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Article

Morphology effect of zirconia support on the catalytic performance of supported Ni catalysts for dry reforming of methane

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ABSTRACT

An immature pinecone shaped hierarchically structured zirconia (ZrO₂-ipch) and a cobblestone-like zirconia nanoparticulate (ZrO₂-cs), both with the monoclinic phase (m-phase), were synthesized by the facile hydrothermal method and used as the support for a Ni catalyst for the dry reforming of methane (DRM) with CO₂. ZrO₂-ipch is a much better support than ZrO₂-cs and the traditional ZrO₂ irregular particles made by a simple precipitation method (ZrO₂-ip). The supported Ni catalyst on ZrO₂-ipch (Ni/ZrO₂-ipch) exhibited outstanding catalytic activity and coke-resistant stability compared to the ones on ZrO₂-cs (Ni/ZrO₂-cs) and ZrO₂-ip (Ni/ZrO₂-ip). Ni/ZrO₂-ip exhibited the worst catalytic performance. The origin of the significantly enhanced catalytic performance was revealed by characterization including XRD, N₂ adsorption measurement (BET), TEM, H₂-TPR, CO chemisorption, CO₂-TPD, XPS and TGA. The superior catalytic activity of Ni/ZrO₂-ipch to Ni/ZrO₂-cs or Ni/ZrO₂-ip was ascribed to a higher Ni dispersion, increased reducibility, enhanced oxygen mobility, and more basic sites with a higher strength, which were due to the unique hierarchically structural morphology of the ZrO₂-ipch support. Ni/ZrO₂-ipch exhibited better stability for the DRM reaction than Ni/ZrO₂-ip, which was ascribed to its higher resistance to Ni sintering due to a strengthened metal-support interaction and the confinement effect of the mesopores and coke deposition resistance. The higher coking resistance of Ni/ZrO₂-ipch for the DRM reaction in comparison with Ni/ZrO₂-ip originated from the coke-removalability of the higher amount of lattice oxygen and more basic sites, confirmed by XPS and CO₂-TPD analysis, and the stabilized Ni on the Ni/ZrO₂-ipch catalyst by the confinement effect of the mesopores of the hierarchical ZrO₂-ipch support. The superior catalytic performance and coking resistance of the Ni/ZrO₂-ipch catalyst makes it a promising candidate for synthesis gas production from the DRM reaction.

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1. Introduction

The dry reforming of methane (DRM) has attracted considerable attention because CO₂ is the primary greenhouse that

has brought about significant climate change, and methane as the main component of natural gas used in combustion leads to a great deal of CO₂ emission. Thus, the DRM reaction converts two greenhouse gases to the industrially important synthesis

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gas (H_2 and CO), which serves as the platform for downstream liquid fuels and valuable chemicals [1–8].

Although the noble metal catalysts have exhibited high catalytic performance and low carbon deposition, their high cost and low availability limit their large scale application in industry [9–13]. Ni-based catalysts have been established as potential catalysts for industrial application in synthesis gas production from the DRM reaction owing to their low cost and comparable activity and selectivity to noble metal catalysts. Unfortunately, Ni-based catalysts have a bottleneck issue of rapid deactivation due to the carbon deposition as well as the sintering and oxidation of metallic Ni under the harsh reaction conditions [14–22]. Among these, carbon deposition has been accepted as the main reason of catalyst deactivation [23–25]. Many reports have focused on retarding coke deposition [7,26–31]. Typically, the coke can be efficiently suppressed by Ni-support interface tuning [32] and enhancing heat transfer [33,34]. There is agreement in the references that the coke originates mainly from the two reactions of the decomposition of methane and the Boudouard reaction of CO , which are strongly dependent on the nature of support.

In the references [35–39], ZrO_2 has been widely used as the catalyst support for diverse transformations including DRM, owing to its high thermal stability, unique acid-base properties and surface oxygen mobility. It was found that the crystalline phase, crystalline size, and pore structure of the ZrO_2 support significantly affected the catalytic performance of the supported catalysts [40–42]. Zheng et al. [43] compared the catalytic performance of supported Ni catalysts on a ZrO_2 prepared by flowing nitrogen (ZrO_2 -AN) and air (ZrO_2 -CP). It was found that Ni/ZrO_2 -AN exhibited much higher stability than Ni/ZrO_2 -CP, which was ascribed to the different nature but not to the amount of coke. Change et al. [44] confirmed that the simultaneous alteration of the support and Ni surface of Ni/ZrO_2 with a Ce modifier and a Ca promoter led to a high performance catalyst, mainly ascribed to a synergy effect of the Ca promoter and Ce modifier for coke resistance and high temperature catalyst aging. Gonzalez-Delacruz et al. [3] found that the size of metallic Ni of the Ni/ZrO_2 catalyst can be efficiently tuned by a H_2/CO treatment, which significantly affects the catalytic performance for DRM. Xu et al. [45] explored the size effect of ZrO_2 support particles on the catalyst and catalytic performance of a Ni/ZrO_2 catalyst for the utilization of natural gas through dry reforming by CO_2 , and found that the supported Ni catalyst on the ZrO_2 support with a smaller particle size exhibited much higher catalytic stability, ascribed to the enhancing effect of reducing the particle size on oxygen transfer ability. It was found that the shape of the supports (e.g., CeO_2 , ZnO , and La_2O_3) strongly affected their catalytic performance [47–49]. In many cases, the morphology effect of CeO_2 and doped CeO_2 has been widely used on a catalyst support to promote the activation of CO_2 and oxidative removal of surface carbon species [7,46,49–51]. However, to the best of our knowledge, few reports regarding the morphology effect of the ZrO_2 support on Ni-based catalysts for DRM reaction can be found.

