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Full Length Article

Highly dispersible cerium-oxide modified Ni/SBA-15 for steam reforming of bio-mass based JP10

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ABSTRACT

Ni/SBA-15 modified by highly dispersed cerium-oxide was prepared with the aid of sucrose for steam reforming of JP10 (C₁₀H₁₆). Their characterization showed that addition of appropriate amount ceria led to the formation of highly dispersed CeO₂ and Ni, and the CeO₂ covered smaller nickel particles like strawberry seeds to form much more interface between them. Their catalytic activity exhibited higher stability over time on stream of 6.5 h with conversion higher than 95% and higher carbon resistance (mass loss less than 4.5% by TG), which may derive from good properties below: (1) much more interface enhanced cooperation effect and increased turnover frequency at the interface; (2) the stronger interaction between Ni and ceria to suppress sintering by formation of Ni-O-Ce solid solution; (3) the large amount of oxygen vacancies from the formation of Ni-O-Ce solid solution and highly dispersed CeO₂ to facilitate the water-gas-shift reaction and carbon removal.

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1. Introduction

Hydrogen, being sustainable and high-energy-content carrier, draw a potential application interest as a fuel in internal combustion engines or as resource for fuel cell to produce electricity without pollution emission and its use was one way to CO₂ emission mitigation [1–4]. But its storage and transport was high-investing and dangerous in a form of high density, or suffered from the inevitable losses arising from boil-off and extreme load, or introduced extra-carriers and -processes [3]. A potential method to this problem is producing hydrogen on site and on demand by reforming various high-energy density fuels, such as gasoline, kerosene or jet fuel and diesel, especially for the application on aircraft [5–8]. As one of widely used jet fuels, JP10 (C₁₀H₁₆) had better performance in volumetric energy density, freezing point, and thermal stability and wide source and could be synthesized by bio-energy, such as lignocellulosic platform compound [9,10]. Moreover, it was feasible to reform JP10 with steam by catalyst to produce hydrogen and to be with better hydrogen production efficiency, which was firstly studied in our previous article [11].

For the production of hydrogen by steam reforming of JP10, catalyst was the key importance. Benefit from lower cost and higher catalytic efficiency, Ni-based catalyst was chosen for the steam reforming process by many researchers [6,12–14] and also applied in steam reforming of JP10 in our previous work [11]. But, problems were confronted including severe coking and aggregation of active Ni metal, especially for steam reforming of high-density fuel including JP10 [11,15,16]. To probe into these problem, some studies made clear that small Ni particle with several nanometers enable the inhibition of filamentous carbon and its subsequent transformation to inactive graphite in methane reforming due to high saturation concentration of carbonaceous species over smaller Ni particles to lower the driving force for carbon diffusion through the Ni crystals [17–19]. Some reports confirmed that good dispersion and smaller particles could bring about the higher activity of the catalyst [20,21]. And some others found enhanced interaction between metal and support took an important role to keep metal particle size stable [22,23]. Thus diverse catalyst preparation methods for smaller Ni particles and strong interaction between metal and support were developed, including dispersing and confining the Ni particles in the mesoporous alumina [24] and silica [25,26]. Among these mesoporous material, SBA-15 was more popular for its bigger and ordered pore structure to host enough active metal particles, partially maintaining good dispersion [27,28] and promoting mass transfer character, especially for the big molecular

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hydrocarbons [29] or bigger metal complex [30]. Despite of above advantages, disadvantages were still found for the spent catalyst that nickel particles grew up by migrating from the internal channel to the outer or by mesoporous silica structure collapse to accelerate the sintering and then covered by the heavy carbon deposited, which deactivated the catalyst [25,26]. To improve the stability of these catalysts, the researchers induced promoters (Ce, La, Zr, Ca, Mg or Ti etc.) to strengthen the interaction between nickel particles and support [25,26,31–33]. Comparing to the others, addition of Ce took more extra effects including promoting the dispersion of nickel particles, gasification of carbon deposited on the nickel particles by the mobile oxygen released from the ceria lattice [34,35], enhancing the mesoporous structure by producing surface Si–O–Ce bonds with higher steam resistance than Si–O–Si [36] and accelerating the dissociation of H₂O to facilitate the reaction of WGS [37]. Therefore, Ce was doped or used as support in the nickel-based catalyst to improve the stability by many reporters just like mentioned above. However, ceria itself also exhibited unfavorable features, such as relatively lower surface area, less-pore, aggregation and growth at elevated temperatures which resulted in dramatic drop of surface area of supports especially for higher loading [38,39]. Therefore, highly dispersed loading of Ce on high surface area support was necessary. And also, its good dispersion offered more oxygen vacancies leading to higher coke resistance and better stability [39,40]. On the other hand, the incorporation of Ni atoms into the ceria lattice led to charge unbalance and lattice distortion, which also generates more oxygen vacancies and better reducibility [41]. Thus, ceria modified catalyst with better dispersion of both Ceria and nickel, stronger interaction between them and higher surface area, could contribute to the good performance for steam reforming of high-density fuel.

In this work, Ce-promoting Ni/SBA-15 with higher dispersion of Ce and Ni and higher surface area was prepared by addition of sucrose and was used to perform the steam reforming of JP10.

2. Experimental

2.1. Catalyst preparation

The catalysts, 8Ni/Ce/SBA-15, were prepared by a modified incipient wetness impregnation method with aid of sucrose. Typically, 1 g pre-dried (120 °C) SBA-15 (Nanjing XFNANO Materials Tech. Co. Ltd.), 0.432 g Ni(NO₃)₂·6H₂O (Aladdin Industrial Corp.), 0.36 g sucrose (Tianjin Guangfu Technology Development Co. Ltd.), and a certain amount Ce(NO₃)₃·6H₂O (Aladdin Industrial Corp.) were mixed in 15 ml of water to form a slurry. The following procedure of preparation could refer to the reference [11]. The amount of Ce(NO₃)₃·6H₂O was determined according to the Ni/Ce atomic ratio (8:0, 8:2, 8:4) and the prepared samples were denoted as 8Ni0Ce, 8Ni2Ce, 8Ni4Ce. The reason for the addition of sucrose was that it can react with Ce³⁺ and Ni²⁺ and formed complex, which would improve the dispersion of metal.

2.2. Characterization

N₂ adsorption/desorption at –196 °C was performed to study the surface areas and pore structures of catalysts using a Micro Active for ASAP 2460 Version 2.01 analyzer. Before the measurement, degas was performed for all materials at 350 °C for 8 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface areas, and the Barret–Joyner–Halenda (BJH) method was used to obtain the pore distribution and the cumulative volumes of pores based on the adsorption branches of the N₂ isotherms.

