Syngas Production via CO₂ Reforming of Methane over Aluminum-Promoted NiO–10Al₂O₃–ZrO₂ Catalyst

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ABSTRACT: CO₂ reforming of methane was studied at medium temperature (700 °C) using a GHSV of 48,000 h⁻¹ over nickel catalysts supported on ZrO₂ promoted by alumina. The catalysts were prepared by a one-step synthesis method and characterized by BET, H₂-TPR, XRD, XPS, TEM, Raman spectroscopy, and TGA. The NiO–10Al₂O₃–ZrO₂ catalyst exhibited higher catalytic performance in comparison with the NiO–ZrO₂ catalyst. The enhancement of catalytic activity in dry reforming could be associated with the alterations in surface properties due to Al promotion. First, the Al promoter could modify the structure of ZrO₂, leading to an increase of its pore volume and pore diameter. Second, the NiO–10Al₂O₃–ZrO₂ catalyst exhibited high resistance to sintering. Third, the NiO–10Al₂O₃–ZrO₂ catalyst showed high suppression to the loss of nickel during a long-term catalytic test. Finally, the addition of Al could inhibit the reduction of ZrO₂ during the reduction and reaction, endowing further the stability.

INTRODUCTION

In recent years, the reaction of carbon dioxide reforming of methane, which is defined as the dry reforming of methane (DRM), has garnered extensive attention among scientific researchers. It utilizes two greenhouse gases (CO₂ and CH₄) to produce syngas (CO and H₂), which can be further converted to methanol or fuels through Fisher–Tropsch synthesis.⁴⁻⁶ Therefore, the global warming issues could be mitigated through the deep investigation of the DRM reaction.

According to the literature, a large number of parallel side reactions, such as the CO disproportionation, CH₄ decomposition, reverse water gas shift, and so on (Table 1), might take place during the DRM reaction.⁴⁻⁶ The reverse water gas shift reaction would consume H₂ and reduce the H₂/CO molar ratio. The CO disproportionation and CH₄ decomposition led to carbon deposition.

Nickel shows excellent catalytic activity as noble ones (Pt, Ru, and Rh), and Ni-based catalysts have been widely reported for the DRM reaction.⁷⁻¹⁰ Pompeo et al.⁹ compared the catalytic performance of Ni and Pt supported on α-Al₂O₃, ZrO₂ and α-Al₂O₃–ZrO₂ catalysts for the dry reforming of methane. They found that nickel was slightly more active than platinum. Moreover, the nickel-based catalysts served as the optimal alternatives considering economic viability.¹¹ However, the deactivation of Ni-based catalysts due to sintering and/or carbon deposit needs to be addressed in order to achieve facile scaling-up in the industrial process. Thus, tremendous efforts have been focused on the development of promoters or novel support materials to address these two problems, further contributing to the design of catalysts with higher stability.¹²,¹³

It has been found that aluminum (Al) as a promoter and/or support could enhance the catalytic performance mainly because Al could improve the reducibility and dispersion of nickel. Liu et al.¹⁴ investigated the effect of La, Al, and Mn promoters on Fe-modified natural clay-supported Ni catalysts for the dry reforming of methane. The promotion of La increased the activity of the catalyst, while the addition of Al inhibited the sintering of Ni catalysts. However, it is necessary to carry out experiments to clarify the mechanism of the promotion process. Moreover, it is also necessary to identify which conditions should be used for Ni-based catalysts to achieve the highest activity and stability during the DRM reaction.
reforming of methane, and confirmed that the Al-promoted catalyst exhibited the highest catalytic performance in the dry reforming of methane since Al could improve the dispersion and reducibility of nickel species. Talkhoncheh and Haghighi found that Ni/Al2O3 nanocatalysts exhibited the best performance among Ni/clinoptilolite and Ni/CeO2 due to the higher specific surface area, homogenous distributions, and good dispersion of Ni species. Various supports have been employed, such as CeO2, ZrO2, SiO2, La2O3, and Al2O3. ZrO2 exhibits favorable properties such as thermal stability, oxygen storage capacity, enhancement of the metallic dispersion, and the ability of CO2 adsorption. Therefore, many researchers have focused on the utilization of ZrO2 support for DRM. Pompeo et al. found that ZrO2 as a basic support could promote the adsorption of CO2, thereby inhibiting the carbon deposition. Mesoporous La2O3–ZrO2 could promote the stability of the catalyst due to the high dispersion of nickel species. Miao et al. found that mesoporous-ZrAl-10 (M-ZrAl-10) with the Al content of 10% exhibited better physical properties than the mesoporous-ZrO2 (M-ZrO2) support. The specific surface area increased from 9.8 to 56 m2/g, the pore volume increased from 0.07 to 0.13 cm3/g, and the pore size distribution decreased from 23.9 to 8.2 nm by the addition of 10 wt % Al. On one hand, the properties of ZrO2 support could be modified by the introduction of alumina species. On the other hand, ZrO2 could enhance the performance of the catalyst with Al2O3 support for the dry reforming of methane. Therdthianwong et al. demonstrated that the Ni/Al2O3 catalyst modified by ZrO2 exhibited higher stability for the dry reforming of methane because ZrO2 could promote the elimination of carbon deposition by the dissociation of CO2 to form oxygen intermediates. The spinel NiAl2O4 that formed under the reduction process at higher temperature results in lower activity. The zirconia addition could avoid the formation of spinel NiAl2O4. Li and Wang also found that the interaction between nickel and the Al2O3–ZrO2 support could avoid the formation of spinel NiAl2O4.

