence state [50–52]. Therefore, it could be concluded that there were +4 and +3 cerium surface types of the 15Ni2R/M-Ce80Zr20 catalysts studied, and Ce<sup>4+</sup> was the predominant species. The Zr 3d spectra of catalysts are displayed in Figure 7b. As could be observed, almost all catalysts displayed the Zr 3d spectra with Zr 3d<sub>5/2</sub> peaks centered around 182.0 eV, which corresponded to the  $Zr^{4+}$  in the +4 oxidation state [53]. From the O 1s spectra of these catalysts in Figure 7c, it was noteworthy that almost all catalysts had main peaks and shoulder peaks at 530.0 eV and 533.0 eV, respectively, indicating the presence of O<sup>2-</sup>. The appearance of acromion was related to the nonequivalence of the oxidation environment. It has been reported that the acromial peak near 533.0 eV corresponds to  $O^{2-}$  bound with  $Ce^{3+}$ . As a result, the oxygen vacancy was formed around the Ce<sup>3+</sup> species to maintain the charge neutrality [49,54]. Thus, the O 1s shoulder peak at higher binding energy could be generated. The Ni 2p spectra of these catalysts are shown in Figure 7d. It can be clearly seen that each catalyst had a Ni  $2p_{3/2}$  main peak at 854.0 eV and a Ni 2p1/2 main peak at 872.0 eV. Compared with pure NiO (Ni 2p3/2, 853.6eV), the 15Ni2R/M-Ce80Zr20 catalysts had a higher binding energy [55,56]. Therefore, the above H<sub>2</sub>-TPR analysis confirmed that the oxidation state of Ni species in these catalysts mainly existed in the form of Ni<sup>2+</sup>, and there was a strong metal-support interaction.



**Figure 7.** X-ray photoelectron spectroscopy (XPS) spectra of (**a**) Ce 3d, (**b**) Zr 3d, (**c**) O 1s, and (**d**) Ni 2p of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts.

Furthermore, the XPS spectra of the Pr 3d, Sm 3d, Yb 4d, and La 3d of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts are shown in Figure 8. As showen in Figure 8a, the Pr 3d spectra of the 15Ni2Pr/M-Ce80Zr20 catalyst displayed a Pr  $3d_{5/2}$  peak at 933.0 eV. This was different from the Pr  $3d_{5/2}$  peaks of PrO<sub>2</sub> (935.0 eV) and Pr<sub>2</sub>O<sub>3</sub> (932.9 eV), and might be a mixture of PrO<sub>2</sub> and Pr<sub>2</sub>O<sub>3</sub> [57]. During the methanation of CO<sub>2</sub>, the change in valence state would produce an oxygen vacancy and activate the C=O bond of CO<sub>2</sub>.

The Sm 3d spectrum of 15Ni2Sm/M-Ce80Zr20 (Figure 8b) showed the Sm  $3d_{5/2}$  peak near 1082.0 eV and the Sm  $3d_{3/2}$  peak near 1110.0 eV. This indicated that the Sm element existed in the form of Sm<sup>3+</sup> in the 15Ni2Sm/M-Ce80Zr20 catalyst [57]. The Yb 4d spectrum in Figure 8c of 15Ni2Yb/M-Ce80Zr20 displayed the Yb  $4d_{5/2}$  centered at 183.0 eV, suggesting the presence of Yb<sup>3+</sup> cation species in the +3 valence [58]. As can be seen in Figure 8d, the peak of La  $3d_{5/2}$  was located at about 834.0 eV, and the peak of the satellite was located at about 838.0 eV. The  $\Delta$ E between the two was about 4.0 eV, which was the characteristic feature of the La<sup>3+</sup> in La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>. The surface La<sub>2</sub>O<sub>3</sub> and CO<sub>2</sub> interacted to form La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, when the 15Ni2La/M-Ce80Zr20 catalyst was exposed to the atmosphere [59].



**Figure 8.** XPS spectra of (**a**) Pr 3d, (**b**) Sm 3d, (**c**) Yb 4d and (**d**) La 3d of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts.

In addition, the binding energies of the surface elements of the catalysts based on XPS in Table 2. The results showed that almost all the catalysts had the same Ni  $2p_{3/2}$ , O 1s, Ce  $3d_{5/2}$ , and Zr  $3d_{5/2}$  binding energies of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts. As shown in Table 3, it could be seen that rare earth doped Ni-based mesoporous Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalysts had different O 1s shoulder peak area ratios, which further affects the catalytic performance of CO<sub>2</sub> methanation. Among them, the O 1s shoulder peak area of the 15Ni2La/M-Ce80Zr20 catalyst was larger than that of the other catalysts, which indicated that the surface redox performance of the 15Ni2La/M-Ce80Zr20 catalyst was obviously better than that of other catalysts in terms of the number of oxygen vacancies on the surface.