Low-angle and wide-angle XRD patterns were collected using a Rigaku D/max-2500 diffractometer employing the graphite filtered Cu K_α radiation ($\lambda = 0.154056$ nm).

Transmission electron microscope (TEM) images were used to acquire the morphology of catalysts by a FEI Tecnai G2 F20 at 200 kV. The ethanol suspension with sample powder was dropped onto a copper grid-supported transparent carbon foil. The loaded foil was dried in air and used for detection.

H₂-TPR was conducted on a TPR Win v3.52 apparatus (Chem. Star). Firstly, pretreatment was carried out to remove moisture and impurities of the powder sample (50 mg) at 300 °C for 1 h in flowing He (50 ml·min^{–1}) and then cooled down to 50 °C. After that, reduction was conducted under the temperature programed from 50 °C to 800 °C at a rate of 10 °C·min^{–1} and a flow rate of 30 ml·min^{–1} of 10% (vol) H₂-He.

A chemisorption analyzer (Micromeritics Autochem II 2920) was used to perform H₂ pulse chemisorption experiments. First, the reduction of catalyst was carried out in H₂ flow at 600 °C for 1 h. After the temperature reached to 45 °C, 10% H₂/Ar mixed gas was injected in pulses until the TCD signal intensity unchanged.

A thermal analysis system (TGA Q500 V20.13 Build 39, TA Instrument) was used to obtain TGA with a heating rate of 10 °C·min^{–1} and a flow air of 50 ml·min^{–1}.

2.3. Catalytic activity measurements

The steam reforming of JP10 were performed in a stainless-steel tube reactor with 4 mm inner diameter and 400 mm length. The mixed sample (0.15 g catalyst, 0.6 g quartz sand as diluent, 20–40 mesh) was packed in the middle part of tube located between the two K-type thermocouples to keep the uniform temperature. The conditions was fixed to S/C ratio (ratio of steam to carbon) = 5, LHSV (liquid hourly space velocity) = 10 ml·(g cat)^{–1}·h^{–1} and the detailed procedure and calculation method was described in our previous work [11].

3. Results and Discussion

3.1. Characterization of catalysts

3.1.1. Textural properties

The nitrogen sorption isotherms for all the samples (Fig. 1(a), (b)) displayed typical IV hysteresis loop isotherms at high relative pressure, indicating the still presence of meso-pores after loading metal oxide. The inflection point of hysteresis loop of loaded samples shifted to the lower p/p^0 derived from the narrowing pore size of mesopores due to the filling of loadings and typically characterized as H₂ type by a percolation effect due to nanoparticles located inside the mesopores, effectively forming ink-bottle type pores [42]. This change in hysteresis loop led to validity to determination of pore size distribution by adsorption branch according to the study of Vradman and plotted in Fig. 1(c) [43]. It can be seen that addition of ceria took nil effect on pore size of 8Ni2Ce while brought 8Ni4Ce to a broad distribution with diverse pore size from micropore to hundred nm pore. Moreover, the addition of ceria took significant effect on the pore volume and BET surface. With the increase in ceria amount, they all increased firstly and then reduced, especially for the BET surface area, just like Table 1. The highest value of pore volume and BET surface was observed over 8Ni2Ce (618 cm²·g^{–1}, 0.8 cm³·g^{–1}), which was obviously larger than that for 8Ni0Ce (488 cm²·g^{–1}, 0.65 cm³·g^{–1}) and 8Ni4Ce (388 cm²·g^{–1}, 0.77 cm³·g^{–1}) and was also the largest comparing to the other reports even with such higher loading, shown in Table 1. To understand the effect of Ce on BET surface, normalized surface area (NSA, Equation below Table 1) was adopted according

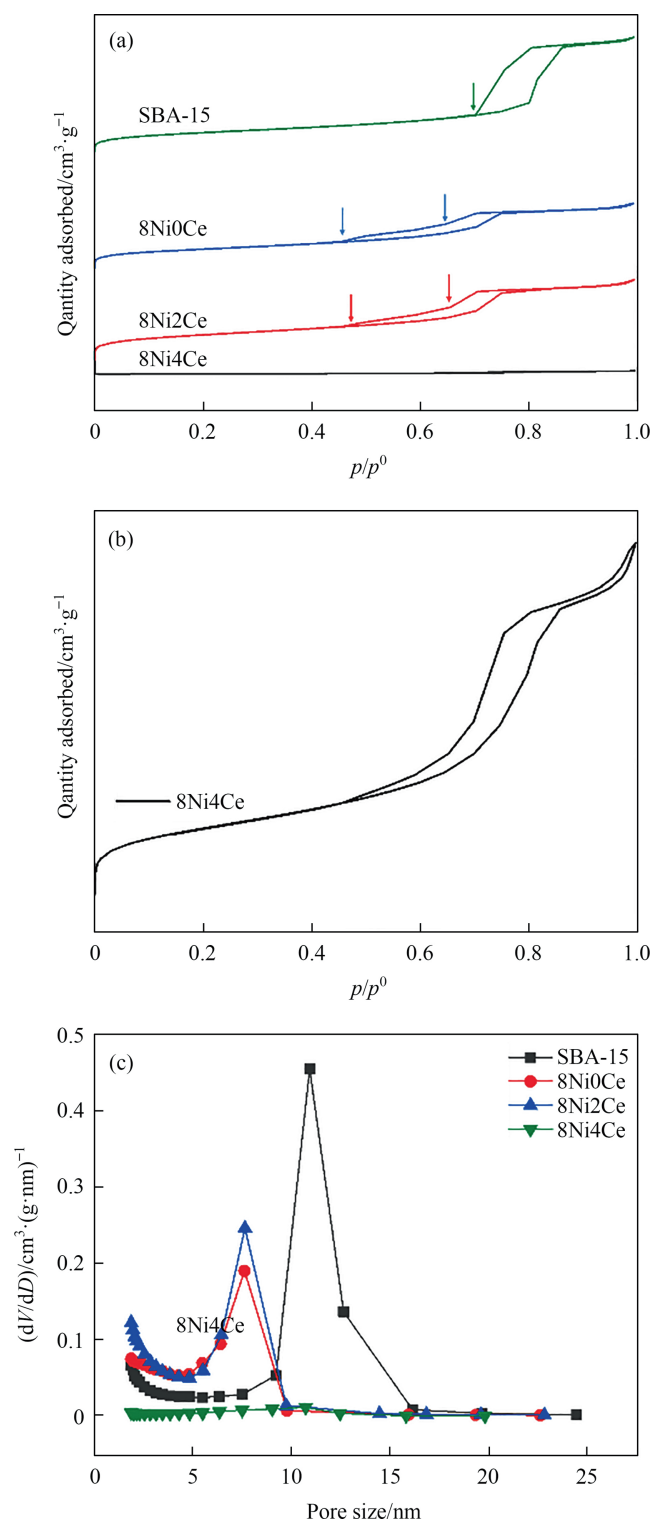


Fig. 1. N₂ adsorption-desorption isotherms (a, b) and pore size distribution (c).