Thus, to combine the advantages of Al and Zr, a series of 10NiO–xAl2O3–(90–x)ZrO2 (x = 0, 10, 20, 45, 90) catalysts were prepared by a one-step synthesis method and tested in the dry reforming of methane. A correlation between the structure and reactivity of promoted and non-promoted catalysts was proposed here in order to highlight the positive effects of aluminum promotion on the catalytic activity in the DRM reaction.

## RESULTS AND DISCUSSION

### Catalytic Performance in the Dry Reforming of Methane

The catalytic results of the DRM in terms of CO2 and CH4 conversion and the ratio of H2/CO with the range of 550–800 °C are presented in Figure 1. Within the series of 10NiO–xAl2O3–(90–x)ZrO2 catalysts, NiO–10Al2O3–ZrO2...
exhibited the highest CH4 conversion in the whole temperature range during the DRM experiment. This advantage became more prevalent with the decrease of reaction temperature, especially at 550 °C. On all the catalysts, the obtained CH4 conversion was always lower than the equilibrium conversions of CH4. From Figure 1A, the conversion of methane at 550 °C obtained for NiO–ZrO2, NiO–10Al2O3–ZrO2, NiO–20Al2O3–ZrO2, NiO–45Al2O3–ZrO2, and NiO–Al2O3 catalysts were 54, 62, 43, 45, and 42%, respectively. A similar trend was observed in CO2 conversion with the following results obtained at 550 °C: 56, 59, 53, 50, and 48% for NiO–ZrO2, NiO–10Al2O3–ZrO2, NiO–20Al2O3–ZrO2, NiO–45Al2O3–ZrO2, and NiO–Al2O3 catalysts, respectively (Figure 1B). The CO2 conversion of all studied catalysts was also found higher than the equilibrium conversions of CO2. Meanwhile, the conversion of CO2 on the NiO–ZrO2 catalyst was higher than the CH4 conversion, which indicated that the reverse water gas shift reaction (RWGS) occurred. The RWGS reaction would lead to lower the H2/CO ratio; therefore, the H2/CO ratio on catalysts was lower than the unity H2/CO ratio (Figure 1C). In addition, the H2/CO ratio increased by adding aluminum, indicating that the aluminum could enhance the selectivity to H2 of the catalyst. Similar results on the effect of Al have also been reported by Liu et al.\textsuperscript{14} and Chai et al.\textsuperscript{28}

The stability runs were performed on NiO–10Al2O3–ZrO2 and NiO–ZrO2 catalysts at 700 °C, and the results are presented in Figure 1. At 550 °C, the conversions of CH4 and CO2 on the NiO–10Al2O3–ZrO2 catalyst were higher than those on the NiO–ZrO2 catalyst, while the H2/CO ratio on the NiO–10Al2O3–ZrO2 catalyst was lower than the one on the NiO–ZrO2 catalyst with time on stream. Both catalysts exhibited stable catalytic performance for the DRM reaction. At 700 °C, for the methane conversion, a decrease was observed from 89 to 84% on the NiO–ZrO2 catalyst within 1 h. The NiO–10Al2O3–ZrO2 catalyst exhibited higher methane conversion, and its conversion remained almost constant at ca. 92%. For the CO2 conversion, an increase was observed with time on stream on the NiO–ZrO2 catalyst, which was slightly higher than the one on the NiO–10Al2O3–ZrO2 catalyst after an 8 h run. Meanwhile, the H2/CO ratio on the NiO–ZrO2 catalyst was slightly lower than the one on the NiO–10Al2O3–ZrO2 catalyst.

**Carbon Formation on NiO–ZrO2 and NiO–10Al2O3–ZrO2 Catalysts.** The carbon deposition of both catalysts was followed by TGA experiments and is shown in Figure 2. The carbon formation on the NiO–10Al2O3–ZrO2 catalyst (5.5%) (Figure 2B) was slightly higher than that found for the NiO–ZrO2 catalyst (4.4%) (Figure 2A), which can be ascribed to a slight decrease in CO2 conversion on the NiO–10Al2O3–ZrO2 catalyst during 8 h on-stream. In addition, an increase peak in the sample weight curve could be observed on both NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts due to the oxidation of the Ni0 species, implying that there was nickel metal on both catalysts after reaction.\textsuperscript{29,30} More carbon that can be removed obtained by the elimination of carbon deposition, and similar results have been reported.\textsuperscript{29} More carbon that can be removed at 420 °C formed on NiO–10Al2O3–ZrO2 catalysts after reaction, resulting in the mass value not over 100%. From the DSC curve, one peak corresponding to the maximum of carbon formation on the NiO–ZrO2 catalyst, which was slightly lower than the one on the NiO–10Al2O3–ZrO2 catalyst after an 8 h run. Meanwhile, the H2/CO ratio on the NiO–ZrO2 catalyst was slightly lower than the one on the NiO–10Al2O3–ZrO2 catalyst.

