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CeZrO_x Promoted Water-Gas Shift Reaction under Steam–Methane Reforming Conditions on Ni-HTASO₅

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Abstract: Ni-based catalysts (Ni- γ -Al₂O₃, Ni-HTASO₅ and Ni-CeZrO_x) were prepared by impregnation method and characterized by BET, AAS, XRD, H₂-TPR, CO-TPD, NH₃-TPD, XPS, TG-DSC-MS and Raman spectroscopies. Using CeZrO_x-modified Al₂O₃ (HTASO₅) as support, the catalyst exhibited good catalytic performance (TOF_{CH₄} = $8.0 \times 10^{-2} \text{ s}^{-1}$, TOF_{H₂} = $10.5 \times 10^{-2} \text{ s}^{-1}$) and carbon resistance for steam-methane reforming (SMR) reaction. Moreover, CeZrO_x was able to enhance water-gas shift (WGS) reaction for more hydrogen production. It was found that the addition of CeZrO_x could increase the content of active nickel precursor on the surface of the catalyst, which was beneficial to the decomposition of water and methane on Ni-HTASO₅. Furthermore, Ni-HTASO₅ could decrease the strong acid sites of the catalyst, which would not only contribute to the formation of low graphited carbon, but also decrease the amount of carbon deposition.

Keywords: steam-methane reforming; water-gas shift reaction; CeZrO_x; hydrogen; carbon deposition

1. Introduction

Hydrogen is considered an important part of future energy systems. With the development of the hydrogen fuel cell, the application of H₂ in vehicles and energy fields has aroused the interest of many researchers. Using Ni-based catalysts, methane can react with H₂O, O₂ or CO₂ to produce hydrogen and carbon monoxide [1–3]. Because of its high H₂/CO ratio, steam–methane reforming reaction (Equation (1)) is the main approach of hydrogen production in industry. When water-gas shift (WGS) reaction (Equation (2)) occurs simultaneously, it will increase the yield of hydrogen. Removing the products (H₂, CO₂) or enhancing adsorption of CO and H₂O on the catalyst are both beneficial to WGS reaction for hydrogen production.



Although compared with precious metals, nickel is not the most active catalyst, it is the most attractive because of its low cost and promising catalytic performance [4]. It has been reported that coke formation and metal sintering are the main reasons that lead to the deactivation of Ni-based catalysts in SMR reaction [5]. With the stoichiometric steam-to-methane ratio (H₂O/CH₄ = 1), graphite carbon is formed on the nickel-based catalyst, leading to reactor blockage and further deactivation of the catalyst [6]. High water–methane ratio can decrease the formation of carbon. In actual industrial

production, the molar ratio of steam to methane is in the range of 2–5 [7]. Meanwhile, the reaction conditions can also result in technical problems associated with industrial catalysts. In order to obtain a high methane conversion and avoid the formation of carbon deposits through methane cracking or CO disproportionation reaction, one approach is controlling the reaction conditions, e.g., temperature, water–methane ratio, gaseous hourly space velocity, etc. [8]

Another approach is controlling the preparation of the catalyst. The support plays an important role in controlling the properties of the catalyst. The most commonly used support for commercial steam–methane reforming catalyst is α - Al_2O_3 , which has good mechanical properties and thermal stability. Nevertheless, alumina is an acidic support that can catalyze secondary reactions such as polymerization and cracking, resulting in carbon deposition on the catalyst surface and blockage of the active sites [9]. In recent years, Mg, Fe, K, Ag, Pt, Pd, Rh, Ru and other elements have been used as additives to inhibit catalyst deactivation in catalytic systems of methane steam reforming [1,10–13]. Some researchers have studied different supports such as CeO_2 , MgAl_2O_4 , MgO , hydrotalcite, NiAl_2O_4 , ZrO_2 and perovskite [11,14,15]. CeO_2 , ZrO_2 and $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ are known for their properties of storing, releasing and exchanging oxygen in lattice structures, and then enhancing methane steam reforming activity in terms of catalytic activity, stability and carbon deposition resistance [16–19]. Furthermore, CeO_2 could contribute to avoid the active metal sintering and phase inversion from γ - Al_2O_3 to α - Al_2O_3 , which could promote the stability of the catalyst. As a promising support or promoter, ZrO_2 is proved to have acid–basic sites [20–23]. It has been demonstrated that cerium doped with zirconia has higher oxygen storage properties, which is beneficial to the oxidation process [24,25]. A solid mixture of CeO_2 – ZrO_2 deposited on Al_2O_3 , used as support for a Ni-based catalyst during SMR reaction was studied by de Abreu et al. [26]. It was found that the high content of Ce would promote the reduction of nickel species and the adsorption of H_2O , which inhibited carbon deposition. Roh et al. [27] found that stable NiO_x , which was the precursor of active Ni site, would form on $\text{Ni/Ce-ZrO}_2/\theta\text{-Al}_2\text{O}_3$ catalyst. The high catalytic activity and stability were owed to Ce– ZrO_2 promoted formation of NiO_x species. Macroporous CeO_2 – ZrO_2 oxygen support for SMR reaction was studied [28], and it was discovered that good oxygen mobility and higher reducibility were due to the porous structure, which could be favorable for the release of oxygen from bulk to surface. Meanwhile, it also promoted methane and steam to diffuse into the catalyst. Wang et al. [29] found that a $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ layer precoated on SBA-15 could promote the formation of high activity Ni species rather than bulk NiO and was beneficial to the formation of mobile oxygen species. Therefore, $\text{Ni/Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{SBA-15}$ catalyst exhibited high catalytic activity and stability. Iglesias et al. [14] studied nickel catalysts supported on $\text{Ce}_{1-x}\text{Zr}_x\text{O}_{2-\delta}$, the Ce/Zr ratio was optimized for SMR at severe reaction conditions, i.e., low temperature and low $\text{H}_2\text{O}/\text{CH}_4$ ratio. They found that zirconium was effectively incorporated into ceria cubic lattice and the support's reducibility and metallic dispersion could be enhanced by the addition of Zr. These characteristics were determined by the structure, and then the physical and chemical properties of the catalyst were adjusted in the preparation of the catalyst.