to Vradman *et al* shown in Table 1 [43]. A small addition of Ce enable large increase in NSA (0.84–1.12), indicating smaller nanocrystals formed in mesochannels of SBA-15. These smaller nanocrystals packed in the mesochannels owned bigger surface area, which partially contributed to the BET surface area, and their packing in mesochannels of SBA-15 formed ink-bottle type mesopores. But the further increase in Ce led to NSA < 1 (8Ni4Ce, 0.74), implying the bigger nanoparticles formed with size compa-

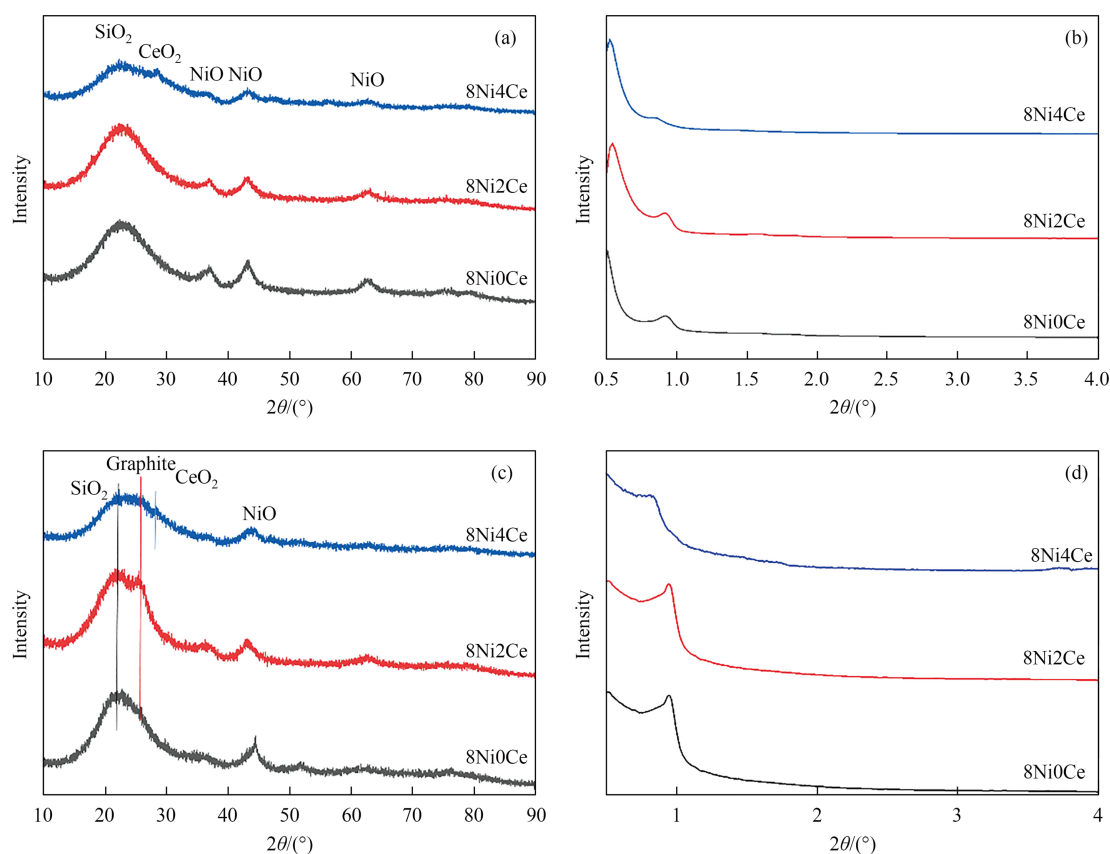
table or higher than mesopore of SBA-15. These bigger particles may block the channel of SBA-15, which resulted in widened pore size distribution (Fig. 1(c)). Both the bigger particles and blocking was negative to BET surface and caused dramatically drop in surface area just seen in Table 1. In previous works, BET area was all declined with the addition of Ce (part in Table 1) despite of improvement in nickel dispersion [25,26,34,36,40]. But, small addition of Ce was favorable for higher BET area in our work. We ascribed the positive effect of Ce addition on BET surface to our preparation method by addition of sucrose. With sucrose as ligand, both Ni and Ce ions could form complex and be isolated by carbon after calcination in N₂ at 550 °C, which produced much smaller separated particles and packed in mesochannels with higher surface area after calcined in air.