![Figure 2](https://doi.org/10.1021/acsomega.1c03174)
adsorbed oil pump molecules (C−C and C−H species). Another peak at 285.5 eV was assigned to the C−O and C−C species. The proportions of C−C and C−H species on NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts were 66 and 63%, respectively.

Another peak at 285.5 eV was assigned to the C−O and C−O species. The proportions of the surface C−C, C−O, and C−O species are listed in Table 2. The proportions of C−C and C−H species on NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts were 66 and 63%, respectively.

Table 2. Results of the TGA, XPS, and Raman Experiment for NiO−ZrO2 and NiO−Al2O3−ZrO2 Catalysts after Reaction at 700 °C for 8 h

| Catalyst          | Position/°C | Carbon Content/% | C−H | C−C | C−O+ | C=O | ID/IG |
|-------------------|-------------|-----------------|-----|-----|------|-----|-------|
| NiO−ZrO2          | 630         | 4.4             | 66  | 34  | 0.6  |
| NiO−10Al2O3−ZrO2  | 560         | 5.5             | 63  | 37  | 0.8  |

The carbon was determined by the TGA method. The C−X (X = H, O or C) species was determined by XPS. The ID/IG was determined by Raman spectroscopy.

From the Raman experiment, three distinct peaks (1345, 1580, and 2694 cm−1) could be observed for both NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts. The peaks at about 1345 and 1580 cm−1 were assigned to D (disorder) and G (graphite) bands of carbon materials, respectively. The peak at about 2694 cm−1 was ascribed to the overtone of the D band (2 × 1345 cm−1 = 2690 cm−1). The intensity of D and G bands is named as ID and IG, respectively. The ratio of ID/IG on NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts are 0.6 and 0.8 (Table 2), respectively. Namely, the type of carbon deposition was mainly in the form of graphite on both catalysts and more graphite formed on the NiO−ZrO2 catalyst. Combined with XPS and Raman results, the graphite consisted of C−C species, while disorder carbon materials were composed of C−O and C=O species. Those phenomena indicated that the carbon deposition on both NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts was presented as containing graphitic carbon (C−C species). The graphite carbon is generally very difficult to be removed, and the amorphous carbon is easy to be removed. Combined to the results of TGA, XPS, and Raman spectroscopy, the higher content of carbon that is easy to be removed formed on the NiO−10Al2O3−ZrO2 catalyst.

The morphology of carbon deposition on NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts was determined by using transmission electron microscopy. The results are presented in Figure 3. A large amount of carbon in the form of a nanotube were deposited on the NiO−ZrO2 catalyst (Figure 3A,C), while only some amorphous carbon could be observed on the NiO−10Al2O3−ZrO2 catalyst (Figure 3B,D), which was consistent with the results of XPS and Raman. In addition, the amount of carbon deposition on the NiO−ZrO2 catalyst (4.4%) was lower than the one on the NiO−10Al2O3−ZrO2 catalyst (5.5%), while the intensity of the C 1s curve in XPS spectra on the NiO−ZrO2 catalyst.
catalyst was stronger than that on the NiO−10Al2O3−ZrO2 catalyst. There are three reasons. First, the C species determined by XPS could be affected by the polluted carbon that came from the oil in the pump. Second, the content of C species determined by XPS was the surface content, not the real value of carbon. The TGA presented the real value of carbon deposition. Lastly, the amorphous carbon formed in the pore of the NiO catalyst, which cannot be detected by XPS, while more amorphous carbon formed in the pore of the NiO catalyst. A part of CO2 reacted with hydrogen rather than reverse water-gas shift (RWGS) reaction occurred on the NiO catalyst. Also, according to the results of stability test, the rate of carbon deposition was higher than the one on the NiO−10Al2O3−ZrO2 catalyst. The specific surface area could be influenced by the pore volume, pore diameter, particle size, and so on. The large particle size of Ni species can lead to a lower surface area. The NiO species with the crystallite size of 10 nm (Table 3) could be detected on the NiO−10Al2O3−ZrO2 catalyst, while almost no NiO species could be found on the NiO−ZrO2 catalyst. Thus, the physical properties (pore volume and pore diameter) could be promoted by the introduction of aluminum. This large pore volume and pore diameter may cause an increase in the proportion of metal nickel dispersed in the porous structure of the catalysts. The reducibility of NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts were determined by H2-TPR experiments, as shown in Figure 5. The reduction temperatures on the NiO−10Al2O3−ZrO2 catalyst shifted toward higher values as compared to the NiO−ZrO2 catalyst, which was an indication for a stronger interaction between Ni and the support on the promoted catalyst. This stronger metal−support interaction could inhibit the sintering of Ni particles, hence enhancing the stability of the catalyst.31