Samples	Ni 2p <sub>3/2</sub>	O 1s	Ce 3d <sub>5/2</sub>	Zr 3d <sub>5/2</sub>
15Ni2La/M-Ce80Zr20	853.40	529.16	882.20	182.10
15Ni2Pr/M-Ce80Zr20	853.35	529.14	882.22	182.05
15Ni2Sm/M-Ce80Zr20	853.30	529.16	882.24	182.10
15Ni2Yb/M-Ce80Zr20	853.45	529.10	882.35	182.10
15Ni/M-Ce80Zr20	853.55	529.20	882.10	182.23

**Table 2.** Binding energies (eV) of the surface elements of the catalysts based on X-ray photoelectron spectroscopy (XPS).

Table 3. O 1s peak areas of the catalysts based on XPS.

Samples	O 1s Main Peak Area	O 1s Shoulder Peak Area	O 1s Shoulder Peak Area Ratio (%)
15Ni2La/M-Ce80Zr20	62695.89	63689.8	50.39
15Ni2Pr/M-Ce80Zr20	80514.51	67103.99	45.46
15Ni2Sm/M-Ce80Zr20	56684.18	50302.07	47.02
15Ni2Yb/M-Ce80Zr20	78341.24	66003.99	45.72
15Ni/M-Ce80Zr20	31806.181	28467.17	47.23

## 2.2. Catalytic Performance toward CO<sub>2</sub> Methanation

# 2.2.1. The Promoting Effect of Rare Earth Doping on Catalytic Activity

The catalytic activity of 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts at different reaction temperatures was investigated under the specified conditions ( $H_2/CO_2 = 4$ , GHSV = 12,000 mL/(g·h), 1 atm), and their catalytic performances are shown in Figure 9. As can be seen from Figure 9a, the rare earth doped 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts had the higher  $CO_2$  conversion rate than that of the original 15Ni/M-Ce80Zr20catalyst. Specifically, 15Ni2La/M-Ce80Zr20 had a much higher CO<sub>2</sub> conversion rate than the other catalysts, especially in the low temperature range. In addition, it can be found that the trend of the CO<sub>2</sub> conversion curve of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts were completely different from that of the equilibrium  $CO_2$  conversion curve. This was mainly due to the contradiction between kinetics and thermodynamics. In particular, according to previous literature [60], CO<sub>2</sub> methanation is controlled by the kinetics at low temperatures due to the inert property of the stable  $CO_2$  molecule, which is then controlled by thermodynamics at high temperature. Although the lower reaction temperature was theoretically conducive to achieving a higher equilibrium CO<sub>2</sub> conversion rate, the large kinetic barrier limited the methanation of CO<sub>2</sub> activity at low-temperature. Therefore, the doping of rare earth can greatly improve the  $CO_2$  methanation activity of Ni-based catalysts, and La was considered to be the best rare earth modifier among these rare earths. The CH<sub>4</sub> selectivity of 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts at different temperatures is shown in Figure 9b. It can be seen that with the increase in reaction temperature, the equilibrium selectivity of CH<sub>4</sub> gradually decreased, which was due to the generation of CO gas at the water gas shift (RWGS) side of the reaction, which reduces the selectivity of CH<sub>4</sub> [9,61]. In addition, the CH<sub>4</sub> selectivity of the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts were higher than that of the 15Ni/M-Ce80Zr20 catalyst. This indicates that rare earth elements also promoted the selectivity of CH<sub>4</sub>.



**Figure 9.** The curves of the (**a**) CO<sub>2</sub> conversion and (**b**) CH<sub>4</sub> selectivity versus reaction temperature over the 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts; reaction condition:  $H_2/CO_2 = 4$ , GHSV = 12,000 mL/(g·h), 1 atm.

In general, these rare earth doped 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb) catalysts have higher catalytic activity at low temperature than the original 15Ni/M-Ce80Zr20 catalyst. The results showed that the rare earth dopants (La) played an important role in improving the catalytic activity of the catalysts at low temperature.