3.1.2. Crystallinity structures

The fraction patterns of small-angle and wide-angle XRD was present in Fig. 2. In Fig. 2(a), the first broadening peak centering at $2\theta \approx 25^\circ$ was assigned to the reflection peaks of the SiO₂ frameworks of SBA-15 support. Fraction peaks at $2\theta \approx 37^\circ$, 43° , 63° , 75° were corresponding to the (111), (200), (220) and (311) facets of NiO cubic crystalline structure [1]. The intensity of these peaks reduced with the addition of Ce, suggesting that the NiO particles became smaller and high dispersible. This could attribute to the strong interaction between NiO and CeO₂ and dilution effect of CeO₂ to disperse the NiO particles, which suppressed their aggregation during reaction [36]. Meanwhile, the fraction peaks of CeO₂ was hardly observed for 8Ni2Ce, revealing that CeO₂ was amorphous and also dispersed perfectly. The amorphous form of CeO₂ was usually thought to take a key effect on regulating Ni dispersion during the reduction process via interaction between Ni and ceria and preferable affinity of cerium oxide toward silica matrix [44]. Further increase in amount of Ce, a little fraction peak at $2\theta \approx 28.5^\circ$ was present for 8Ni4Ce, indicating some bulk CeO₂ formed. Whereas, the intensity of this CeO₂ peak of 8Ni4Ce was still weak and the majority of CeO₂ could remain amorphous. This amorphous form was also identified by the Raman spectra with no obvious peak located at 464 cm^{-1} featured cubic fluorite phase of CeO₂ (F_{2g} band), seen in Fig. S2 (Supplementary Material) [45]. Despite of less bulk CeO₂, it still take risk of formation of bigger particles to block the meso-channel and cover the surface of nickel [25]. To investigate coverage of Ni, the surface metal area was detected by the H₂ pulse chemisorption. It was found that the surface metal area of 8Ni0Ce (S_H) was the highest, even comparing to other only nickel supported catalysts (Table 1), indicating the preparation method in this report was more efficient. But, interestingly, the S_H reduced with the addition of CeO₂. According to the results of XRD and TEM, the addition of CeO₂ made the nickel particles smaller, namely, enhanced the dispersion of nickel (Fig. 2(a), Fig. 3). Therefore, the reduction of S_H was not ascribed to the formation of bigger nickel particles, but to the covering by CeO₂ or blocking of mesochannel. In consideration of the high dispersed amorphous morphology of CeO₂, the covering could be like strawberry seeds surrounding the nickel particles (Scheme 1), which could significantly increase the interface between Ni and CeO₂ and enhance the cooperation effect at the interface. This kind enhancement was also found on a sample with higher dispersed CeO₂ located on the metal Au surface, and the higher dispersion of CeO₂ led to more Ce³⁺ cations and more oxygen vacancies. Both the enhanced cooperation effect and more oxygen vacancies led to higher reactivity for WGS reaction [46]. With the further addition of CeO₂, the bulk CeO₂ and smaller nickel particles was formed (Fig. 2(a), Fig. 3). For these smaller nickel particles, much large surface area over them was easily covered and even buried by the bulk CeO₂, which caused interface between Ni and CeO₂ reduced and active sites unavailable. Moreover, more CeO₂ could make

Table 1Textural properties of Ni_xCe/SBA-15 catalysts and comparison with previous reports

Sample	$A_{\text{BET}}^{\text{①}}/\text{m}^2\cdot\text{g}^{-1}$	$V_{\text{p}}^{\text{①}}/\text{cm}^3\cdot\text{g}^{-1}$	$D_{\text{p}}^{\text{①}}/\text{nm}$	NSA ^②	$D^{\text{③}}(\%)/S_{\text{H}}^{\text{③}}(\text{m}^2\cdot\text{g}^{-1})$	Ni/Ce content/% (mass)	Reporter
SBA-15	687	0.93	–	–	–	–	Li et al. [25]
Ni/SBA-15	616	0.90	–	0.93	0.64/4.3	2.8	
1CeNi/SBA-15	538	0.79	–	0.88	2.06/13.8	2.8/7.1	
SBA-16	837	0.514	8.2	–	–	–	Zhang et al. [36]
5Ni5Ce/SBA-16	375	0.238	7.2	0.54	13.3/89	5/14.7	
SBA-15	799	10.9	5.7	–	–	–	Shanmugam et al. [26]
Ni/SBA-15	582	10.7	4.6	0.83	9.6/64	11.9	
Ni/CeO ₂ -SBA-15	453	10.6	4.7	0.66	18.7/126	11.8/2.71	
SBA-15	648	1.18	9.3	–	–/–	–	This work
8Ni/SBA-15	488	0.65	5.7	0.84	16.1/106	7.4	
8Ni2Ce/SBA-15	618	0.8	5.7	1.12	–/37	7.8/2.7	
8Ni4Ce/SBA-15	388	0.77	7.9	0.74	–/34	6.2/3.8	Spent catalysts in this work
8Ni/SBA-15	328	0.47	5.7	–	–	–	
8Ni2Ce/SBA-15	359	0.53	5.9	–	–	–	
8Ni4Ce/SBA-15	324	0.61	7.5	–	–	–	

① A_{BET} —BET surface area; V_{p} —Pore volume; D_{p} —Pore size.② Normalized surface area $\text{NSA} = \frac{S_{\text{A catalyst}}}{(1-y)S_{\text{A support}}}$, y —mass fraction of the loaded metal oxide in the sample, S_{A} —BET surface area of catalyst sample or support (SBA-15).③ D —dispersion (%); S_{H} —metal surface area ($\text{m}^2\cdot\text{g}^{-1}$).**Fig. 2.** Wide-angle, small-angle patterns of the fresh samples (a, b) and spent samples (c, d).

its surrounding shell over the nickel particle thickened or several smaller nickel particles bonded together, which easily led to large particles to block the mesochannels and reduce the BET surface area of catalyst, just like shown in Table 1. Both the covering and the blocking could cause the reduction in S_{H} . For 8Ni2Ce, because BET surface area (Table 1) was the highest indicating non-existence of blocking and formation of smaller particles in the mesochannel just like the discussion above (smaller than average size of 5.3 nm for 8Ni0Ce derived from H_2 pulse chemisorption measurement), the covering was the only reason to less S_{H} . That is to say, the high dispersed CeO_2 may be like strawberry seeds sur-

rounding the nickel particles (Scheme 1) and contributed to the increase in interface between Ni and CeO_2 . But for 8Ni4Ce, BET surface area dropped dramatically implying blocking of partial mesochannel and appearance of bigger particles (Table 1). In consideration of the smallest nickel particles and high dispersed CeO_2 over this sample (Fig. 2(a), Fig. 3), the bigger particles could be formed only by bonding several nickel particles or thickening the surrounding shell by more CeO_2 , which brought out covering of relative large surface area. As result, the interface between Ni and CeO_2 and cooperation effect at the interface was also reduced despite of the close value in S_{H} (Table 1).