### Table 3. Results of the BET, XRD, and TEM Experiment for NiO−ZrO2 and NiO−10Al2O3−ZrO2 Catalysts after Reduction and after Reaction at 700 °C for 8 h

| Catalyst         | Dp (nm) | SP2 (m2/g) | VP (cm3/g) | Ni0 crystallite sizes (nm) | Particle size of Ni (nm) |
|------------------|---------|------------|------------|--------------------------|--------------------------|
| NiO−ZrO2         | 3       | 113        | 0.18       | 10−12                    | 5−10                     |
| NiO−10Al2O3−ZrO2 | 6       | 86         | 0.25       | 10−12                    | 5−10                     |

*The pore diameter (Dp) and the pore volume (VP) were determined by the BJH method, and the specific surface area ($S_{BET}$) was determined by the BET method. *The Ni0 crystallite sizes were determined by XRD (Scherrer equation). *The particle size of Ni was determined by TEM.*

Physicochemical Features of NiO−ZrO2 and NiO−10Al2O3−ZrO2 Catalysts. Figure 4 presented the adsorption/desorption isotherms of the non-promoted and promoted catalysts. The adsorption isotherms for NiO−10Al2O3−ZrO2 and NiO−ZrO2 catalysts were both type IV isotherms, with an H2 hysteresis loop according to the literature, which is typical of mesoporous materials. The pore size distribution (Figure 4B) indicated that the pore size of NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts is almost distributed at about 3 and 6 nm, respectively. The pore volume (VP) and the specific surface area ($S_{BET}$) are listed in Table 3. A large pore volume (0.25 cm3/g) and pore diameter (6 nm) were observed on the NiO−10Al2O3−ZrO2 catalyst.

However, the specific surface area on the NiO−ZrO2 catalyst was higher than the one on the NiO−10Al2O3−ZrO2 catalyst. The specific surface area could be influenced by the pore volume, pore diameter, particle size, and so on. The large particle size of Ni species can lead to a lower surface area. The NiO species with the crystallite size of 10 nm (Table 3) could be detected on the NiO−10Al2O3−ZrO2 catalyst, while almost no NiO species could be found on the NiO−ZrO2 catalyst. Thus, the physical properties (pore volume and pore diameter) could be promoted by the introduction of aluminum. This large pore volume and pore diameter may cause an increase in the proportion of metal nickel dispersed in the porous structure of the catalysts.

The reducibility of NiO−ZrO2 and NiO−10Al2O3−ZrO2 catalysts were determined by H2-TPR experiments, as shown in Figure 5. The reduction temperatures on the NiO−10Al2O3−ZrO2 catalyst shifted toward higher values as compared to the NiO−ZrO2 catalyst, which was an indication for a stronger interaction between Ni and the support on the promoted catalyst. This stronger metal−support interaction could inhibit the sintering of Ni particles, hence enhancing the stability of the catalyst.

![Figure 4. Isotherm (A) and pore size distribution (B) of NiO−ZrO2 and NiO−Al2O3−ZrO2 catalysts.](https://doi.org/10.1021/acsomega.1c03174)

![Figure 5. H2-TPR profiles of NiO−ZrO2 and NiO−Al2O3−ZrO2 catalysts.](https://doi.org/10.1021/acsomega.1c03174)
Three peaks could be distinguished (denominated α, β, and γ) on both catalysts, and the content of each peak is presented in Table 4. The first peak (α) at 400–500 °C was related to the reduction of NiO species with weak interaction between zirconia, which might be easy to sinter during the DRM reaction.42,43 The second peak (β) at 500–600 °C corresponded to the reduction of NiO species inside the mesoporous network with strong interaction between zirconium, which could maintain the original state even after reduction and reaction.44–46 The third peak (γ) at 600–800 °C was assigned to the NiO species in the skeleton of ZrO2 and ZrO2 species.47,48 The proportion of three peaks on NiO–10Al2O3–ZrO2 and NiO–ZrO2 catalysts is shown in Table 4. The content of the β peak was about 40% on the NiO–10Al2O3–ZrO2 catalyst, which was higher than the one on the NiO–ZrO2 catalyst (15%) because the NiO–10Al2O3–ZrO2 catalyst exhibited a large pore volume and pore diameter. Considering the content of the α peak, about 44% (40 + 4 = 44%) H2 consumption came from the reduction of NiO species out of the skeleton. The ratio of the NiO species out/in the skeleton was about 24:51 on NiO–ZrO2 and 44:47 on NiO–10Al2O3–ZrO2 catalysts, respectively. In addition, a part of nickel species could be released and distributed on the surface of ZrO2 or enter into the porosity. Then, this shift could lead to an increase in the proportion of NiO species on the surface, which could promote the activity of the catalyst, due to the probability of the contact of the reactant with the active metal. In addition, the total H2 consumption on the NiO–10Al2O3–ZrO2 catalyst was about 479 μmol H2/g (Table 4), which was higher than the theoretical value (434 μmol H2/g), indicating that this 9% ((479 − 434)/479 × 100% = 9%) of H2 consumption was assigned to the reduction of Zr4+ to Zr3+, as proved by Zr 3d of XPS spectra, which was consistent with the results of the activity test.