## 2.2.2. Catalytic Stability Tests

An important problem for  $CO_2$  methanation is to conduct long-term stability experiments on catalysts because the exothermic property, the hot sintering of metal Ni active site, led to rapid subsequent deactivation. The 40 h catalytic stability tests at 400 °C were also conducted over 15Ni/M-Ce80Zr20 and 15Ni2La/M-Ce80Zr20 catalysts under the specified conditions ( $H_2/CO_2 = 4$ , GHSV = 12,000 mL/(g·h), 1 atm) and their profiles are exhibited in Figure 10. As shown in Figure 10a, the  $CO_2$  conversions over the 15Ni/M-Ce80Zr20 and 15Ni2La/M-Ce80Zr20 catalysts did not decrease after 40 h stability tests. Furthermore, the 15Ni2La/M-Ce80Zr20 catalyst doped with rare earth also displayed higher activity than the 15Ni/M-Ce80Zr20 single metal counterparts. Its excellent performance should be attributed to the limiting effect of mesoporous skeleton on the stabilization of metal Ni active sites, forming a strong metal-skeleton interaction in the mesoporous skeleton. Similarly, it was noticeable in Figure 10b that the  $CH_4$  selectivity over the 15Ni/M-Ce80Zr20 and 15Ni2La/M-Ce80Zr20 catalysts were also stable during the stability tests, suggesting that severe hot sintering of the metal Ni active center had been effectively avoided. The stable catalytic activities and selectivity over the 15Ni/M-Ce80Zr20 and 15Ni2La/M-Ce80Zr20 catalysts could be attributed to the outstanding sintering-proof properties. In general, the 15Ni2La/M-Ce80Zr20 catalyst was provided with not only advanced low-temperature activity, but also outstanding catalytic stability. Figure 11 shows the XRD analysis of the spent 15Ni/M-Ce80Zr20 and 15Ni2La/M-Ce80Zr20 catalysts after 40 h long-term stability tests. The results showed that the catalyst exhibited the characteristic peak of Ni (PDF-#-45-1027) after the stability test. Moreover, the metal Ni peak of 15Ni2La/M-Ce80Zr20 was weaker than that of 15Ni/M-Ce80Zr20, which indicated that 15Ni2La/M-Ce80Zr20 had better dispersion of metal Ni. The FWHM reflected the diameter of metal Ni in the catalysts. The smaller the diameter, the larger the FWHM that can be obtained. It could be obtained that the FWHM of the metal Ni diffraction peak of 15Ni2La/M-Ce80Zr20 was higher than that of 15Ni/M-Ce80Zr20, which indicated that the metal Ni in 15Ni2La/M-Ce80Zr20 was smaller and could be uniformly distributed in the catalysts. Therefore, due to the mesoporous structure of M-Ce80Zr20, 15Ni2La/M-Ce80Zr20 showed excellent thermal sintering resistance.



**Figure 10.** Forty hour long-term stability tests over the 15Ni/M-Ce80Zr20 and 15Ni2La/M-Ce80Zr20 catalysts: (a) CO<sub>2</sub> conversion, (b) CH<sub>4</sub> selectivity; reaction conditions:  $H_2/CO_2 = 4$ , GHSV = 12,000 mL/(g·h), 400 °C, 1 atm.



**Figure 11.** XRD patterns of the spent 15Ni/M-Ce80Zr20 and 15Ni2La/M-Ce80Zr20 catalysts after 40 h long-term stability tests.

## 3. Experimental and Methods

#### 3.1. Catalyst Preparation

# 3.1.1. The Fabrication of the Mesoporous Ce-Zr Solid Solution Support

The mesoporous Ce–Zr solid solution material (Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>) was synthesized by the EISA strategy reported elsewhere [38,62]. In the preparation process, 1.0 g of P123 (Molecular Weight (MW) = 5800, EO20PO70EO20, Aladdin, Shanghai, China) was first dissolved in 20.0 mL of anhydrous ethanol (C<sub>2</sub>H<sub>5</sub>OH) and the P123 was completely dissolved by strong magnetic stirring. Then, 8 mmol of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>Oand 2 mmol of ZrOCl<sub>2</sub>·8H<sub>2</sub>O were added to the above solution and magnetic agitation was performed with strong force until the solution was transparent. The transparent solution was stirred into a culture dish and covered with a PE membrane with small holes. The final solution was moved to a culture dish and placed in a 100 °C convection oven with relative humidity less than 50% for solvent volatilization and template assembly. After experiencing the 48 h EISA process, the golden yellow dried gel in the culture dish was transferred to the crucible and calcined at 500 °C for 5 h. The final mesoporous Ce–Zr solid solution with the 80/20 Ce/Zr molar ratio was abbreviated as M-Ce80Zr20.

#### 3.1.2. The Preparation of the Catalysts

The Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Yb(NO<sub>3</sub>)<sub>3</sub>· 5H<sub>2</sub>O were selected as the metal precursors and all catalysts were prepared by the incipient impregnation method using the M-Ce80Zr20 as the support. The weight percentages of the Ni and rare earth (R = La, Sm, Pr, Yb) were controlled at 15.0 wt.% and 2.0 wt.%, respectively. The catalyst precursors were dried at 100 °C in a convection oven overnight and then calcined at 500 °C for 5 h. The final bimetal catalysts with 15.0 wt.% Ni and 2.0 wt.% rare earth were denoted as 15Ni2R/M-Ce80Zr20 (R = La, Sm, Pr, Yb).