Obviously, reducible CeZrO_x has good catalytic effects and anti-carbon properties when it was used as support or promoter on heterogeneous catalytic reaction [30–32]. In order to combine the characteristics of Al_2O_3 : high specific surface, good mechanical property, thermal stability, and the oxygen transfer ability of cerium and zirconium oxide, the CeZrO_x -modified Al_2O_3 support (HTASO5) is applied on SMR reaction so as to enhance the reaction performance.

2. Results and Discussion

2.1. The Catalytic Activity of the Catalysts

The turnover frequency (TOF) of CH_4 and H_2 at 600 °C for 9 h are depicted in Figure 1. The initial TOF of CH_4 conversion (for one hour) on $\text{Ni-}\gamma\text{-Al}_2\text{O}_3$, Ni-HTASO5 and Ni-CeZrO_x are $5.1 \times 10^{-2} \text{ s}^{-1}$, $8.0 \times 10^{-2} \text{ s}^{-1}$ and $5.5 \times 10^{-2} \text{ s}^{-1}$, respectively. The corresponding initial TOF of H_2 (for one hour) are $7.0 \times 10^{-2} \text{ s}^{-1}$, $10.5 \times 10^{-2} \text{ s}^{-1}$ and $6.8 \times 10^{-2} \text{ s}^{-1}$, respectively. The higher TOF of H_2 implies that WGS

reaction may occur simultaneously. In the activity test, the Ni-HTASO5 exhibited the best catalytic performance while that of the other two catalysts were close. The repeatability of the catalyst was good, and the relative error between the two repeated experiments was 3.22% (Supplementary Materials Figure S2, Table S2). In terms of stability, the TOF of H_2 on Ni- γ - Al_2O_3 and Ni-HTASO5 were stable at around $6.5 \times 10^{-2} s^{-1}$ and $8.7 \times 10^{-2} s^{-1}$, respectively after reaction for five hours, while that of Ni-CeZrO_x gradually decreased. Meanwhile, the ratio of the content of CO_2 to CO on Ni-CeZrO_x was higher than those on the other two catalysts and that on Ni-HTASO5 was higher than on Ni- γ - Al_2O_3 . It could be inferred that CeZrO_x as additive or support can promote WGS reaction, which is beneficial to H_2 production. Compared to other results from the literature, the catalytic effect of CeZrO_x on WGS reaction was generally observed, and the modified Ni-HTASO5 catalyst was more conducive to the simultaneous production of hydrogen in the two-step reaction [14,26,28].

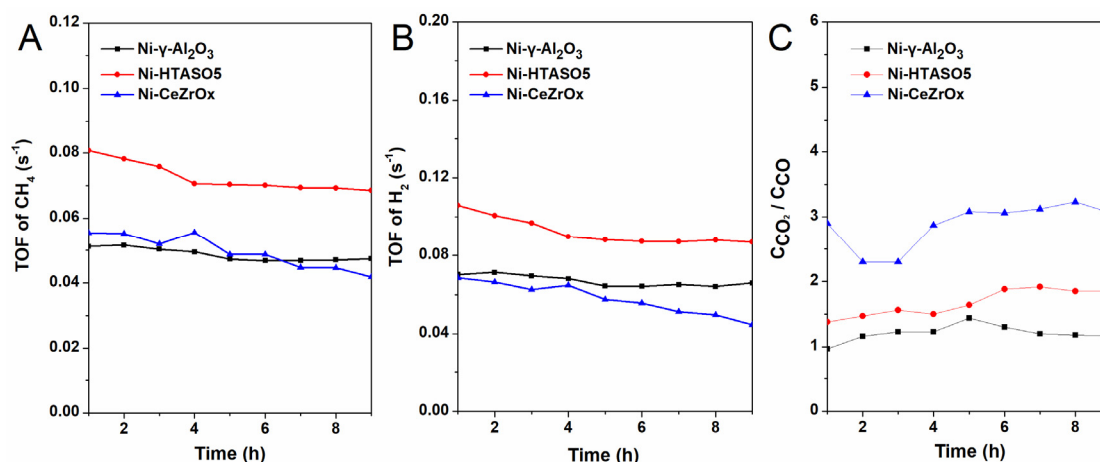


Figure 1. (A) Turnover frequency of CH_4 , (B) turnover frequency of H_2 and (C) the content ratio of CO_2 to CO on Ni- γ - Al_2O_3 , Ni-HTASO5 and Ni-CeZrO_x catalysts at 600 °C with the mixed flow of $H_2O:CH_4 = 3:1$.