Herein, we successfully prepared two m- ZrO_2 supports with different morphologies including an immature pinecone

shaped hierarchically structured zirconia (ZrO_2 -ipch) and a cobblestone-like zirconia nanoparticulate (ZrO_2 -cs), and tested the catalytic performance of the supported Ni catalysts (Ni/ZrO_2 -ipch and Ni/ZrO_2 -cs) on the two supports for the DRM reaction. Ni/ZrO_2 -ip was also prepared and tested for comparison. It was found that the Ni/ZrO_2 -ipch catalyst exhibited much higher catalytic activity than Ni/ZrO_2 -cs or Ni/ZrO_2 -ip, and it also exhibited higher coke-resistant stability. Characterization techniques including X-ray diffraction (XRD), N_2 adsorption measurement (BET), transmission electron microscopy (TEM), temperature-programmed reduction of hydrogen (H_2 -TPR), CO chemisorption, temperature-programmed desorption of CO_2 (CO_2 -TPD), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) were employed to investigate the morphology effect of the ZrO_2 support on the supported Ni catalyst for DRM. The origin of the high activity and coke-resistant stability of Ni/ZrO_2 -ipch was explored.

2. Experimental

2.1. Catalyst preparation

All chemicals (Sinopharm Chemical Reagent Co., Ltd) were used as purchased without further purification. For ZrO_2 -ipch, 3.22 g (7.5 mmol) of $Zr(NO_3)_4 \cdot 5H_2O$ was dissolved in de-ionized water under magnetic stirring, followed by adding 1.5 g (10.7 mmol) of hexamethylenetetramine aqueous solution to the $Zr(NO_3)_4 \cdot 5H_2O$ aqueous solution. Then NH_4F was introduced into the above mixture. The resulting solution was transferred into a Teflon-lined autoclave and hydrothermally treated for 24 h. After the autoclave was cooled down to room temperature, the suspension was separated by filtration, washed with de-ionized water several times, and then dried at 105 °C overnight. The solid was subsequently calcinated at 550 °C for 5 h in a muffle furnace, and ZrO_2 -ipch was obtained. For ZrO_2 -cs, a solution containing 3.22 g (7.5 mmol) of $Zr(NO_3)_4 \cdot 5H_2O$ was transferred into a Teflon-lined autoclave and was hydrothermally treated at the same conditions as above. After the autoclave was naturally cooled down to room temperature (RT), the solid was recovered by filtration, washed with de-ionized water several times, and then dried at 105 °C overnight. The solid was calcined at 550 °C for 5 h in a muffle furnace, and the ZrO_2 -cs sample was obtained. For comparison, a traditional ZrO_2 -ip support was also prepared by the common precipitation method by using 35% ammonia as precipitant.

The supported Ni catalysts on the ZrO_2 -ipch, ZrO_2 -cs and ZrO_2 -ip supports (10% Ni loading) were prepared by using the previously established LA-IWI method [52]. The NiO/ZrO_2 -ipch, NiO/ZrO_2 -cs and NiO/ZrO_2 -ip samples were reduced at 850 °C for 2 h under a mixture of 20% H_2 in 80% N_2 at a flow rate of 30 mL/min to obtain the reduced samples, which were denoted as Ni/ZrO_2 -ipch, Ni/ZrO_2 -cs and Ni/ZrO_2 -ip, respectively.

2.2. Catalyst characterization

TEM images were obtained by using a Tecnai F30 HRTEM

instrument (FEI Corp.) at an acceleration voltage of 300 kV. The sample was dispersed in ethanol with ultrasonic treatment for 10 min, and a drop of the suspension was placed on a copper grid for TEM observation. FE-SEM experiments were performed on a JEOL JSM-5600LV SEM/EDX instrument.

Nitrogen adsorption and desorption isotherms were determined on a Beishide apparatus Model 3H-2000PS1 at $-196\text{ }^{\circ}\text{C}$. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the mesopore size distribution was calculated from the adsorption branch of the isotherm by the BJH model.

XRD patterns were collected from 10° to 80° at a step width of 0.02° using a Rigaku Automatic X-ray Diffractometer (D/Max 2400) equipped with a $\text{Cu K}\alpha$ source ($\lambda = 0.15406\text{ nm}$). The average crystallite size was estimated on the basis of the Scherrer formula from the characteristic diffraction peaks by the MDI Jade 5 software.

TGA analysis was conducted to study the amount of coke deposited on the spent $\text{ZrO}_2\text{-ipch}$ and $\text{ZrO}_2\text{-ip}$ catalysts using a Perkin-Elmer STA 6000 with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ from 30 to $800\text{ }^{\circ}\text{C}$ in an air stream.

The Ni dispersion of the two catalysts was measured by CO titration at $35\text{ }^{\circ}\text{C}$ using a Builder PCA-1200 Pulsar TPR/TPD equipment by pulse chemisorption ($300\text{ }\mu\text{L}$ for each pulse, 10% $\text{CO}/90\%$ He , purity of He is 99.999%). The catalyst ($\sim 100\text{ mg}$) was reduced in situ with H_2 at $850\text{ }^{\circ}\text{C}$ for 1.5 h, then flushed at $400\text{ }^{\circ}\text{C}$ with He for 50 min. After pre-reduction, the catalyst was cooled to $30\text{ }^{\circ}\text{C}$ and CO chemisorption was carried out. The Ni dispersion was calculated by

$$D_M = 100\% \times ((V_s \times \text{SF}) / (\text{SW} \times 22414)) \times \text{MW}$$

where D_M , V_s , SF, SW and MW were metal dispersion (%), volume of active gas chemisorbed (cm^3 at STP), stoichiometric factor, catalyst mass (g), and molecular mass of metallic Ni (g/mol), respectively [53].