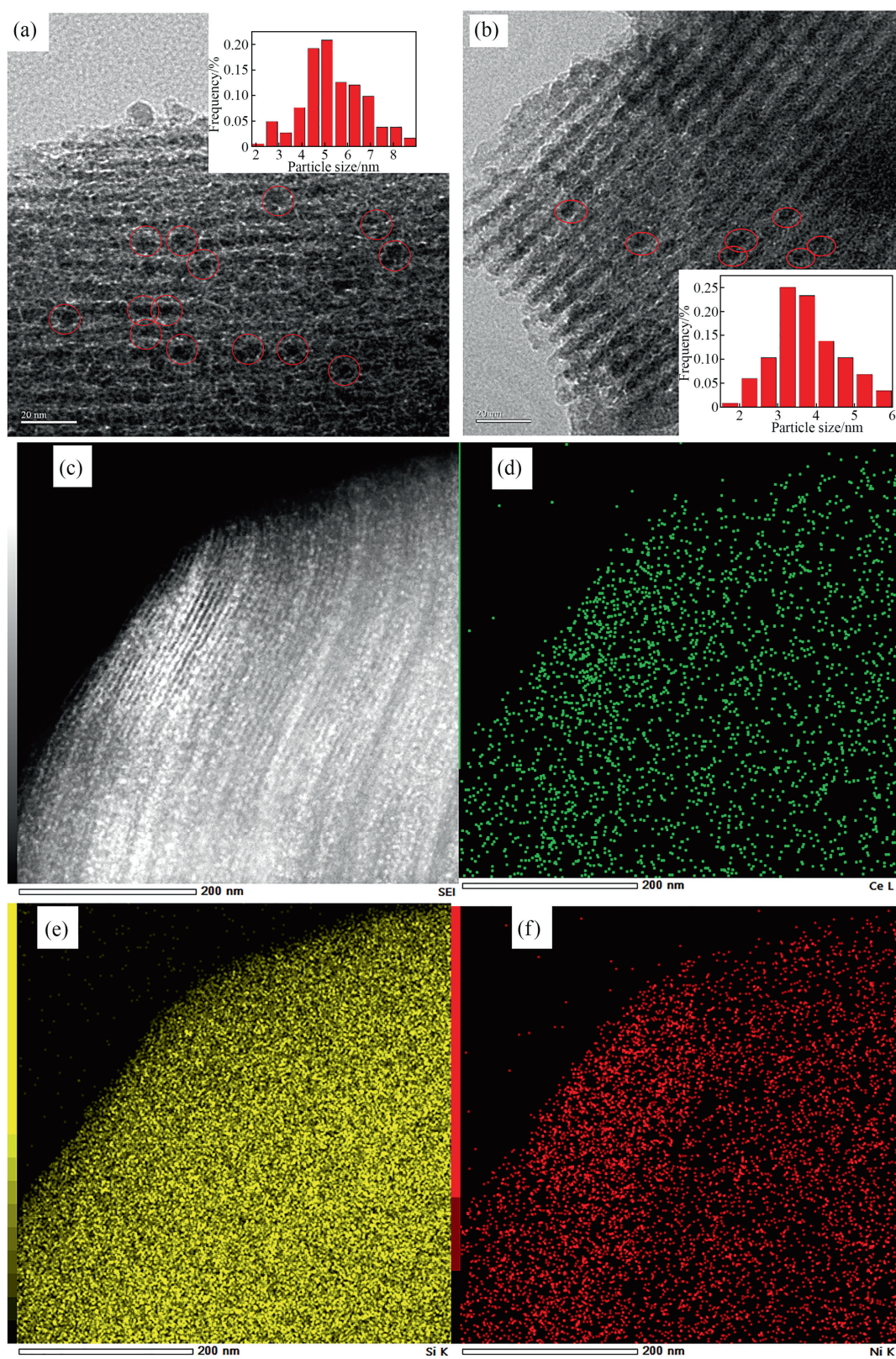


Fig. 3. TEM images (a) 8Ni0Ce (b) 8Ni2Ce and STEM-EDS elemental maps (c), (d) Ce, (e) Si, (f) Ni of sample catalyst.

Fig. 2(b) showed the fraction patterns of small angle XRD. It could be seen that mesopore characteristic peaks were still remained and the peak intensity reduced with the ceria amount increased.

3.1.3. Oxygen vacancies

The XP spectra of Ni 2p_{3/2}, Ce3d and O1s and H₂-TPR profile were shown in Fig. 4 and their deconvolution patterns were shown in Fig. S1. Fig. 4(a) showed Ni 2p_{3/2} main peaks located on

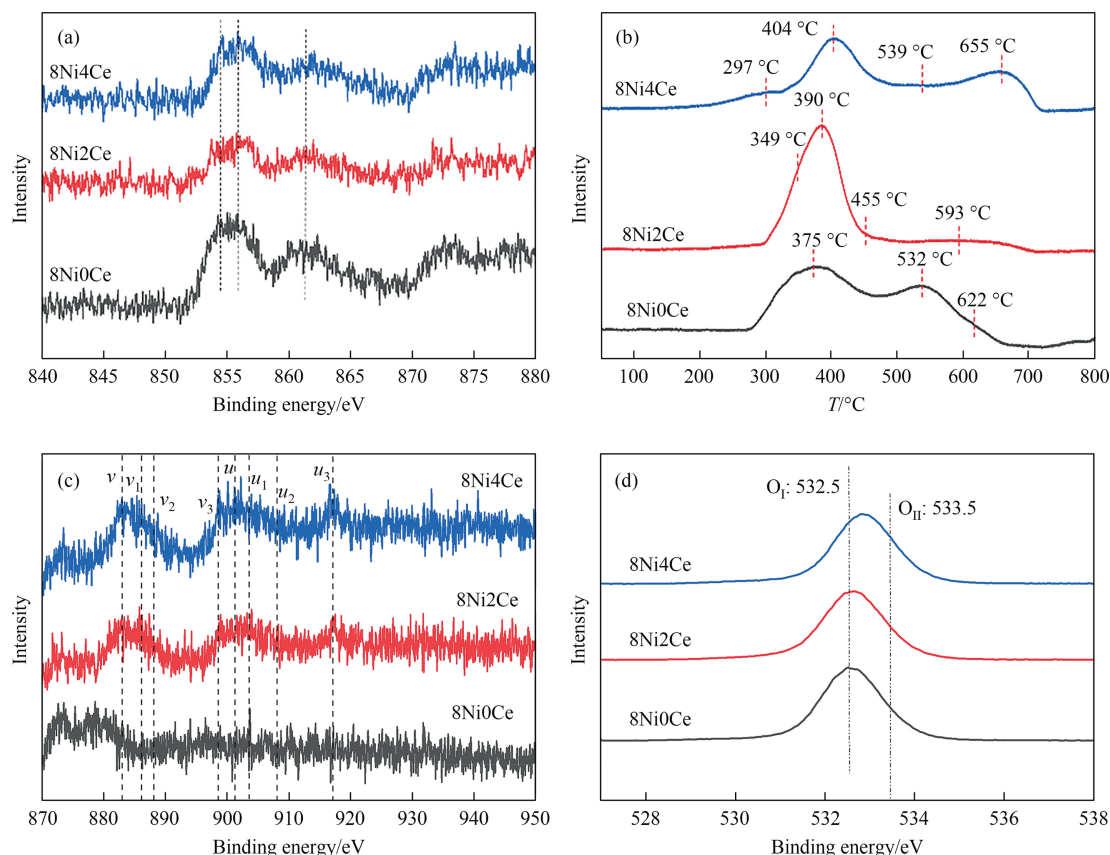
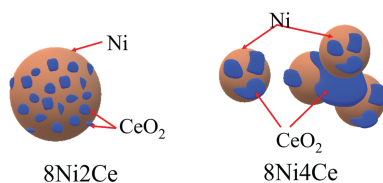


Fig. 4. Ni 2p XPS (a), H₂-TPR (b), Ce 3d XPS (c) and O 1s XPS (d) profiles of fresh NiCe/SBA-15.