2.2. BET Results of the Catalysts

The specific surface area (S_{BET}) and dispersion of pore volume (V_p) and pore size (D_p) of the catalysts are shown in Figure 2 and Table 1. The isotherm curves of the three catalysts are all type IV and the ratio of P to P_0 for the hysteresis loop is over the range of 0.45 to 1.0, which indicates that they are all mesoporous materials [33]. The BET result (Table 1) showed that HTASO5 retained a relatively larger surface area of the catalyst than CeZrO_x. The specific surface area of Ni- γ - Al_2O_3 , Ni-HTASO5 and Ni-CeZrO_x are $141.9 m^2 g^{-1}$, $67.6 m^2 g^{-1}$ and $49.0 m^2 g^{-1}$, respectively. The addition of Ce, Zr in Al_2O_3 support decreased the surface area of the catalyst. The pore volume also decreased significantly compared with Ni- γ - Al_2O_3 . However, the Ni-HTASO5 catalyst remained relatively larger surface area of than Ni-CeZrO_x catalyst, which could promote the dispersion of nickel. The pore size distribution of Ni-HTASO5 was concentrated around 10–20 nm, while the other two catalysts were more widely distributed from 10 to 80 nm. As seen in Figure 2A, after being reduced in H_2 atmosphere at 600 °C, the mesopores in Ni- γ - Al_2O_3 and Ni-CeZrO_x could be classified into H3-type, which indicated an irregular pore structure and it is similar with that observed in nanorod and/or nanofiber [34]. However, the shape of hysteresis loop for Ni-HTASO5 was grouped within H1-type, which is typically found in spheroidal particles of uniform size and array [35,36].

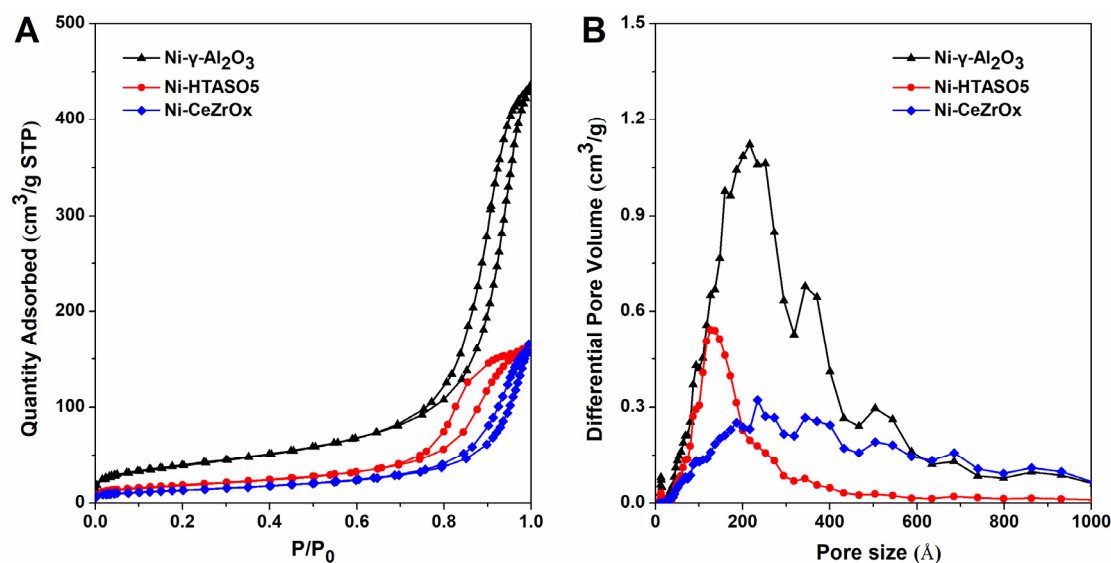


Figure 2. (A) N_2 adsorption–desorption isotherm curve and (B) pore-volume and size-distribution for different Ni-based catalysts after reduction.

Table 1. Physical properties of different Ni-based catalysts and different supports, the surface area was determined by BET method, the pore size (Dp) and the pore volume (Vp) were both determined by BJH method. The loading content of Ni was detected by atomic absorption spectrum (AAS).

Samples	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	Dp (nm)	Ni (%)
Ni- γ - Al_2O_3	141.9	0.65	16	9.8
Ni-HTASO5	67.6	0.25	12	8.9
Ni-CeZrO _x	49.0	0.22	16	7.0
γ - Al_2O_3	151.2	0.68	16	/
HTASO5	71.5	0.22	11	/
CeZrO _x	51.6	0.17	15	/

The actual loading of nickel was characterized by atom adsorption spectrum, and the results are shown in Table 1. The content of Ni on Ni- γ - Al_2O_3 , Ni-HTASO5 and Ni-CeZrO_x are 9.8%, 8.9% and 7.0%, respectively. Combining this result with that of surface area, the lower surface area was responsible for lower Ni-loading, which would influence the conversion of CH_4 .

2.3. The Reducibility and Distribution of Ni Species on the Catalysts

The reducibility of the Ni-based catalysts with different supports is shown in Figure 3A. Two peaks around 286 °C and 401 °C are observed on Ni-CeZrO_x catalyst. The reducibility curve of Ni-HTASO5 is similar to Ni- γ - Al_2O_3 . The peaks are around 450 °C (A peak) and 750 °C (B peak). Compared to the other two catalysts, the Ni species on Ni-CeZrO_x could be reduced at lower temperature, which is attributed to weak interaction between metal Ni and CeZrO_x support. The two reduction peaks of Ni-HTASO5 both shifted to lower temperatures when compared with Ni- γ - Al_2O_3 . Furthermore, the ratio of A peak to B peak on Ni- γ - Al_2O_3 was lower than that of Ni-HTASO5. They both indicated that the addition of CeZrO_x to Al_2O_3 can weaken the interaction between Ni species and the support.