H_2 -TPR experiments were performed on a Builder PCA-1200 automated system. 100 mg of catalyst was placed in a U-shape quartz tube in a temperature-controlled oven. The catalyst was first purged under $30\text{ cm}^3/\text{min}$ of Ar flow at $300\text{ }^{\circ}\text{C}$ for 30 min (using a ramp rate of $10\text{ }^{\circ}\text{C}/\text{min}$) and then cooled down to RT. After that, it was reduced with a 10% H_2 -90% Ar mixture ($30\text{ mL}/\text{min}$) by heating to $800\text{ }^{\circ}\text{C}$ at a ramp rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The amount of hydrogen consumption was measured using a thermal conductivity detector.

CO_2 -TPD was performed using a Builder PCA-1200 automated instrument. The catalyst was pre-reduced under a 10% H_2 /Ar mixture gas flow ($30\text{ mL}/\text{min}$) by ramping to $800\text{ }^{\circ}\text{C}$ ($10\text{ }^{\circ}\text{C}/\text{min}$). Then, the system was purged with He at $800\text{ }^{\circ}\text{C}$ for 30 min, and then cooled down to RT. The adsorption of CO_2 was performed at $50\text{ }^{\circ}\text{C}$ in a pure CO_2 (99.999%) flow with a rate of $30\text{ mL}/\text{min}$, and the catalyst was purged with a He stream at $50\text{ }^{\circ}\text{C}$. After that, the system was cooled down to RT in a He stream until the baseline was steady. Finally, CO_2 -TPD was performed with a ramp of $10\text{ mL}/\text{min}$ from the RT to $800\text{ }^{\circ}\text{C}$ in a $30\text{ mL}/\text{min}$ He stream.

The XPS experiments were carried out on an ESCALAB 250 XPS system with a monochromatized Al $\text{K}\alpha$ X-ray source (15 kV, 150 W, $500\text{ }\mu\text{m}$, pass energy = 50 eV). The binding energy was

calibrated by the C 1s photoelectron peak at 284.6 eV . The binding energy of O 1s was analyzed using the Shirley baseline correction method.

2.3. Catalytic performance measurement

The catalytic performance measurement of the catalysts was performed in a quartz tube fixed-bed reactor (6 mm O.D. and 4 mm I. D.) at atmospheric pressure. Typically, 30 mg catalyst with the 40–60 mesh particle size was loaded between two quartz wool plugs. The temperatures were measured using K Type thermocouples and controlled by a PID controller. Before the reaction, the catalyst was reduced at $850\text{ }^{\circ}\text{C}$ for 2 h using a mixture of 20% H_2 in 80% N_2 at a flow rate of $30\text{ mL}/\text{min}$. The reaction feed contained CH_4 , CO_2 and N_2 (N_2 was used as the internal standard gas), which was controlled by mass flow controllers. The reforming reaction was performed at 650, 750 and $850\text{ }^{\circ}\text{C}$, and the N_2 was used an internal standard to calculate the CH_4 and CO_2 conversion. The effluent gas was passed through a trap and then analyzed by a gas chromatograph online with a molecular sieve column and a Porapak Q column. The stability was tested by using the following conditions: $m_{\text{cat}} = 30\text{ mg}$, $\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:3$, $\text{GHSV} = 100000\text{ mL h}^{-1}\text{ g}^{-1}$, $T = 850\text{ }^{\circ}\text{C}$ and atmospheric pressure. The conversions of CH_4 (X_{CH_4}) and CO_2 (X_{CO_2}), the selectivity of H_2 (S_{H_2}), as well as H_2/CO ratio were calculated as follows:

$$X_{\text{CH}_4} = (F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) / F_{\text{CH}_4,\text{in}} \times 100\%$$

$$X_{\text{CO}_2} = (F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}) / F_{\text{CO}_2,\text{in}} \times 100\%$$

$$S_{\text{H}_2} = F_{\text{H}_2,\text{out}} / 2(F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) \times 100\%$$

$$\text{H}_2/\text{CO} = [\text{H}_2]_{\text{out}} / [\text{CO}]_{\text{out}}$$

3. Results and discussion

3.1. Morphology and texture of the ZrO_2 supports

The morphology of the three synthesized ZrO_2 supports was examined by FE-SEM. Fig. (1a–c) displays typical FE-SEM images. From Fig. 1(a), a panoramic view revealed particles with different shapes including rice-like ones for $\text{ZrO}_2\text{-ipch}$. The enlarged FE-SEM image of $\text{ZrO}_2\text{-ipch}$ (inset in Fig. 1(a)) further suggested that $\text{ZrO}_2\text{-ipch}$ has an immature pinecone shaped hierarchical structure composed of ZrO_2 nanoparticles. However, $\text{ZrO}_2\text{-cs}$ has cobblestone-like agglomerated ZrO_2 nanoparticles (Fig. 1(b)). Fig. 1(c) shows that $\text{ZrO}_2\text{-ip}$ has an aggregate shape of irregular particles. The TEM images of $\text{ZrO}_2\text{-ipch}$, $\text{ZrO}_2\text{-cs}$ and $\text{ZrO}_2\text{-ip}$ (Fig. 1(d–f)) present further views of their morphology. From Fig. 1(d), the hierarchical structure feature with mesopores of $\text{ZrO}_2\text{-ipch}$ can be further confirmed. More interestingly, in Fig. 1(e), the nanopores (less than 20 nm) of the cobblestone-like agglomerated ZrO_2 nanoparticles can be clearly seen. From Fig. 1(f), the structural characteristic of aggregation of $\text{ZrO}_2\text{-ip}$ composed of irregular particles can be further confirmed. From the above, it was confirmed that an immature pinecone shaped hierarchical structure with mesopores ($\text{ZrO}_2\text{-ipch}$) and a cobblestone-like agglomerated ZrO_2 nanoparticles with nanopores in the nanoparticles ($\text{ZrO}_2\text{-cs}$) were successfully prepared. The

Fig. 1. FE-SEM (a–c) and TEM (d–f) images of ZrO₂-ipch (a,d), ZrO₂-cs (b,e) and ZrO₂-ip (c,f) samples. Insets in Fig. 1(d,e) are the magnified images of selected regions.

textural properties of the two synthesized ZrO₂ supports were measured by nitrogen adsorption.