845.5 eV and 856.2 eV representing separately NiO and Ni₂O₃ interacting with support. With the addition of CeO₂ by our preparation method, their peaks all shifted to a little higher binding energy, implying a stronger interaction between Ni and support [47]. Fig. 4(b) showed three quite different TPR patterns. For 8Ni0Ce, two main peaks were observed located on 371 °C and 534 °C as well as a shoulder peak at the temperature range of 600–650 °C, assigned as bulk-phase NiO species with weak interaction located on the outside surface of silica support, smaller NiO particles confined in the meso-channels with strong contact with the silica and the Ni silicates [25,26]. With the addition of Ce, the first peak of 8Ni2Ce shifted downward from 375 °C to 349 °C, and that of 8Ni4Ce shifted further to 297 °C, which representing the formation of smaller NiO particles outside the support and easier to be reduced and agreed with the result of XRD. The second peak in case of 8Ni2Ce took a dramatic change in temperature and shifted from 523 °C to 390 °C, and so did for 8Ni4Ce. The temperature downward shift, namely high reducibility, was supposed to be the result from higher mobility and activity of surface oxygen species, which was ascribed to the formation of plenty of oxygen vacancies. And the oxygen vacancies mainly derived from the formation of Ni-O-Ce solid solution by incorporation of Ni into the CeO₂ lattice, which also meaning a much stronger interaction between Ni and Ce [26,41,48]. The second peak temperature difference between 8Ni2Ce and 8Ni0Ce in this work was so large (133 °C) comparing to the previous reports (less than 50 °C) that the oxygen vacancies over 8Ni2Ce was supposed to be very large amount, also implying formation of large amount of Ni-O-Ce solid solution [26,47,49]. Namely, large amount of Ni interacted strongly with CeO₂, which could inhibit the sintering of Ni and kept the stability of this catalyst. Meanwhile, the large amount of oxygen vacancies had higher capability of dissociation adsorption of H₂O, which would facilitate the WGS reaction and the carbon removal

[37]. From Fig. 4(b), it was also found that the intensity of the second reduction peak for the sample with became much stronger comparing to the first one, indicating much more NiO with stronger interaction and more oxygen vacancies was confined in the mesochannels. With further addition of CeO₂, the second peak for 8Ni4Ce shifted to higher temperature in contrast to 8Ni2Ce (390–404 °C), representing strong interaction between part NiO and CeO₂ [49]. However, more amount ceria addition led to blockage of mesopore and larger particles by bonding nickel particles together or thickening the surrounding shell of CeO₂ over nickel particles, which caused both reduction in interface between Ni and CeO₂ and active sites just like in Table 1. These disadvantages may balance off above mentioned favorable properties (higher NiO dispersion, formation of Ni-O-Ce solid solution and more oxygen vacancies) for 8Ni4Ce. The rest shoulder peaks of 8Ni2Ce and 8Ni4Ce were classified to reduction of CeO₂ with temperature range of 500–700 °C, which was attributed to reduction of surface CeO₂ or highly dispersed CeO₂, being in consistent with XRD (reduced temperature of bulk CeO₂ is higher than 700 °C) [50]. The higher dispersion of CeO₂ could also supply more Ce³⁺ cations and large amount of oxygen mobility and vacancies [46]. The similar situation was found in Sun's work that the surface oxygen mobility of Y₂O₃ nanocrystal increases with decreasing crystal size [51]. And Carrettin *et al.* also confirmed that the reduced CeO₂, Ce₆O₁₁, was found in smaller crystalline ceria particles (mean CeO₂ particle size of 4 nm), which led to the formation of more oxygen vacancies [52]. To identify the oxygen vacancy on these samples, XPS of Ce-3d were performed (Fig. 4(c)). The two groups of spin orbital multiplets are denoted as U and V corresponding to 3d_{3/2} and 3d_{5/2}, respectively. For all the samples, three main 3d_{3/2} peaks are located at about 901.3 (U), 908.1 (U₂), and 917.1 (U₃) eV and three main 3d_{5/2} peaks at about 882.8 (V), 888.1 (V₂), and 898.1 (V₃) eV, all of which are assigned to the state of Ce⁴⁺ cation.



Scheme 1. Morphology of Ni and CeO₂ in the mesochannels.

The peaks at around 886.2 eV (V_1) and 904.0 eV (U_1) could be assigned to the Ce³⁺ state [53]. It was obvious that the intensity of V_1 and U_1 were relatively higher, especially for 8Ni2Ce, implying the Ce³⁺ state took a relative high proportion among the fresh Ce-promoting catalysts (Fig. 4(c)). That is to say, more oxygen vacancies were present, which also made the samples reduced more easily. Moreover, the oxygen vacancies were confirmed by O 1 s XPS (Fig. 4(d)). As seen in Fig. 4(d), the main peak was located at 532.5 eV (Q_1) representing of lattice oxygen, while the peak at 533.5 eV (Q_2) was assigned to adsorbed oxygen which were usually trapped by oxygen vacancies [47]. All these oxygen vacancies were favorable to adsorption of CO₂ and H₂O and then facilitate to the removal of deposited carbon and WGS reaction [37,47].

3.1.4. Morphology by TEM

The morphology and dispersion of metal oxide particles was determined by TEM and STEM-EDS. Based on the map of TEM (Fig. 3(a), (b)), the particle size of 8Ni2Ce (a maximum centered at 3–4 nm, average particle size of 3.8 nm) was obviously smaller than 8Ni0Ce (a maximum centered at 5–6 nm), indicating that addition of ceria dispersed the NiO particles perfectly and kept them isolated. This smaller particle size contributed to the inhibition of filamentous carbon and its subsequent transformation to inactive graphite. It was also identified by the STEM-EDS mapping of 8Ni2Ce (Fig. 3(d), (f)). From the mapping, it can be seen that the most part of nickel and ceria were all kept good dispersion both outside and inside mesochannels of SBA-15, which proved the preparation method with addition of sucrose led to a good dispersion for both nickel and ceria on silica SBA-15. This was agreed with the result of wide-angle XRD.