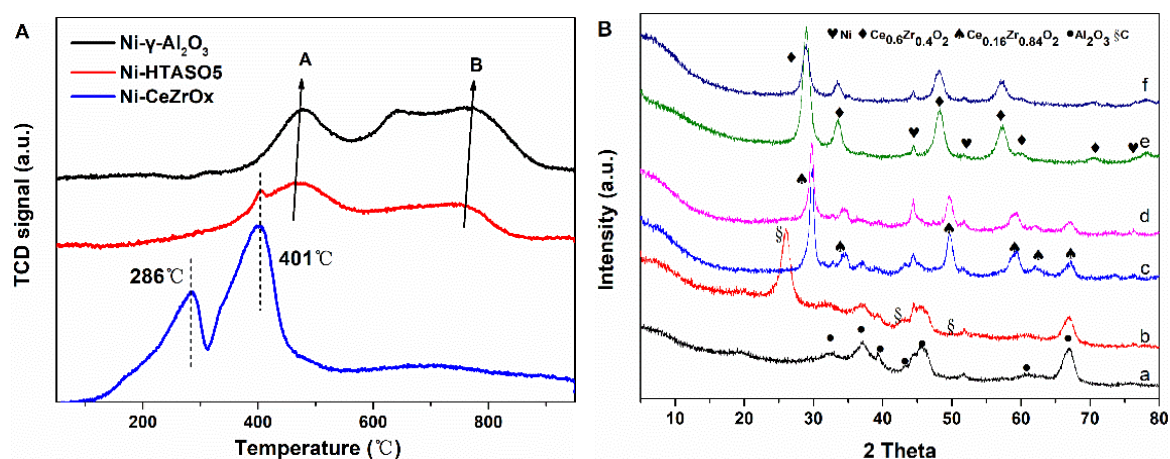


Figure 3. (A) H₂-TPR profile and (B) XRD result of Ni-based catalysts with different supports: Ni-γ-Al₂O₃ (a) after reduction (b) after reaction, Ni-HTASO5 (c) after reduction (d) after reaction and Ni-CeZrO_x (e) after reduction (f) after reaction.

The XRD result of Ni-based catalysts with different supports is shown in Figure 3B. It can be seen that the diffraction peak of $2\theta = 44.5^\circ, 51.9^\circ, 76.4^\circ$ (PDF# 04-0850) of metal Ni⁰ appears on all the catalysts after reduction and reaction. The Ce_{0.6}Zr_{0.4}O₂ crystalline phase appeared on Ni-CeZrO_x catalyst, while Ce_{0.16}Zr_{0.84}O₂ crystalline phase was shown on Ni-HTASO5. Therefore, different CeZrO_x were formed on Ni-CeZrO_x and Ni-HTASO5. There was no significant change of the crystal size of Ni⁰ on the catalysts before and after the reaction (see in Table 2). The crystal size of Ni⁰ on Ni-γ-Al₂O₃ was smaller than the other two catalysts, which is owed to the high dispersion of Ni on the support. Furthermore, the carbon diffraction peak (PDF# 41-1487) appeared on Ni-γ-Al₂O₃ after reaction while it cannot be seen on the other catalysts, which means graphite carbon did form on Ni-γ-Al₂O₃. The grain size of Ni did not change significantly before and after the reaction of Ni-HTASO5 and Ni-CeZrO_x and the grain size of them was similar.

Table 2. Crystal size of nickel on Ni-γ-Al₂O₃, Ni-HTASO5 and Ni-CeZrO_x after reduction and reaction as determined by XRD. The intensity ratio of G bond to D bond of deposited carbon after reaction at 600 °C for 9 h, tested by Raman spectroscopy.

Catalyst	Ni ⁰ (nm)		I _G /I _D
	Reduction	Reaction	
Ni-γ-Al ₂ O ₃	12	12	0.58
Ni-HTASO5	18	19	0.47
Ni-CeZrO _x	19	18	0.20

The information of different surface species on the catalyst was determined by X-ray photoelectron spectrum (XPS). As seen in Figure 4, for Ni 2p, all the catalysts have three peaks. The binding energy at 854.5 eV, 855.8 eV were regarded as NiO_x species and Ni²⁺ species, respectively [14,25,37]. Furthermore, NiO_x species was regarded as the precursor of active nickel species [27,38]. From quantitative analysis results in Table 3, among the three catalysts, Ni-HTASO5 catalyst had the highest content of precursor of the active species nickel (NiO_x), which play very important roles in the catalytic activity and stability [27,38]. Comparing the binding energy of Zr, Ce and O on Ni-HTASO5 and Ni-CeZrO_x, it was found that the peak location of Ce had little change while that of Zr on Ni-HTASO5 shifted to higher binding energy. This means that Zr on Ni-HTASO5 had a stronger ability to donate electrons, which may contribute to the reduction of Ni species. The result of O 1s-binding energy showed that the ratio of lattice oxygen (O²⁻, 529.6 eV) to surface oxygen (OH⁻, 531.6 eV) on Ni-CeZrO_x was much higher than that on Ni-HTASO5 [39,40]. Therefore, CeZrO_x had the property of storing oxygen while the

HTASO5 support contained Al_2O_3 , which made the surface of Ni-HTASO5 contain more OH^- . It has been reported that the lattice oxygen could promote activation of water [21,23], which may promote WGS reaction. The high surface content of active nickel could promote methane decomposition and hydrogen production, which made high catalytic activity of SMR reaction. Although there was more active lattice oxygen to promote the WGS reaction on Ni-CeZrO_x, the low content of active nickel limited the SMR reaction for H_2 production. Therefore, the TOF of hydrogen on Ni-HTASO5 was higher than that on Ni-CeZrO_x.