Fig. 2 presents the nitrogen adsorption of ZrO₂-ipch, ZrO₂-cs and ZrO₂-ip (the insets in Fig. 2(a) are specific surface area and pore volume). The most probable pore size are listed in Table 1. In Fig. 2(a), the isotherm of ZrO₂-ipch is of type IV with a H3 hysteresis loop, indicating the presence of narrow slit-shaped mesopores (less than 20 nm) [54,55], which agreed with the TEM observation (Fig. 1(a)). The isotherm corresponding to the ZrO₂-cs support showed the type IV feature with a H3 hysteresis loop. However, in comparison with the isotherm of ZrO₂-ipch, there was a capillary condensation step at 0.9–0.95 in the high relative pressure region, indicating the formation of macropores [56]. In Fig. 2(b) and in Table 1, the mesopores with the size 4 nm can be ascribed to the pores of the cobblestone-like nanoparticulates shown in Fig. 1(b), whereas the macropores with the size of 20–70 nm with bimodal pores (12.4 and 42.0 nm) resulted from the pores of agglomerated cobblestone-like nanoparticles. ZrO₂-ip has the most probable pore diameter of 12.8 nm. The hierarchically structured ZrO₂-ipch has a lower surface area (15.3 m²/g, the inset in Fig. 2(a)) and smaller pore volume (0.07 cm³/g) than those of ZrO₂-cs (33.2 m²/g and 0.29 cm³/g, respectively) and ZrO₂-ip (39.5 m²/g and 0.16 cm³/g, respectively), which might be ascribed to the denser accumulation of nanoparticles in the hierarchical structure.

The crystalline structure of the three synthesized supports was investigated by XRD analysis. Fig. 3 presents XRD patterns of the ZrO₂-ipch, ZrO₂-cs and ZrO₂-ip supports. From Fig. 3, the m-phase ZrO₂ can be confirmed for both of them (JCPDS

Fig. 2. Nitrogen adsorption isotherms (a) and BJH pore size distribution from adsorption branch (b) of the ZrO₂-ipch, ZrO₂-cs and ZrO₂-ip supports. Insets: specific surface area and total pore volume.

Table 1

Physicochemical properties of the ZrO_2 -ipch, ZrO_2 -cs and ZrO_2 -ip supports.

Support	Average crystalline size ^a (nm)		Pore diameter (nm)
	550 °C	850 °C	
ZrO_2 -ipch	13.6	17.2	4.0
ZrO_2 -cs	12.1	21.9	12.4, 42.0
ZrO_2 -ip	14.0	16.8	12.8

^a Comparison of average crystallite sizes of the synthesized ZrO_2 from calcination at 550 and 850 °C, estimated by the Scherrer equation from the m- ZrO_2 (11 $\bar{1}$) and (111) planes.

37–1484) [57]. The ZrO_2 -ipch demonstrated a higher intensity of the XRD peaks than ZrO_2 -cs, indicating higher crystallinity. The weaker and broader XRD peaks for ZrO_2 -cs than those for ZrO_2 -ipch suggest a smaller average crystalline size. The narrowest XRD peaks were observed with ZrO_2 -ip, indicating the largest average crystallite size. The average crystalline sizes of m- ZrO_2 for the two supports were estimated by the Scherrer equation from the peaks for the (111) and (11 $\bar{1}$) planes of monoclinic ZrO_2 (Table 1). The average crystalline size of m- ZrO_2 for the ZrO_2 -ipch support (13.6 nm) is larger than that for the ZrO_2 -cs support (12.1 nm). However, these two crystallite sizes were smaller than that of ZrO_2 -ip (14.0 nm). A high thermal stability is indispensable for the catalyst support to satisfy the requirement imposed by the harsh conditions for the DRM reaction. Therefore, we compared the thermal stability of the two ZrO_2 supports by performing an XRD analysis on the ZrO_2 supports after calcinating at 850 °C. The

Fig. 3. XRD patterns of ZrO_2 -ipch (1), ZrO_2 -cs (2) and ZrO_2 -ip (3) supports.

estimated average crystalline sizes of the m- ZrO_2 for the two supports calcined at 850 °C are listed in Table 1. From Table 1, the crystalline size of m- ZrO_2 for ZrO_2 -cs increased from 12.1 to 21.9 nm (81.0% growth, the percentage of the increased size over the original size), suggesting its poor thermal stability. However, only 26.5% growth (from 13.6 to 17.2 nm) for the ZrO_2 -ipch support and 20.0% of growth (from 14.0 to 16.8 nm) for ZrO_2 -ip were observed. This revealed that both ZrO_2 -ipch and ZrO_2 -ip have superior thermal stability in comparison to the ZrO_2 -cs sample.