3.2. Catalytic performance test

The steam reforming of JP10 was performed with the temperature of 680 °C, LHSV = 10 (ml JP10)·(g cat)⁻¹·h⁻¹ and S/C of 5 for a time on stream of 6.5 h over all the sample catalysts, and the result was shown in Fig. 5. It showed that the conversion of 8Ni2Ce was higher than 95% and quite stable in time of 6.5 h (Fig. 5(a)). This made it superior to the others. At the beginning (TOS = 1.5 h), the conversion and yield of H₂, CO₂ all raised while yield of CO decreased with the addition of CeO₂ (8Ni2Ce, 8Ni4Ce) due to facilitating the WGS reaction and carbon removal capability caused by much more oxygen vacancies and oxygen mobility (Fig. 4(b)) and higher Ni dispersion just like mentioned above (Fig. 5(b)) [25,37]. With the process of reaction, the 8Ni0Ce and 8Ni4Ce deactivated slowly and their conversion and yield of H₂, CO₂ was below 8Ni2Ce, especially the 8Ni4Ce, at the time on stream of 6.5 h (Fig. 5(c)). The good performance of 8Ni2Ce may be caused by the formation of large amount of Ni-O-Ce solid solution, high dispersed CeO₂ and smaller nickel particles surrounded with highly dispersed CeO₂. Large amount of Ni-O-Ce solid solution strengthened the interaction between Ni and CeO₂ to inhibit the sintering of nickel particles and carbon deposition [26]. Both large amount of Ni-O-Ce solid solution and high dispersed CeO₂ supplied large amount oxygen vacancies, which facilitated the dissociation of H₂O and contributed to WGS reaction and gasification of carbon deposited

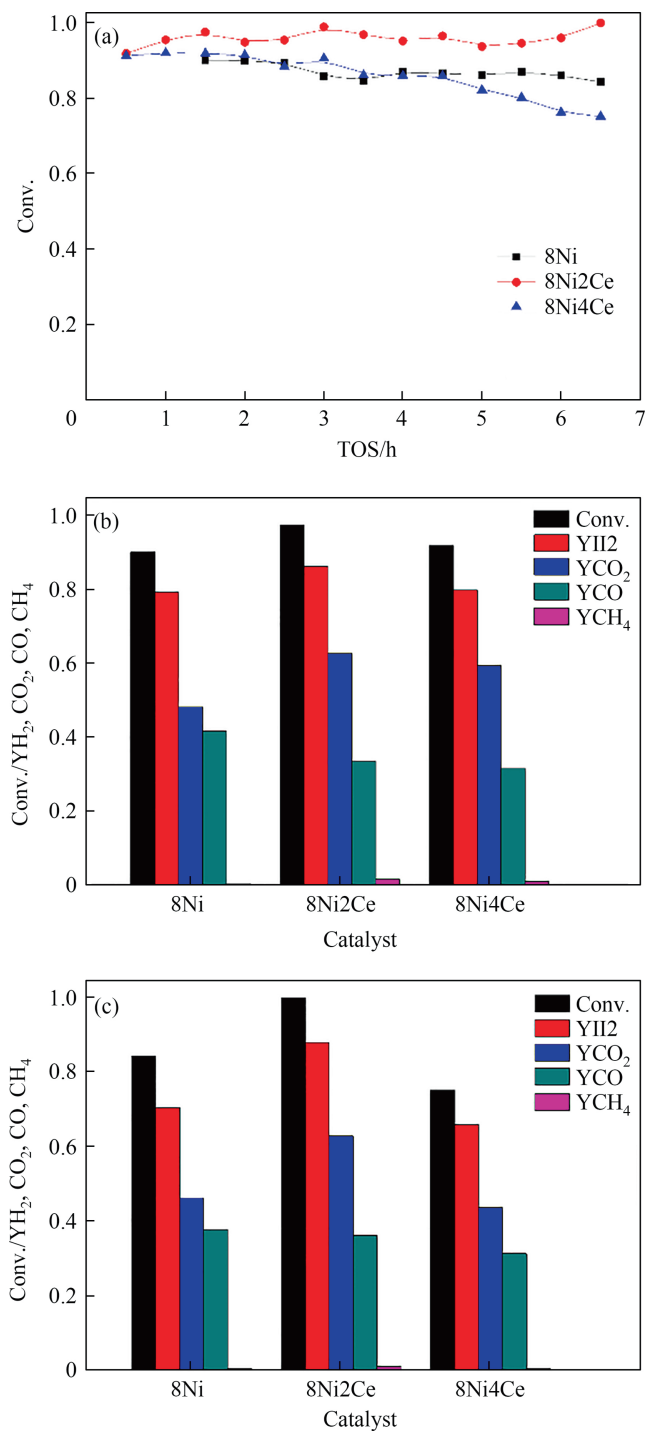


Fig. 5. JP10 conversion as a function of time on stream (TOS) (a), products yield at TOS = 1.5 h (b) and 6.5 h (c) for different catalysts. (S/C = 5, 680 °C).

[26,37,46]. Smaller nickel particles surrounded with highly dispersed CeO₂ supplied more interface between Ni and CeO₂, namely, supplied more opportunity to cooperation between them. The cooperation at the interface not only enhanced dissociation adsorption of H₂O but contributed to the formation of intermediate (HOCO) that precedes the production of CO₂ and H₂, which usually formed between OH adsorbs on the sites of CeO₂ and CO adsorbs on the sites of Ni. Furthermore, the cooperation effect could significantly increase turnover frequency (TOF) for WGS reaction that could be 40–50 times higher than that of Cu (100) [37,46]. All these

merits contributed to WGS reaction and led to a higher yield of CO_2 . Moreover, they could compensate the loss in S_H and enable a good activity over 8Ni2Ce even its S_H reduced comparing to 8Ni0Ce. However, excessive addition of CeO_2 led to bond nickel particles together or thicken its surrounding shell over nickel particles which caused much less interface between Ni and CeO_2 and cooperation effect at the interface. The reduced interface and the cooperation effect could not compensate the loss in S_H . Once part of active sites was covered, there are serious negative effect on the activities. As result, 8Ni4Ce exhibited a less stable performance despite of the close value of S_H to 8Ni2Ce. The catalytic performance of 8Ni2Ce was also compared with the previously reported catalysts (Table 2) and turned out to be a very efficient catalyst for steam reforming of heavy carbon compound.

3.3. Structure and properties of spent catalyst

TEM, wide-angle and small-angle XRD, TG, Raman spectrum and N_2 adsorption–desorption isotherms were adopted to characterize the spent catalyst and investigate the reason to stability and deactivation of catalyst.