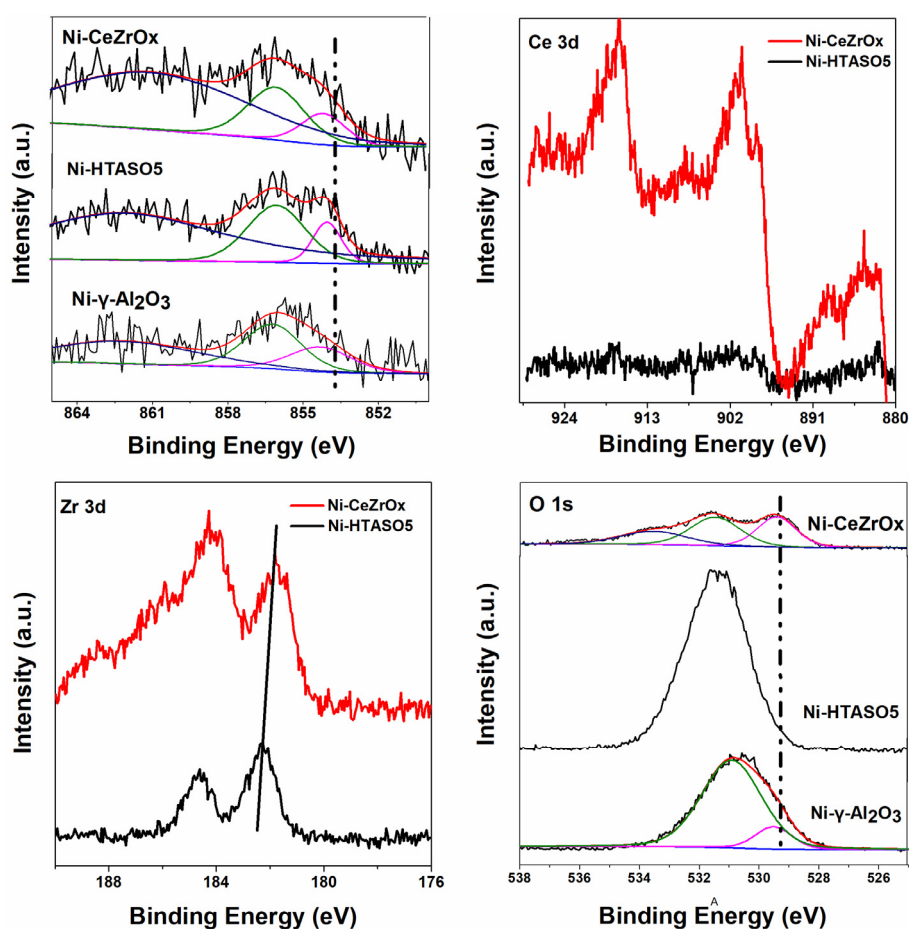


Figure 4. Ni 2p, Ce 3d, Zr 3d and O 1s binding energy of Ni- γ - Al_2O_3 , Ni-HTASO5 and Ni-CeZrO_x catalysts.

Table 3. Surface content of different nickel species on reduced catalysts determined by XPS.

Catalyst	Content (%)	
	NiO _x	Ni ²⁺
Ni- γ - Al_2O_3	28	72
Ni-HTASO5	34	66
Ni-CeZrO _x	25	75

2.4. The Acidity and Carbon Deposition of the Catalysts

The acidity of Ni- γ - Al_2O_3 , Ni-HTASO5 and Ni-CeZrO_x catalysts was characterized by temperature programmed NH_3 desorption experiment. Three NH_3 desorption peaks, which are ascribed to weak, medium and strong acid sites, over the range of 50–500 °C on all the catalysts are shown in Figure 5. The desorption peak at the range of 50–150 °C (peak 1) was attributed to weak Lewis acid site, and the peak with maximum at 150–250 °C (peak 2) was regarded as NH_4^+ bound to medium acid site [41]. The peak at above 250 °C (peak 3) was attributed to NH_3 bound to strong Lewis acid site and NH_4^+ .

bound to strong Brønsted acid site [41–43], which may be due to the presence of surface OH^- on the support. Moreover, the amount of desorbed ammonia was calculated from NH_3 desorption peak area and the result is shown in Table 4. The tendency of acid strength was as follows: $\text{Ni-}\gamma\text{-Al}_2\text{O}_3 > \text{Ni-HTASO}_5 > \text{Ni-CeZrO}_x$. The medium and strong acid site (peak 2 and peak 3) gradually increased with the increase of Al_2O_3 content. That was due to the acidity of Al_2O_3 support. The weak acid site (peak 1) increased by the addition of CeZrO_x . The acidity of Ni-HTASO_5 was lower than $\text{Ni-}\gamma\text{-Al}_2\text{O}_3$, which was due to the addition of CeZrO_x to the support.