Fig. 4. CH_4 rate (a), CO_2 rate (b), H_2 selectivity (c) and H_2/CO ratio (d) at different temperatures for DRM over Ni/ZrO_2 -ipch, Ni/ZrO_2 -cs and Ni/ZrO_2 -ip catalysts. Reaction conditions: $m_{\text{cat}} = 50$ mg, $\text{CH}_4/\text{CO}_2/\text{N}_2 = 1:1:3$, GHSV = 60 000 $\text{mL h}^{-1} \text{g}^{-1}$, and atmospheric pressure.

3.2. Morphology effect of the ZrO₂ support on the supported Ni catalysts for DRM reaction

The initial catalytic performance evaluation of Ni/ZrO₂-ipch, ZrO₂-cs and Ni/ZrO₂-ip catalysts was performed to explore the effect of the morphology of the support (Fig. 4). From Fig. 4(a,b), it can be observed that the CH₄ and CO₂ rates of all the supported Ni catalysts were strongly dependent on the reaction temperature, indicating the thermodynamic control of the DRM. The order of the CH₄ and CO₂ rates was Ni/ZrO₂-ipch > Ni/ZrO₂-cs > Ni/ZrO₂-ip. Moreover, it can be observed that the CO₂ rate was higher than CH₄ rate over the catalysts, especially at lower reaction temperatures, which might be due to the simultaneous occurrence of the reverse water gas shift (RWGS) reaction [58]. The RWGS reaction results in the H₂/CO ratio being less than 1 (Fig. 4(d)). From Fig. 4(c,d), an increasing reaction temperature does not result in a visible change in H₂ selectivity, but led to an increase in the H₂/CO ratio, which might be attributed to an enhanced water gas shift (WGS) reaction by the increased temperature.

Table 2 shows that the Ni/ZrO₂-ipch catalyst has a lower surface area (17 m²/g) than Ni/ZrO₂-cs (20 m²/g) and Ni/ZrO₂-ip (32 m²/g). Generally, supported Ni catalysts show a lower surface area than their corresponding support. Interestingly, the Ni/ZrO₂-ipch catalyst showed a higher specific surface area than the ZrO₂-ipch support (15.3 m²/g), which was ascribed to a high Ni dispersion and higher thermal stability of the ZrO₂-ipch support (Table 1). On correlating the surface area data to reaction results, in comparison with Ni/ZrO₂-cs or Ni/ZrO₂-ip, the lower surface area of the Ni/ZrO₂-ipch catalyst did not reduce the rate for CH₄ and CO₂ transformation, implying that there were other aspects that resulted in its higher catalytic activity. Therefore, XRD, CO chemisorption, H₂-TPR, CO₂-TPD and XPS experiments were further performed to reveal the origin for the higher catalytic activity of the Ni/ZrO₂-ipch catalyst in comparison with Ni/ZrO₂-cs or Ni/ZrO₂-ip for the DRM reaction.

Fig. 5 presents the XRD patterns of the Ni/ZrO₂-ipch, Ni/ZrO₂-cs and Ni/ZrO₂-ip catalysts. In Fig. 5, the XRD peaks appearing at 44.5°, 51.8° and 76.4° can be well resolved, and were assigned to the reflections of the (111), (200) and (220) planes of the face centered cubic (fcc) Ni phase (JCPDS No. 65-2865), respectively. The weaker and broader XRD peaks corresponding to the (111), (200) and (220) planes of Ni for the Ni/ZrO₂-ipch catalyst in comparison with those for Ni/ZrO₂-cs or Ni/ZrO₂-ip can be clearly seen, which suggested a better dispersion of Ni on ZrO₂-ipch. The average crystalline

Fig. 5. XRD patterns of Ni/ZrO₂-ipch (1), Ni/ZrO₂-cs (2) and Ni/ZrO₂-ip (3) catalysts, and bulk Ni (4) included for reference.

size of Ni for the two catalysts was estimated by the Scherrer equation based on the above three typical reflections planes. The results are listed in Table 2. From Table 2, the 12.7, 13.3 and 20.4 nm of the average crystalline size of Ni for Ni/ZrO₂-ipch, Ni/ZrO₂-cs and Ni/ZrO₂-ip, respectively, can be seen. The smaller average crystalline size of Ni for Ni/ZrO₂-ipch may be one reason for its higher catalytic activity for DRM in comparison with Ni/ZrO₂-cs or Ni/ZrO₂-ip catalyst. CO chemisorption was performed to measure the Ni dispersion. The chemisorption stoichiometry of CO to Ni was assumed to be 1 [52]. The results are listed in Table 2. The higher Ni dispersion (5.3%) of the Ni/ZrO₂-ipch catalyst than that of Ni/ZrO₂-cs (3.8%) and Ni/ZrO₂-ip (3.1%) can be observed, revealing the effect of the morphology of the support on Ni dispersion of a supported Ni catalyst. The higher Ni dispersion of the Ni/ZrO₂-ipch catalyst endowed it with a higher catalytic activity for the DRM by the increased active sites.

The H₂-TPR technique is a powerful tool for unveiling the reducibility and metal-support interaction of supported metal catalysts. Fig. 6 presents the H₂-TPR profiles for the Ni/ZrO₂-ipch, Ni/ZrO₂-cs and Ni/ZrO₂-ip catalysts. The quantitative analytical results are listed in Table 2. In Fig. 6, the H₂-TPR profiles for the two catalysts can be roughly divided into two reduction regions (region I and region II). Region I can be assigned to the reduction of free NiO on the support surface and the reduction of NiO with a weak metal-support interaction [59–61], whereas region II can be assigned to the reduction of NiO with a strong Ni-ZrO₂ interaction [52]. The initial reduction temperature for region I corresponding to the Ni/ZrO₂-ipch catalyst was shifted to a lower temperature, which might be ascribed to the reduction of surface oxygen species. From Table

Table 2

Characteristics of the Ni/ZrO₂-ipch, Ni/ZrO₂-cs and Ni/ZrO₂-ip catalysts.