## 3.2. Catalyst Characterizations

The XRD patterns of the catalysts were recorded on a XRD-6100 diffractometer (Shimadzu, Kyoto, Japan) with Cu K $\alpha$  radiation and scanning rate of 3°/min in the range of 20–80°.

The  $N_2$  physisorption analysis was carried out on an Autosorb-iQ-AG-MP instrument (Quantachrome, Boynton Beach, US). The Brunauer–Emmett–Teller (BET) specific surface area, Barret–Joyner–Halenda (BJH) pore volume, and pore size distribution of the sample were calculated based on the  $N_2$  adsorption branch of the isotherm.

The TEM images, STEM images, and EDS mapping were taken on a high-resolution transmission electron microscopy (FEI TECNAI G2 F20, Hillsboro, OR, USA). The sample was uniformly dispersed in absolute ethanol with the assistance of ultrasonic and then dropped on the copper grid sample holder coated with a carbon layer.

The valence state and composition of the surface elements in the catalysts were characterized by XPS. The binding energy of the catalyst was calibrated by using C1s (284.5 eV) as the internal standard.

The H<sub>2</sub>-TPR analyses of the catalysts were carried out on a micro fixed reactor with a LC-D200 mass spectrometer (TILON, US) as the detector. In a specific test, 200 mg of sample was loaded in a quartz tube (i.d. = 5.0 mm). The sample was first purged with Ar (20.0 mL/min) at 300 °C for 30 min before the regular analysis. Then, the 5 vol.% H<sub>2</sub>-95 vol.% Ar mixture stream (50.0 mL/min) was introduced. After the baseline of the H<sub>2</sub> mass signal (m/z = 2) was stable, the temperature was programmatically increased from 25 °C to 800 °C with the rate of 20 °C /min and the H<sub>2</sub> mass signal was recorded with the LC-D200 mass spectrometer during the whole H<sub>2</sub>-TPR process.

The CO<sub>2</sub>-TPD analyses of the samples were analyzed on the same apparatus of the H<sub>2</sub>-TPR described above. Specifically, 100 mg of catalyst was loaded and absorbed CO<sub>2</sub> in a CO<sub>2</sub> stream (10.0 mL/min) at 25 °C for 30 min. Then, the sample was purged by the Ar stream until the CO<sub>2</sub> baseline (m/z = 44) was stable. Finally, the sample was programmatically heated from 25 °C to 800 °C with a ramp of 20 °C/min under Ar stream (40.0 mL/min) and the CO<sub>2</sub> signal during the CO<sub>2</sub>-TPD was recorded by the mass spectrometer.

#### 3.3. Catalyst Evaluation

Catalytic activity tests were conducted in a micro fixed bed reactor equipped with a quartz tube (i.d. = 10 mm) and the reaction quartz tube was placed vertically in a tube furnace. The temperature of the reaction was detected and controlled by the thermocouple located in the center of the catalyst bed. The gas flows of the feed gases were controlled by the mass flow controllers (MFC, Brooks Instrument, Hatfield, UK) and the ratio of the reactants (H<sub>2</sub>/CO<sub>2</sub>) was controlled at 4/1 without any dilution. The reaction pressure is controlled at 1.0 atm and the reaction temperature was investigated in the range of 200–450 °C. For each test, 100 mg of catalyst was loaded and the space velocity was set as 12,000 mL/(g·h). The 40 h stability tests were performed at 400 °C with the GHSV of 12,000 mL/(g·h). Before the catalytic reactions, the catalyst in the reactor was first prereduced with  $H_2/N_2 = (10.0/10.0 \text{ mL/min})$  at 500 °C for 3 h. A Perkin Elmer GC-680 gas chromatograph equipped with a thermal conductivity detector (TCD) and a hydrogen flame detector (FID) was used for online analysis of the products.

## 4. Conclusions

The rare earth (R = La, Sm, Pr, Yb) doped Ni-based mesoporous  $Ce_{0.8}Zr_{0.2}O_2$  were prepared via the incipient co-impregnation method for  $CO_2$  methanation. Compared with the Ni-based single catalyst, the rare earth doped catalysts showed much higher low-temperature activities. The addition of rare earth greatly improved the surface basicity and electronic properties of the catalysts, and promoted the chemisorption and activation of CO<sub>2</sub>. Thus, the results showed that the 15Ni2La/M-Ce80Zr20 catalyst had the optimum catalytic performance. In addition, by limiting the Ni species in the mesoporous carrier, a strong interaction between the active site of Ni and the mesoporous skeleton is formed, which can effectively stabilize the metallic nickel nanoparticles through the restriction effect. In addition, the 15Ni2La/M-Ce80Zr20 and 15Ni/M-Ce80Zr20 catalyst had excellent stability without any deactivation after 40 h tests. In summary, a series of the rare earth doped Ni-based mesoporous Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> catalysts prepared in this study can be used as CO<sub>2</sub> methanation catalysts with strong low temperature activity.

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