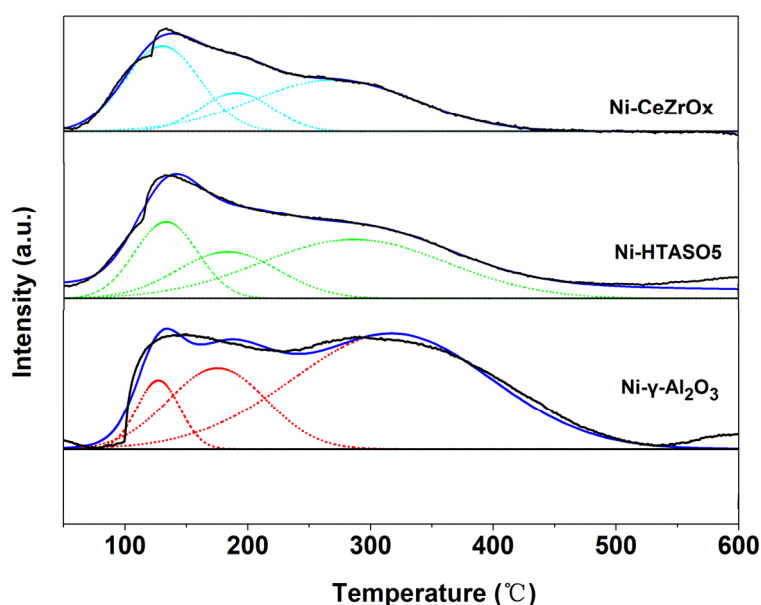


Figure 5. Temperature-programmed NH_3 desorption (NH_3 -TPD) profile of $\text{Ni-}\gamma\text{-Al}_2\text{O}_3$, Ni-HTASO_5 and Ni-CeZrO_x catalysts.

Table 4. Acidity measured by temperature programmed NH_3 desorption experiment on $\text{Ni-}\gamma\text{-Al}_2\text{O}_3$, Ni-HTASO_5 and Ni-CeZrO_x catalysts and weight loss of catalysts determined by thermogravimetric analysis.

Catalysts	Peak 1		Peak 2		Peak 3		Total (mmol/g)	Weight Loss (%)
	T1	Amount (mmol/g)	T2	Amount (mmol/g)	T3	Amount (mmol/g)		
$\text{Ni-}\gamma\text{-Al}_2\text{O}_3$	127	108	175	311	317	906	1325	24.01
Ni-HTASO_5	133	161	183	161	286	373	695	12.77
Ni-CeZrO_x	130	169	191	70	270	221	460	9.43

T1, T2, T3—center temperature of the peak.

The amount and type of carbon deposition were investigated by thermogravimetric analysis combined with differential scanning calorimeter and mass spectrometer (TG-DSC-MS). The result is shown in Figure 6. In terms of the amount of deposited carbon, there was the highest amount of coke on $\text{Ni-}\gamma\text{-Al}_2\text{O}_3$ (24.01%) catalyst and the least on Ni-CeZrO_x (9.43%) catalyst. It had previously been indicated that carbon was more likely to deposit on $\text{Ni-}\gamma\text{-Al}_2\text{O}_3$. This may be attributed to the acidic site of Al_2O_3 , which could catalyze polymerization and cracking, resulting in more carbon deposition on the catalyst surface [44]. Meanwhile, the addition of Zr or Ce could increase the ability of carbon resistance [44–46]. Comparing with $\text{Ni-}\gamma\text{-Al}_2\text{O}_3$ catalyst, Ni-HTASO_5 catalyst had less carbon deposition. Meanwhile, the CO_2 MS signal on Ni-HTASO_5 shifted to lower temperature. It means that the deposited carbon on Ni-HTASO_5 was more easily removed. There was the least amount of coke on Ni-CeZrO_x , furthermore the coke was of easy removal character. Combined with the result of NH_3 -TPD, it was inferred that the increase of weak acid sites would decrease the amount of carbon

deposition and inhibit the growth of coke, which could then easily be removed. That is to say, the Ni-HTASO5 modified by CeZrO_x could not only form easily removable carbon, but also reduce the amount of carbon formation.