The crystallite sizes on NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts were determined by XRD, as shown in Figure 7. The diffraction peak corresponding to NiO could not be observed on both catalysts after reduction, indicating that all the NiO species were reduced. Ni metal peaks were obvious on both catalysts before and after the reaction, and the crystallite size of Ni metal is shown in Table 3. Before the reaction, those two catalysts exhibited the same Ni0 crystallite size (12 nm), which was consistent with the TEM results. According to the H2-TPR results, the NiO–ZrO2 catalyst exhibited a higher content of the α peak (the NiO is well-known to be easily sintered) and lower content of the β peak (the NiO was more difficult to sinter), which led to very severe sintering. Therefore, the Ni metal particle size increased to 24 nm on the NiO–ZrO2 catalyst after the reaction, which corresponded to the nickel particle size determined by the TEM experiment, concentrated at 15–20 nm (Table 3). On the contrary, it decreased to 11 nm on NiO–10Al2O3–ZrO2 catalyst after reaction, and according to the TEM results, the nickel particle size mainly distributed at 10–15 nm. The lower content of the α peak and higher content of the β peak formed on the NiO–10Al2O3–ZrO2 catalyst, and thus, the Ni species might be better to stay pristine in the porosity, as compared with the NiO–ZrO2 catalyst. There were two reasons to explain the decrease of the Ni metal particle size. First, the Ni metal can be redispersed during reaction. Second, part of metallic Ni (Ni0) could be oxidized to NiO or NiCOx by CO, and CO2 could be adsorbed on NiO.49,50

Obviously, the structure of the nickel particle on the NiO–10Al2O3–ZrO2 catalyst was more stable, contributing to the stability of the catalyst. Therefore, the NiO–10Al2O3–ZrO2 catalyst exhibited higher stability for the dry reforming of methanol. In addition, the large nickel metal particle size could affect the selectivity of catalyst toward carbon deposition.52,53 Hence, the carbon deposited on the NiO–ZrO2 catalyst was difficult to be removed because of its graphite form.

From XPS, the Zr 3d in XPS profiles of NiO–10Al2O3–ZrO2 and NiO–ZrO2 catalysts before and after reduction were studied and the results are presented in Figure 8A. The intensity of the surface Zr species decreased on both catalysts after the reaction because the formation of carbon would cover on the NiO in the γ peak was 51 and 47% on NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts, respectively. This fact suggested that more NiO and ZrO2 species were reduced on the NiO–ZrO2 catalyst.

The morphology of reduced NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts was determined by TEM, as shown in Figure 6. A similar distribution of nickel particles could be observed on both catalysts, almost at 5–10 nm. The highly dispersed Ni species on reduced catalysts could promote the activity of the DRM reaction. Herein, the similar distribution of Ni species resulted in similar initial activity on NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts, which was consistent with the results of the activity test.

### Table 4. Consumption of H2 and the Proportion of Three Peaks on the H2-TPR Experiment

| catalyst          | total μmol H2/g | α (%) | β (%) | γ (%) | NiO | NiO | NiO | ZrO2 | ratio of out/in |
|-------------------|-----------------|------|------|------|-----|-----|-----|------|----------------|
| NiO–ZrO2          | 626             | 648  | 9    | 15   | 51  | 25  | 25  | 25:41 |
| NiO–10Al2O3–ZrO2  | 479             | 434  | 4    | 40   | 47  | 9   | 9   | 44:47 |

"The H2 consumption of the theory calculated by ICP and the consumption of reduction of pure NiO. bThe proportion of NiO in the skeleton of ZrO2. cThe ratio of the NiO species out/in the skeleton.

### Table 5. Content of Zr, Ni, and O Species on both Catalysts before and after Reaction at 700 °C for 8 h, Determined by XPS

| catalyst          | Zr proportion (%) | initial | 8 h  | Ni content (wt %) | initial | 8 h  | ΔNi0 | ΔNi0 σ | ΔNi0 σ | Oσ/Oads |
|-------------------|-------------------|---------|------|------------------|---------|------|------|--------|--------|--------|
| NiO–ZrO2          | Zr4+              | 11      | 89   | Ni0              | 5.6     | 1.9  | −21% | −21%   | 0.98   | 0.27   |
|                   | Zr3+              | 17      | 25   | Ni0              | 5.8     | 1.0  | −3%  | +10%   | 1.02   | 0.94   |
| NiO–10Al2O3–ZrO2  | Zr4+              | 14      | 86   | Ni0              | 5.6     | 1.1  | −21% | −21%   | 0.98   | 0.27   |
|                   | Zr3+              | 22      | 34   | Ni0              | 5.6     | 1.1  | −3%  | +10%   | 1.02   | 0.94   |

"The loss of surface nickel species after the DRM reaction for 8 h. aThe loss of surface nickel metal species after the DRM reaction for 8 h.