Catalyst	S_{BET} (m ² /g)	CS _{Ni} ^a (nm)		D_{Ni} ^b (%)	H ₂ uptake ^c (mmol/g)		Reduction degree (%)	CO ₂ desorption (μmol/g)	Coke rate (mg g _{cat} ⁻¹ h ⁻¹)
		Fresh	Spent		I	II			
Ni/ZrO ₂ -ipch	17	12.7	13.0	5.3	0.52	0.52	38.1	64.6	1.95
Ni/ZrO ₂ -cs	20	13.3	—	3.8	0.75	0.21	35.8	57.2	—
Ni/ZrO ₂ -ip	32	20.4	25.5	3.1	0.84	—	31.6	36.7	6.19

^a Average crystalline size of Ni for fresh and spent catalysts was estimated by the Scherrer equation based on the Ni(111) plane.

^b Determined by CO chemisorption.

^c Measured by H₂-TPR experiments.

Fig. 6. H₂-TPR profiles of the NiO/ZrO₂-ipch (1), NiO/ZrO₂-cs (2) and NiO/ZrO₂-ip (3) samples.

2, the H₂ uptake for region II of the Ni/ZrO₂-ipch catalyst was much higher than that of the Ni/ZrO₂-cs catalyst, indicating more NiO with a strong metal-support interaction. Interestingly, no peak in region II from Ni/ZrO₂-ip was observed, suggesting the weakest Ni-support interaction. A strong Ni-ZrO₂ interaction is favorable for high Ni sintering resistance, which would improve the catalytic stability for DRM at high temperature. Moreover, from Table 2, the Ni/ZrO₂-ipch catalyst exhibited a higher reduction degree (the percentage of total H₂ consumption to the nominal H₂ uptake for NiO complete reduction, 38.1%) in comparison with that of the Ni/ZrO₂-cs (35.8%) and Ni/ZrO₂-ip (31.6%) catalysts, which allowed the Ni/ZrO₂-ipch catalyst to exhibit superior catalytic activity to the other two catalysts.

CO₂-TPD was conducted to investigate the surface basic properties of the catalysts, which significantly affects the adsorption and activation of CO₂ [62–64]. Fig. 7 presents the CO₂-TPD profiles, and the quantitative results are listed in Table 2. In Fig. 7, besides the desorption peak at 129 °C (weak basic sites) in the CO₂-TPD profile of the Ni/ZrO₂-ipch catalyst, another peak at 247 °C can be clearly observed. However, only one peak occurred at 112 °C in the CO₂-TPD profile of Ni/ZrO₂-cs and at 113 °C in the CO₂-TPD profile of the Ni/ZrO₂-ip catalyst. This result illustrated that the Ni/ZrO₂-ipch catalyst has strong basic sites in addition to the existing weak

Fig. 7. CO₂-TPD profiles of the Ni/ZrO₂-ipch (1), Ni/ZrO₂-cs (2) and Ni/ZrO₂-ip (3) catalysts.

Fig. 8. O 1s region of the XPS spectra for the Ni/ZrO₂-ipch (1), Ni/ZrO₂-cs (2) and Ni/ZrO₂-ip (3) catalysts.

ones. From Table 2, the total desorbed CO₂ from the Ni/ZrO₂-ipch catalyst (64.6 μmol/g) was more than that of the Ni/ZrO₂-cs (57.2 μmol/g) and Ni/ZrO₂-ip catalysts (36.7 μmol/g). In comparison with the Ni/ZrO₂-cs catalyst, more and stronger basic sites can promote the adsorption and activation of CO₂, which can efficiently enhance the DRM reaction. From the references [65,66], lattice oxygen (O²⁻) can activate the C–H bond and also promote coke gasification.

The surface oxygen species were monitored by XPS analysis. Fig. 8 displays the O 1s region of the XPS spectra for the Ni/ZrO₂-ipch, Ni/ZrO₂-cs and Ni/ZrO₂-ip catalysts. In Fig. 8, the O 1s spectra of the two catalysts can be deconvoluted into two peaks. The peaks at 530.1 and 531.4 eV can be assigned to lattice oxygen (O²⁻) and adsorbed oxygen, respectively [55,56]. The percentage of lattice oxygen and adsorbed oxygen to the total amount of O, Ni, and Zr is summarized in Table 3. It can be observed that the percentage of the lattice oxygen on Ni/ZrO₂-ipch (49.7%) was much higher than that on the Ni/ZrO₂-cs (30.7%) and Ni/ZrO₂-ip (23.4%) catalysts. The higher percentage of lattice oxygen allows Ni/ZrO₂-ipch to exhibit higher catalytic activity and coke resistant stability [65,66].

3.3. Morphology effect of the ZrO₂ support on the longterm stability of supported Ni catalysts

Deactivation by coke is still the key problem to be solved for the industrial application of Ni-based catalysts for the DRM reaction. Therefore, the development of stable and coke resistant catalysts is a major concern. Here, the morphology effect of the support on the catalytic stability of the supported Ni catalysts for the DRM reaction was investigated. The results are

Table 3
XPS data for the Ni/ZrO₂-ipch, Ni/ZrO₂-cs and Ni/ZrO₂-ip catalysts ^a.