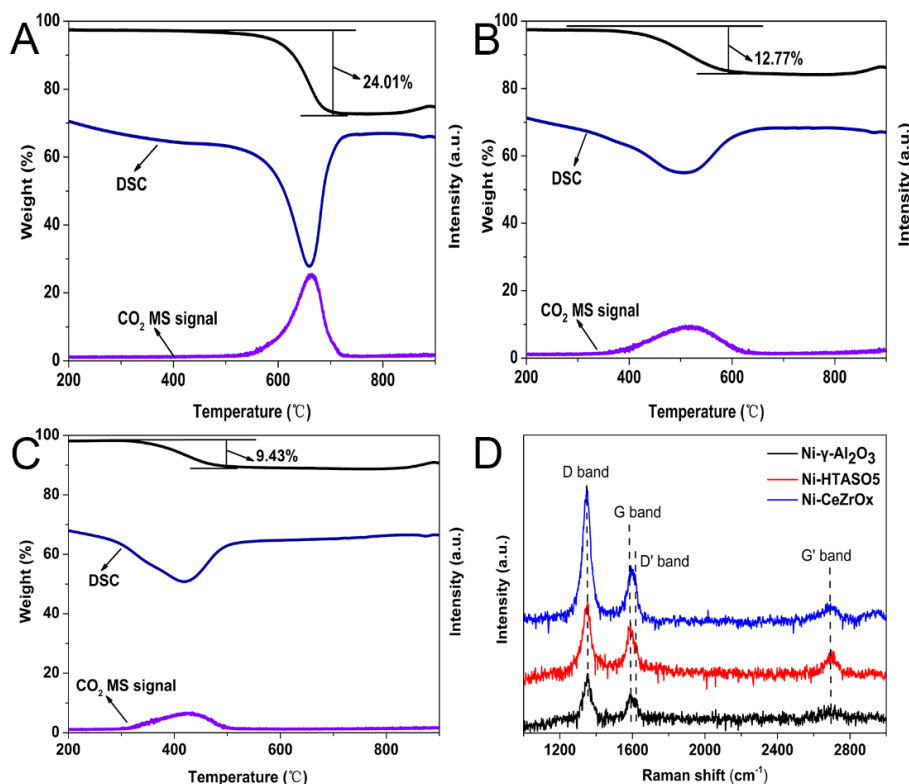


Figure 6. TG-DSC-MS profile. (A) Ni- γ -Al₂O₃; (B) Ni-HTASO₅; (C) Ni-CeZrO_x; (D) Raman spectra of different Ni-based catalysts after reaction at 600 °C for nine hours.

In order to identify the graphitization degree of coke, the Raman spectroscopy analysis was performed (Figure 6D). It could be seen that there were four peaks on all the catalysts. The peak at 1343 cm⁻¹ (D band) was considered to C–C stretch vibration of disordered carbon while the peak at 1579 cm⁻¹ (G band) was regarded as C–C stretch vibration of well-ordered carbon. The ratio of I_G/I_D of Ni- γ -Al₂O₃, Ni-HTASO₅ and Ni-CeZrO_x was 0.58, 0.47 and 0.20 (see in Table 2), respectively. As is shown, the graphitization degree increased with the increase content of Al₂O₃ in the support. Adding CeO₂ and ZrO₂ to the composite support could change the property of carbon deposition, making it decrease the graphitization, which was beneficial to carbon removal.

Combined with the characterization of the catalysts and the results of activity, it could be seen that the highest turnover frequency of hydrogen on Ni-HTASO₅ is owed to its high surface content of active nickel and promising carbon resistance.

3. Materials and Methods

3.1. Synthesis of Catalysts

The γ -Al₂O₃ support was provided by Adamas-beta, Shanghai, China (99.99%). The HTASO₅ support with the composition of CeO₂:ZrO₂:Al₂O₃ = 1:2:7 was provided by Zhongzi Environmental Protection Technology Co., LTD, Chengdu, China.

The CeZrO_x support was prepared by co-precipitation method. Cerium nitrate (99.5%, Kelong, Chengdu, China) and zirconium nitrate (99.5%, Kelong, Chengdu, China) with the mole-ratio of Ce:Zr = 3:2 were dissolved in deionized water. The resulting solution was transferred to a flask and the pH adjusted to 9 using 2.5 M NH₃·H₂O with constantly stirring. The mixture was aged for 2 h at

70 °C, then cooled to room temperature and stored for 12 h. The resulting gel was rinsed thoroughly with deionized water and then it was dried in air overnight. The support was finally calcined at 450 °C for 4 h.

Ni- γ -Al₂O₃, Ni-HTASO5 and Ni-CeZrO_x catalysts were prepared by impregnation method. First, Ni(NO₃)₄·6H₂O (2.1846 g) was added to 20 mL deionized water. The above support (4 g) was added after 20 min ultrasound treatment of the solution. The mixture was impregnated by stirring constantly at room temperature for 24 h, then dried at 80 °C using oil bath and at 110 °C in oven for 4 h. The three catalysts precursors were obtained after being calcined at 600 °C for 4 h.

3.2. Catalytic Activity Test

The catalyst activity was tested in a stainless steel fixed bed reactor at atmospheric pressure. Ni- γ -Al₂O₃ and Ni-HTASO5 were reduced at 800 °C for 1 h under the atmosphere of H₂ and Ar mixture (H₂/Ar = 1) and passivated in the mixture of oxygen and argon (5% O₂ in Ar) at room temperature, while the reduction temperature of Ni-CeZrO_x was 600 °C and passivated under the same conditions. Before the activity test, all the catalysts were reduced again at 600 °C for 1 h. The reaction gases methane (F = 30 mL/min) and H₂O (nH₂O/nCH₄ = 3) were injected after ten min of argon purge. Meanwhile, the gas products were analyzed by gas chromatography (TDX-01 packed column).