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surface of catalyst, especially for the NiO–ZrO₂ catalyst. More surface carbon formed on the NiO–ZrO₂ catalyst, as proved by C 1s in XPS. Similar results had been reported in the literature.54,55 The peaks at about 182.3, 181.4, 180.5, and 179.3 eV are attributed to the Zr⁴⁺, Zr³⁺, Zr²⁺, and Zr¹⁺, respectively.47,56 The proportion of Zr⁴⁺ and Zr³⁺ is listed at Table 5. The proportion of surface Zr³⁺ on NiO–ZrO₂ and NiO–10Al₂O₃–ZrO₂ catalysts were 11 and 14%, respectively, which indicated that a part of Zr⁴⁺ could be reduced to Zr³⁺ after reduction on both catalysts. After the reaction, a part of surface Zr³⁺ species was reduced to lower valence, e.g., Zr²⁺ and Zr¹⁺.57–60 Then, the NiO–ZrO₂ catalyst exhibited a higher content of lower valence zirconium, especially containing Zr¹⁺ species of 35%, while no Zr¹⁺ species could be observed on the NiO–10Al₂O₃–ZrO₂ catalyst, manifesting that the structure of ZrO₂ might be more stable by the modification of Al.

Figure 6. Morphology of reduced NiO–ZrO₂ (A) and reduced NiO–10Al₂O₃–ZrO₂ (B) catalysts determined by TEM.

Figure 7. XRD profiles of (a) NiO–ZrO₂ and (b) NiO–10Al₂O₃–ZrO₂ catalysts and (c) NiO–ZrO₂ and (d) NiO–10Al₂O₃–ZrO₂ catalysts after reduction at 700 °C for 1 h and (e) NiO–ZrO₂ and (f) NiO–10Al₂O₃–ZrO₂ catalysts after reaction at 700 °C for 8 h.

Figure 8. Zr 3d (A), Ni 2p (B), and O 1s (C) profiles of (a) NiO–10Al₂O₃–ZrO₂ and (c) NiO–ZrO₂ catalysts after reduction at 700 °C for 1 h and (b) NiO–10Al₂O₃–ZrO₂ and (d) NiO–ZrO₂ catalysts after reaction at 700 °C for 8 h.
We also followed the Ni species at the surface by XPS. Figure 8B presented the Ni 2p profiles of NiO–10Al2O3–ZrO2 and NiO–ZrO2 catalysts before and after the reaction. The peak at about 852.8 eV was attributed to Ni8 species, while another peak was assigned to Ni6 species. After the reaction (DRM, 700 °C, 8 h), the NiO peak shifted slightly to lower binding energy on NiO–10Al2O3–ZrO2. It suggested that the electrons on the support could transfer to Ni species during the reaction, which might contribute to the catalytic performance of the catalyst.\(^{36,53}\) Whereas, the NiO peak shifted slightly to higher binding energy on the NiO–ZrO2 catalyst, which indicated that the ability of nickel species to receive electrons on the NiO–10Al2O3–ZrO2 catalyst was weaker than the one on the NiO–ZrO2 catalyst.\(^{36,53}\) Except for the electron transfer, the nickel content also varied visibly. Before the reaction, the content of surface nickel species on NiO–ZrO2 catalyst was about 5.6 wt %, while after reaction for 8 h, it decreased by 24% (Table 5). A larger amount of reduction could be observed in the content of surface Ni6 species. It decreased by 42% after reaction. Thus, the activity on the NiO–ZrO2 catalyst also decreased. However, nickel species were relatively stable on the NiO–10Al2O3–ZrO2 catalyst after the reaction, the surface nickel content was 5.8 wt % at the beginning, while it just decreased by 3% after reaction for 8 h.

Meanwhile, the initial content of surface Ni6 species was about 1.0 wt % and increased by 10% on the NiO–10Al2O3–ZrO2 catalyst after reaction for 8 h. The content of nickel species at the surface of the NiO–10Al2O3–ZrO2 catalyst was more stable than that on the NiO–ZrO2 catalyst, which might contribute to the stability of the catalyst. Therefore, the NiO–10Al2O3–ZrO2 catalyst exhibited higher stability for the dry reforming of methane. After reduction, a large amount of Ni6 species could be detected, which may be explained by the following three reasons. First of all, Ni6 species on the surface of the catalyst could adsorb the oxygen in the air; second, the Ni6 species may be re-oxidized when the reduced catalyst exposed to air; and the last, it could be due to the strong interaction between the metal and support.\(^{51,61}\)

The O 1s in XPS profiles of NiO–10Al2O3–ZrO2 and NiO–ZrO2 catalysts before and after the reaction was studied, and the results are presented in Figure 8C. The peaks at 529.0 and 531.2 eV were assigned to the lattice oxygen species (O\(^{2−}\)) and adsorbed oxygen species (O\(_{\text{ads}}\)), respectively.\(^{51,29,62,63}\) The ratio of O\(^{2−}\)/O\(_{\text{ads}}\) is listed in Table 5. After reduction, the ratio of O\(^{2−}\)/O\(_{\text{ads}}\) on NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts was almost the same. After reaction, it decreased from 0.98 to 0.27 on the NiO–ZrO2 catalyst, while it decreased from 1.02 to 0.94 on the NiO–10Al2O3–ZrO2 catalyst. This phenomenon implied that the surface lattice oxygen species on the NiO–ZrO2 catalyst plummeted, which was consistent with that more Zr species were reduced after the reaction on the NiO–ZrO2 catalyst.