Catalyst	Lattice oxygen		Adsorbed oxygen	
	BE (eV)	Percentage (%)	BE (eV)	Percentage (%)
Ni/ZrO ₂ -ipch	530.0	49.7	531.4	20.2
Ni/ZrO ₂ -cs	530.1	30.7	531.4	33.9
Ni/ZrO ₂ -ip	530.1	23.4	531.4	45.1

^a The atom percentage of O atom to total amount of O, Ni, and Zr from XPS analysis.

Fig. 9. CH₄ conversion (a), CO₂ conversion (b), H₂ selectivity (c) and H₂/CO ratio (d) as a function of time on stream for CO₂ dry reforming of methane over the Ni/ZrO₂-ipch and Ni/ZrO₂-ip catalysts. Reaction conditions: $m_{\text{cat}} = 30$ mg, CH₄:CO₂:N₂ = 1:1:3, GHSV = 100 000 mL h⁻¹ g⁻¹, $T = 850$ °C, atmospheric pressure.

displayed in Fig. 9. From Fig. 9, the Ni/ZrO₂-ipch catalyst exhibited higher catalytic activity and stability in comparison with the Ni/ZrO₂-ip catalyst during 30 h of time on stream reaction. From the above analysis, a higher activity of the Ni/ZrO₂-ipch catalyst in comparison with Ni/ZrO₂-ip can be ascribed to the higher Ni dispersion, reducibility, percentage of lattice oxygen, and more basic sites with higher strength. From Fig. 9(c,d), the two catalysts have similar H₂ selectivity and H₂/CO ratio. The Ni/ZrO₂-ipch catalyst exhibited outstanding catalytic stability including the conversion of CH₄ and CO₂, H₂ selectivity and H₂/CO for DRM reaction, which makes it a promising catalyst for synthesis gas production through the DRM reaction.

The XRD, TEM and TGA techniques were used to unveil the reason for the outstanding catalytic stability of the Ni/ZrO₂-ipch catalyst. Fig. 10 displays the XRD patterns of the fresh and spent Ni/ZrO₂-ipch and Ni/ZrO₂-ip catalysts. The average crystalline size of Ni was estimated by the Scherrer equation on the basis of the Ni (111), (200) and (220) planes (Table 2). From Fig. 10 and Table 2, no visible Ni sintering on the two catalysts can be observed, suggesting the existence of a strong Ni–ZrO₂ interaction on the two catalysts. In addition, compared with the fresh catalysts, the spent Ni/ZrO₂-ipch and Ni/ZrO₂-ip catalysts show an obvious diffraction peak ascribed to graphitic carbon located at 26° [67]. The stronger diffraction peak corresponding to graphitic carbon from Ni/ZrO₂-ip than from Ni/ZrO₂-ipch can be observed. Therefore, it can be proposed that the poorer stability of Ni/ZrO₂-ip should be ascribed

to its weaker coke resistance. TEM and TGA measurements were performed to further investigate the coking behavior of the two catalysts.

Fig. 11 displays typical TEM images of the two spent catalysts. In Fig. 11, coke with a nano-tubular feature on the two catalysts can be observed. Moreover, the amount of this kind of tubular carbon on the spent Ni/ZrO₂-ip catalyst was much more than that on the Ni/ZrO₂-ipch catalyst. The amount of

Fig. 10. XRD patterns of fresh and spent supported Ni catalysts (Ni/ZrO₂-ipch and Ni/ZrO₂-ip) and bulk Ni included for reference. (1) Ni/ZrO₂-ipch (fresh); (2) Ni/ZrO₂-ipch (spent); (3) Ni/ZrO₂-ip (spent); (4) Ni/ZrO₂-ip (fresh); (5) metallic Ni.

Fig. 11. TEM images of spent Ni/ZrO₂-ipch (a) and Ni/ZrO₂-ip (b) catalysts.

deposited coke on the two spent catalysts was further investigated by TGA analysis.

Fig. 12 presents the TGA/DTG curves of the spent Ni/ZrO₂-ipch and Ni/ZrO₂-ip catalysts. The coking rate calculated on the basis of the TGA analysis is summarized in Table 2. From Fig. 12 and Table 2, the Ni/ZrO₂-ipch demonstrated a lower mass loss (9.0 wt%) and coking rate (1.95 mg g⁻¹ h⁻¹) than the Ni/ZrO₂-ip catalyst (35.1%, 6.19 mg g⁻¹ h⁻¹). In comparison with the previously reported Ni/ZrO₂-AN catalyst, the developed supported Ni catalyst on ZrO₂ exhibited

Fig. 12. TGA (a) and DTG (b) curves for the spent Ni/ZrO₂-ipch (1) and Ni/ZrO₂-ip (2) catalysts.

obviously better coking resistance [43]. Even if when compared with a supported Ni nanosheet catalyst, Ni/ZrO₂-ipch still exhibited a much lower coke formation rate [68]. According to the literature [65,69], lattice oxygen can react with deposited carbon on the surface of catalysts, and the residual vacancies can be supplied by CO₂. Moreover, the promoted adsorption and activation by the more basic sites of Ni/ZrO₂-ipch catalyst also can eliminate deposited coke [70,71]. Furthermore, from Figs. 1 and 2, one can clearly see that the ZrO₂-ipch sample contains mesopores with a narrow pore size distribution in the region of 4 nm, which may endow it with good catalytic stability through the stabilization effect on nickel particles against sintering and coke deposition by the confinement effect of the mesopores [33,69,72,73]. The much smaller crystallite size of Ni on Ni/ZrO₂-ipch was also one reason for its higher coke tolerance than Ni/ZrO₂-ip [17,62,74–76]. From Fig. 12(b), only one peak in the DTG curves of the two catalysts can be observed, suggesting only one type of coke on the two catalysts. The lower temperature for the DTG peak on Ni/ZrO₂-ipch in comparison with that on Ni/ZrO₂-ip indicated the more active coke species on Ni/ZrO₂-ipch. The more active the coke is, the easier the coke gasification is. This might also be one reason for the higher coke resistant stability of Ni/ZrO₂-ipch during the DRM reaction. Correlating the XPS and CO₂-TPD to the TGA results, the more lattice oxygen and surface basic sites on the Ni/ZrO₂-ipch catalyst than those on Ni/ZrO₂-ip significantly improve the coke resistant ability of Ni/ZrO₂-ipch, which endowed Ni/ZrO₂-ipch to be a promising catalyst for synthesis gas production through the DRM reaction.