The CH₄ (or H₂) turnover frequencies were calculated by the molar number of CH₄ (or H₂) converted or produced per second per mole exposed Ni atom. The number of exposed Ni atoms was determined by CO temperature programmed experiments (seen in Table S1). The methane conversion rate (X_{CH₄}), H₂ production rate (Y_{H₂}) and the CO₂, CO (C_{CO₂}, C_{CO}) content were calculated as follows:

$$X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\%$$

$$Y_{H_2} = \frac{F_{H_2,out}}{2 \times (F_{CH_4,in} - F_{CH_4,out})} \times 100\%$$

$$C_{CO_2} = \frac{F_{CO_2,out}}{F_{CO_2,out} + F_{CO,out} + F_{H_2,out}} \times 100\%$$

$$C_{CO} = \frac{F_{CO,out}}{F_{CO_2,out} + F_{CO,out} + F_{H_2,out}} \times 100\%$$

$$TOF(CH_4) = m(CH_4)/n(Ni)$$

$$TOF(H_2) = m(H_2)/n(Ni)$$

where F referred to the flow of gas, mL/min and m(CH₄) (or m(H₂)) was the molar number of CH₄ (or H₂) converted per second and n(Ni) was the molar number of exposed Ni atoms per gram of catalyst.

3.3. Characterization Methods

The BET specific area and the distribution of pore volume and pore size of samples were tested in a Micromeritics Tristar II 3020 instrument (Micromeritics, Norcross, GA, USA) by adsorption–desorption of N₂ at −196 °C. Before the test, the sample was activated at 120 °C and 300 °C to eliminate any adsorbed substance.

The actual loading was tested by atom adsorption spectrum in a SpectraAA 220FS instrument (Varian, Palo Alto, CA, USA). The sample was dissolved in aqua regia (HCl:HNO₃ = 3:1) and a small amount of HF. Deionized water was added while heating to nearly complete dissolution. Then water was added repeatedly to remove the acid completely. The grating was holographic diffraction grating with 1200 lines/mm (240 nm).

The temperature-programmed reduction (TPR) was performed to attain the reduction property of the catalysts by the Micromeritics Autochem II 2920 instrument (Micromeritics, Norcross, GA, USA). The test was from 50 °C to 900 °C with a heating rate of 5 °C/min under an atmosphere of 10% H₂/Ar.

The temperature programmed NH₃ desorption (NH₃-TPD) was used to study the acid sites of the sample. First, NH₃ was adsorbed on the reduced catalysts at 50 °C for 1 h under a mixture of 10% NH₃ in He. Then, He was used to clean the excessive unadsorbed NH₃ for 1 h. After this, with a heating rate of 10 °C/min under He flow, the sample was heated to 600 °C. The NH₃ desorbed curve at different temperature was presented.

The CO temperature programmed desorption (CO-TPD) was carried out to study the amount of active centers on the sample. First, the catalyst was reduced at 600 °C under an atmosphere of 10% H₂/Ar. After reduction, the samples were blown with He for 2 h. Then, CO was adsorbed on the reduced catalysts at 50 °C for 1 h under a mixture of 3% CO in He. He was used to clean the excessive unadsorbed CO for 1 h. After this, with a heating rate of 10 °C/min under a He flow, the sample was heated to 800 °C. The CO desorbed curve was presented.

X-ray diffraction (XRD) was conducted to probe the type and the size of formed crystal by an XRD-6100 (SHIMADZU, Japan) instrument. Cu K α radiation of 40 kV and 25 mA was used. The diffraction angle ranged from 5° to 80°.

Thermogravimetric, differential scanning calorimeter and mass combination (TG-DSC-MS) analysis were performed to characterize carbon deposition on used catalysts by TG209F1 (NETZSCH, Selb, Germany) instrument. With the heating rate of 10 °C/min, the test started from 30 °C to 800 °C under an atmosphere of air/N₂ (20/60 mL/min).

X-ray photoelectron spectroscopy (XPS) was carried out to study the surface state of the element on AXIS Ultra DLD (KRATOS, Manchester, UK) instrument equipped with a neutralizer. With monochromatic Al K α as the light source, the acceleration power of 25 W, the binding energies were calibrated using C1s 284.6 eV, and the peak separation was performed with a Lorenz–Gaussian ratio (L/G) of 20%.

Raman spectroscopy analysis was conducted to characterize the deposited carbon on used catalysts. He–Ne laser source (532 nm) was used on LabRAM HR instrument (HORIBA, Kyoto, Japan) for the test. The filter was D1 and the aperture was 200 mm.

4. Conclusions

Nickel-based catalysts were prepared using γ -Al₂O₃, HTASO5 and CeZrO_x as supports and used for steam–methane reforming reaction. Ni-HTASO5 showed good catalytic performance at 600 °C for 9 h while being more responsive to WGS reaction and having a promoting effect on hydrogen production. The high catalytic activity of Ni-HTASO5 was due to the presence of a high amount of active Ni precursor species on its surface as compared with Ni- γ -Al₂O₃ and Ni-CeZrO_x. This could contribute to the decomposition of methane and water. The presence of CeZrO_x promoted the WGS reaction under steam–methane reforming conditions. Furthermore, it was seen that the weak acid sites would decrease on the Ni-based catalyst-doping with CeZrO_x in Al₂O₃ as support, which was beneficial to decrease the amount of carbon deposition and make it easier to be removed with a low graphited structure.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/10/1110/s1>, Figure S1: CO-TPD of Ni- γ -Al₂O₃, Ni-HTASO5 and Ni-CeZrO_x catalysts. Figure S2: The turnover frequency of CH₄. (A) The first activity result and (B) the second activity result. Table S1: The amount of nickel active site determined by CO temperature programmed desorption. Table S2: Two activity experiment error of Ni- γ -Al₂O₃, Ni-HTASO5 and Ni-CeZrO_x catalysts.

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