The ammonia desorption results are shown in Figure 9. A wide composite desorption peak with the temperature range of 50 to 500 °C was obtained on both NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts. According to the literature,\(^{64,65}\) the wide peak could be deconvoluted into three contributions, which corresponds to weak, medium strength, and strong acid sites. The medium strength and strong peaks shifted to higher temperatures on the NiO–10Al2O3–ZrO2 catalyst. In other words, the presence of Al seems generally to enhance the acidity of the catalyst. The deconvolution results of the NH\(_3\)-TPD profiles are presented in Table 6. The total acidity on NiO–10Al2O3–ZrO2 and NiO–ZrO2 catalysts was 466 and 486 \(\mu\)mol NH\(_3\)/g, respectively. In addition, the proportion of weak, medium strength, and strong acid sites on the NiO–ZrO2 catalyst was 48.5, 34.9, and 16.6%, respectively. It was 26.9, 43.7, and 29.4% for weak, medium strength, and strong acid sites on the NiO–10Al2O3–ZrO2 catalyst, respectively. The NiO–ZrO2 catalyst exhibited a higher proportion of weak acid sites, while the NiO–10Al2O3–ZrO2 catalyst presented a higher proportion of medium strength and strong acid sites. Generally, the acidity could result in carbon deposition in the dry reforming of methane.\(^{66}\) The strong acid sites was considered important in the activation of hydrocarbons, and thus, the catalyst with more strong acid sites would promote the activation of methane.\(^{67}\) As a consequence, the NiO–10Al2O3–ZrO2 catalyst exhibited higher methane conversion and carbon deposition.

Meanwhile, the initial content of surface Ni6 species on NiO–ZrO2 catalyst plummeted, which might contribute to the stability of the catalyst. Therefore, the NiO–10Al2O3–ZrO2 catalyst exhibited higher stability for the dry reforming of methane. After reduction, a large amount of Ni6 species could be detected, which may be explained by the following three reasons. First of all, Ni6 species on the surface of the catalyst could adsorb the oxygen in the air; second, the Ni6 species may be re-oxidized when the reduced catalyst exposed to air; and the last, it could be due to the strong interaction between the metal and support.\(^{51,61}\)

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The FT-IR spectra of the adsorption of CO over NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts before and after the reaction are shown in Figure 10. The band at 2172 cm\(^{-1}\) was ascribed to CO interaction with Zr\(^{4+}\) moieties, and the signal at 2115 cm\(^{-1}\) was attributed to the physisorbed CO species.\(^{58-70}\) The intensity of those two peaks became weak when the temperature increased to 200 °C. In addition, two IR bands at 1638 and 1870 cm\(^{-1}\) could be observed on reduced NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts, which were assigned to CO species adsorbed on Ni metal particles.\(^{58,71}\) Both peaks on NiO–ZrO2 catalysts disappeared when the temperature increased to 200 °C, while the band at 1638 cm\(^{-1}\) on the NiO–10Al2O3–ZrO2 catalyst shifted to lower frequencies (1612 cm\(^{-1}\)). This red shift was caused by the decreasing of oxygen concentration on the interface of metal and support due to the desorption of CO species.\(^{2,75}\) A similar phenomenon could be observed on used NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts. In addition, no IR band at 1870 cm\(^{-1}\) could be observed on used NiO–ZrO2 and NiO–10Al2O3–ZrO2 catalysts, which were preferentially interacted with metallic Ni species on the NiO–10Al2O3–ZrO2 catalyst, which might contribute the promotion effect activity for dry reforming of methane.
loss of nickel during the DRM reaction, thereby promoting the stability of the catalyst.

### CONCLUSIONS

In this study, we clearly showed that aluminum (Al), as promoter could enhance the activity, selectivity, and stability of the NiO–ZrO₂ catalyst for dry reforming of methane. The activity tests were conducted from 550 to 800 °C, and the NiO–10Al₂O₃–ZrO₂ catalyst exhibited the highest catalytic performance for dry reforming of methane at lower temperature.

Furthermore, the stability tests, carried out at 700 °C for 8 h, showed that the NiO–10Al₂O₃–ZrO₂ catalyst exhibited the highest catalytic performance for dry reforming of methane at lower temperature. Furthermore, the stability tests, carried out at 700 °C for 8 h, showed that the NiO–10Al₂O₃–ZrO₂ catalyst exhibited the highest catalytic performance for dry reforming of methane at lower temperature.

Therefore, the NiO–10Al₂O₃–ZrO₂ catalyst exhibited higher stability for the DRM reaction. In fact, after 8 h runs, on the NiO–10Al₂O₃–ZrO₂ catalyst, it formed coke that is easier to be eliminated as a form of amorphous and disordered carbon (C—O and C≡O species). Also, on the NiO–ZrO₂ catalyst, a severe metal sintering occurred and more nanotube carbon (graphite) formed, which was very difficult to be removed.