4. Conclusions

An immature pinecone shaped hierarchically structured zirconia (ZrO₂-ipch), agglomerated porous cobblestone-like zirconia (ZrO₂-cs) and traditional irregular ZrO₂ particles (ZrO₂-ip) as supports were synthesized by a facile hydrothermal method. The hierarchically structured Ni/ZrO₂-ipch catalyst exhibited much higher activity and stability in comparison with Ni/ZrO₂-ip. The catalytic performance was significantly dependent on Ni crystalline size, Ni dispersion, reducibility, lattice oxygen percentage, and basic properties, which were notably affected by the morphology of the support. The higher activity and Ni- and coke resistant stability of the Ni/ZrO₂-ipch catalyst makes it a potential candidate for the DRM reaction. Owing to its unique microstructure and high thermal stability, the immature pinecone shaped hierarchically structured zirconia would be a promising support for synthesizing other supported catalysts for diverse transformations, especially for high temperature reactions.

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Graphical Abstract

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Morphology effect of zirconia support on the catalytic performance of supported Ni catalysts for dry reforming of methane

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An immature pinecone shaped hierarchically structured zirconia is a promising support for Ni-based catalysts for hydrogen production by the dry reforming of methane. The origin of its superior catalytic performance was discussed.

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氧化锆担载镍甲烷干重整催化剂的载体形貌效应

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摘要: 煤层气是储量十分丰富的煤炭伴生资源, 也是煤炭开采中最大的安全隐患之一, 同时还是重要的温室气体。研究煤层气的高效、清洁资源化利用具有资源和环境双重意义。因此, 世界主要产煤国均十分重视煤层气的开发和利用。煤层气的主要成分是甲烷, 目前主要通过两种方式实现其资源化利用: (1) 直接转化, 主要通过氧化偶联、催化氧化官能团化或脱氢芳构化等途径将其转化为高碳烃、含氧化合物及芳烃等; (2) 间接转化, 甲烷首先经催化重整反应制取合成气, 而后再经 Fischer-Tropsch 合成、甲醇化和氢甲酰化等过程来合成饱和烃、烯烃、甲醇及其他含氧化物。对于前者, 由于热力学限制, 反应收率很低, 应用前景较差, 而经由合成气这一平台产物的间接转化路线被认为是一条甲烷资源化利用颇具工业前景的转化路线。因此, 甲烷催化重整制合成气备受关注。

研究表明, 贵金属具有较好的甲烷重整催化性能, 但其储量有限、价格昂贵的内在缺陷不利于甲烷大规模转化和资源化利用。Ni 基催化剂具有与贵金属可比的催化活性和选择性, 且其储量丰富, 价格低廉, 因此在甲烷重整反应中备受青睐。但是, 相对于贵金属, Ni 基催化剂易于积碳和烧结失活, 这已成为制约其大规模工业化应用的瓶颈。迄今, 大量文献报道关注如何提高 Ni 基催化剂的催化稳定性。而载体形貌调控是调节负载型催化剂的有效途径。本文开展了用作载 Ni 催化剂的氧化锆载体的形貌调控研究, 以期可以有效调节载 Ni 催化剂的物化性质, 进而调控载 Ni 催化剂的甲烷重整催化性能。

采用水热法成功制备了松球状和鹅卵石状的单斜相氧化锆载体, 进一步负载镍, 制备了载镍催化剂, 用于甲烷重整制合成气反应。具有分级结构的松球状氧化锆载 Ni 催化剂 (Ni/ZrO₂-ipch) 展示出比鹅卵石状氧化锆和常规氧化锆纳米粒子载 Ni 催化剂显著好的催化活性和稳定性。采用 XRD、N₂ 吸附、TEM、H₂-TPR、CO 化学吸附、CO₂-TPD、XPS 和 TGA 等手段研究了松球状氧化锆载 Ni 催化剂高催化活性和稳定性的原因和机制。发现, 其较高的催化活性主要归因于高的 Ni 分散度、改善的可还原性、促进的氧流动性以及较多的碱性位和较强的碱性, 这些物化性质依赖于氧化锆载体的独特形貌。分级结构的松球状氧化锆载 Ni 催化剂高的甲烷重整催化稳定性主要源于催化剂的高抗烧结、抗积碳性能。加强的金属载体效应和介孔限域效应可以阻止金属 Ni 的高温烧结, 而优良的抗积碳稳定性主要源于催化剂良好的氧流动性、较多的碱性位、较强的碱性以及小的 Ni 粒子尺寸。

鉴于分级结构松球状氧化锆载 Ni 催化剂高的催化活性和优良的抗积碳、抗烧结稳定性, 该催化剂用于甲烷重整制合成气具有广阔前景. 而所制备的分级结构松球状氧化锆由于具有独特的结构和优良的热稳定性, 可以作为性能优良的载体用于其他反应, 尤其对于高温转化过程可望表现出明显优势.

关键词: 镍基催化剂; 氧化锆载体; 分级结构; 形貌效应; 甲烷干重整; 合成气; 抗积碳

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