### EXPERIMENTAL SECTION

**Synthesis of a Series of 10NiO–xAl₂O₃–(90−x)ZrO₂ Catalysts.** At the First, the dissolution of Pluronic P123 (amphiphilic block copolymer), Ni(NO₃)₂·6H₂O, ZrO(NO₃)₂·xH₂O, CH₃N₂O, and C₆H₇AlO₃ in 375 mL distilled water was carried out to obtain a mixture slurry under vigorous stirring. The concentration of the Ni(NO₃)₂ solution was about 0.01 mol/L. The molar ratio of Ni, Al, and Zr was 10:x:90 − x (x = 0, 10, 20, 45, 90), respectively. Second, the obtained suspension was heated to 95 °C under vigorous stirring for 2 days to ensure that the suspension was precipitated completely. Next, the suspension was subsequently aged at 100 °C for 1 day since the aging process could increase the average particle size and particle

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Table 6. Deconvolution of the NH₃-TPD Profiles Obtained for the NiO–ZrO₂ and NiO–10Al₂O₃–ZrO₂ Catalysts

| Catalyst          | NH₃ desorbed (%) | 128 | 26.9 | 247 | 43.7 | 357 | 29.4 | 466 |
|-------------------|------------------|-----|------|-----|------|-----|------|-----|
| NiO–ZrO₂          | weak position (°C) | 130 | 48.5 | 233 | 34.9 | 339 | 16.6 | 486 |
| NiO–10Al₂O₃–ZrO₂  | strong proportion (%) | 128 | 26.9 | 247 | 43.7 | 357 | 29.4 | 466 |
|                   | position (°C)     |     |      |     |      |     |      |     |

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Figure 10. FT-IR-CO experiment for reduced NiO–ZrO₂ (A) and NiO–10Al₂O₃–ZrO₂ (B) catalysts and used NiO–ZrO₂ (C) and used NiO–10Al₂O₃–ZrO₂ (D).
The data was collected in the 22392 temperature range from 550 to 800 °C (interval of each 50 °C with 30 min to reach the steady state) in a flow type U microreactor. A thermocouple (Type K) was placed near to the catalytic bed to monitor the reaction temperature for each test. The mixture of reactant gases with a molar composition of CO2:CH4:Ar = 1:1:8 corresponding to the molar composition of H2/CO was described elsewhere.47 The experimental error was ±5%.

Catalyst Characterization. Textural properties were determined by the nitrogen adsorption desorption measurements in a Belsorp Mini II instrument at −196 °C. Prior to measurement, the catalysts were pretreated under a vacuum condition at 200 °C for 120 min. The phase structure of the catalysts was evaluated by XRD (X-ray diffraction) analysis on a diffractometer of DX-1000 CSC using a source of Cu Kα X-ray. The data was collected in the 20 range of 10−80°. The scan step size was 0.03°. The reducibility of catalysts was determined by the H2-TPR (temperature-programmed reduction of H2) on a BELCAT-M instrument. The mass of catalyst was about 60 mg. Before the test, the catalyst was cleaned at 150 °C under helium flow for 30 min. Then, the sample was reduced under a mixture flow of 5 vol % H2 in Ar with a heating rate (10 °C/min) from 100 to 900 °C. The surface elements of catalysts were characterized by XPS (X-ray photoelectron spectroscopy) analysis, which was carried out on a KRATOS spectrometer instrument with monochromated Al radiation. All of the data (the electron binding energy) were referenced to the C 1s peak at 284.5 eV.25 The morphology of catalysts was determined by TEM (transmission electron microscopy) experiments, which was conducted on the FEI Tecnai G2 20 Twin apparatus. The coke of used catalysts was obtained by TGA (thermogravimetric analysis). The mass of the sample was 10 mg. The sample was heated from 30 to 800 °C with a 5 °C/min−1 rate under air of 60 mL·min−1. Raman spectroscopy experiments were conducted on an objective of X50LWD with a laser of 532.17 nm, a grating of 600 gr/mm, a filter of D1, and a hole of 200 μm. The data was collected from the wavenumber values of 40−4000 cm−1. Herein, Raman characterization was carried out for the in-depth study of carbon species deposited on the used catalysts.33,34 The temperature-programmed desorption of NH3 (NH3-TPD) method was carried out using a BELCAT-M instrument. Before the test, the sample (60 mg) was reduced at 700 °C under a mixture flow of 5 vol % H2 in Ar and then cooled down to 50 °C under He flow. Next, NH3 was adsorbed under 10% NH3/He flow for 1 h. After cleaning the weakly adsorbed NH3 on the surface of the sample for 30 min, the material was heated from 50 to 800 °C under He flow with a 10 °C/min heating rate. The outgas was detected by a TCD detector. The CO adsorption FT-IR experiments were carried out on a Bruker infrared spectrometer (FT-IR V70). Before the test, the sample was pretreated at 700 °C under the same condition as the activity test and then cooled down to room temperature. The CO was adsorbed in the dilute feed gas (10% CO) for 1 h at 25 °C. Then, the sample was heated to 400 °C under Ar flow.

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Author Contributions

Y.W. did the conceptualization, investigation, formal analysis, writing of the original draft, review, and editing. Y.W., L.L., C.C., and X.L. did the investigation, writing of the review, and editing. P.D.C. did the conceptualization, supervision, writing of the review, and editing. C.H. did the conceptualization, supervision, writing of the review, and editing.

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Notes

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