Ni based catalysts deactivated usually caused by the sintering of Ni particles and carbon deposition, especially for the steam reforming of high molecular hydrocarbon compounds [57,59]. Thus, the morphology of Ni particles over spent catalysts was firstly observed by TEM image (Fig. 6) and found that the size of Ni particles was centered at 4–7 nm, which was enlarged little comparing to the fresh ones for all the spent samples. Meanwhile, XRD patterns for spent samples (Fig. 2(a), (c)) also implied the stable particle size. This stability could be result from the strong interaction between Ni and ceria by formation of Ni–O–Ce solid solution, confinement of mesochannel, surrounding of CeO_2 over nickel particles. Meanwhile, Ni particles at filamentous carbon tip were scarcely found for 8Ni2Ce and 8Ni4Ce, whereas, they were observed for 8Ni0Ce, indicating a strong interaction between Ni and ceria to restrain the remove of Ni particles from support [26]. And the agglomerated particles were also scarcely observed outside mesochannels for 8Ni2Ce and 8Ni4Ce. But they were found over spent sample of 8Ni0Ce [11], which could formed by the migration of internal particles to the outside due to the collapse of part of mesochannels caused by the hydrolysis and rearrangement of surface Si–O–Si bonds under high temperature in presence of steam [36]. Bigger Ni particles may lead to the formation of encapsulated carbon, which could cover the active site to deactivate the catalyst [26,59,60]. This collapse and the consequently agglomerated particles could also be improved by the addition of ceria to form surface Si–O–Ce bonds. They have higher steam resistance than Si–O–Si bonds and kept the mesochannel structure remained just like Fig. 7 [26,36]. The remained mesochannel both inhibited the part agglomeration of Ni particles outside the SBA-15 and led to the less

drop in BET area over Ce-promoted catalyst ($488\text{--}328\text{ m}^2\cdot\text{g}^{-1}$ for 8Ni0Ce and $388\text{--}324\text{ m}^2\cdot\text{g}^{-1}$ for 8Ni4Ce in Table 1).

From discussion above, Ni particles scarcely sintered and carbon deposited maybe the another reason to deactivation. TG test (Fig. 8) confirmed that the carbon deposited over 8Ni2Ce was less with mass loss of 4.5%, which benefited from the promotion of Ce, including the formation of large amount Ce–O–Ni solid solution and high dispersible CeO_2 . They provided stronger interaction between Ni and CeO_2 to suppress the Ni particles sintering and the further coke [59], much more oxygen vacancies to facilitate WGS reaction [37] and the mobile oxygen released from the ceria lattice to suppress the carbon production over catalyst mentioned above [25]. Moreover, the formation of Si–O–Ce enhanced the resistance to the steam under harsh condition, which remained the mesochannel to confine Ni particles and also inhibit their sintering and consequent coke. All above favorable factors led to the less carbon deposited.

Different carbon species caused different way to deactivate the catalyst. From previous reports, carbon deposited was classified to two types: 1) Ni–encapsulating coke; 2) well-structured coke [61–63]. Some researchers acknowledged that the first one was usually condensed coke with amorphous form and the second one was graphite-like coke produced by the carbon deposition, nucleation and diffusion over aggregated bigger Ni particles [57,59]. But, some others took the different view that the encapsulating coke was classified to the graphite carbon by Raman spectra and the base carbon nanotube deposited on the support was the disorder one and produced by catalysis of the Ni metal with strong interaction with the support [26,60]. Distinguished carefully, the first view was obtained over the catalysts with bigger Ni particles (bigger than 10 nm) with the inclination of sintering and usually with the bigger Ni particles on the tip of filament carbon. The second one was based on performance of the smaller Ni-particles (several nm) with stronger interaction between the metal and support or confinement effect by the mesopores. In our work, the formation of Ni–O–Ce solid solution and the confinement effect of SBA-15 led to the stronger Ni–Ce interaction and the smaller Ni particles (centered between 3–7 nm). Thus, our catalytic process was similar to the second one. In fact, the bigger Ni particles on the tip of filament carbon was not observed over the Ce-promoted Ni/SBA-15 from the discussion above, which implied our catalytic process may differ from the first view. Fig. 9 shown the Raman spectra of spent catalysts and there were two major peaks centered approximately at 1340 cm^{-1} and 1590 cm^{-1} , which were respectively assigned as D (disorder) and G (graphite) bands of carbon [64]. D band ascribed to the poorly structured carbon deposition, whereas G band represented the well-structured coke or graphitic carbon. The ratio of intensity of D band to G (I_D/I_G) for all spent catalysts was greater than 1, indicating more disordered coke produced than well-structured one. These disordered coke was mainly composed of little carbon nanotubes grew from the base under the catalysis

Table 2

Comparison of the catalytic performances between previously reported catalysts and ours

Catalyst	Space velocity	Conditions			TOS/h	Conv./%	Ref.
		Fuel content/(%) (vol)	S/C	T/°C			
3.9% (mass) Ni/Olivine	9 kg cat·h·m ⁻³ (220 g cat·h·mol ⁻¹) [Ⓛ]	0.7	2.3	800	7	85	[54]
NiCe(3%)/SBA-15	16 kg cat·h·m ⁻³ (391 g cat·h·mol ⁻¹) [Ⓛ]	1.1	3	850	28	90	[29]
10Ni–Ce _{0.8} Pr _{0.2} O ₂	15 ml dodecane·(g cat) ⁻¹ ·h ⁻¹ (15.1 g cat·h·mol ⁻¹)	3.1	2	600	6	92	[55]
10 %Ni/Al ₂ O ₃	3.4 g cat·h·(g phenol) ⁻¹ (320 g cat·h·mol ⁻¹)	1.2	13	750	1.4	58	[56]
Ni/SBA-15	6.7 ml guaiacol·(g cat) ⁻¹ ·h ⁻¹ (16.4 g cat·h·mol ⁻¹)	2.7	5	600	6	90	[57]
Ni–Cl/CeO ₂	15 h ⁻¹ (60 g cat·h·(mol glycerol) ⁻¹)	2.1	15	450	8	100	[49]
Ce5Ni5M	10000 h ⁻¹	1.16	4	800	8.5	90	[58]
8Ni2Ce	10 ml JP10·(g cat) ⁻¹ ·h ⁻¹ (14.6 g cat·h·mol ⁻¹)	4.4	5	680	6.5	99	This work

[Ⓛ] The ratio of catalyst mass to the volumetric flow rate of toluene vapor (25 °C).

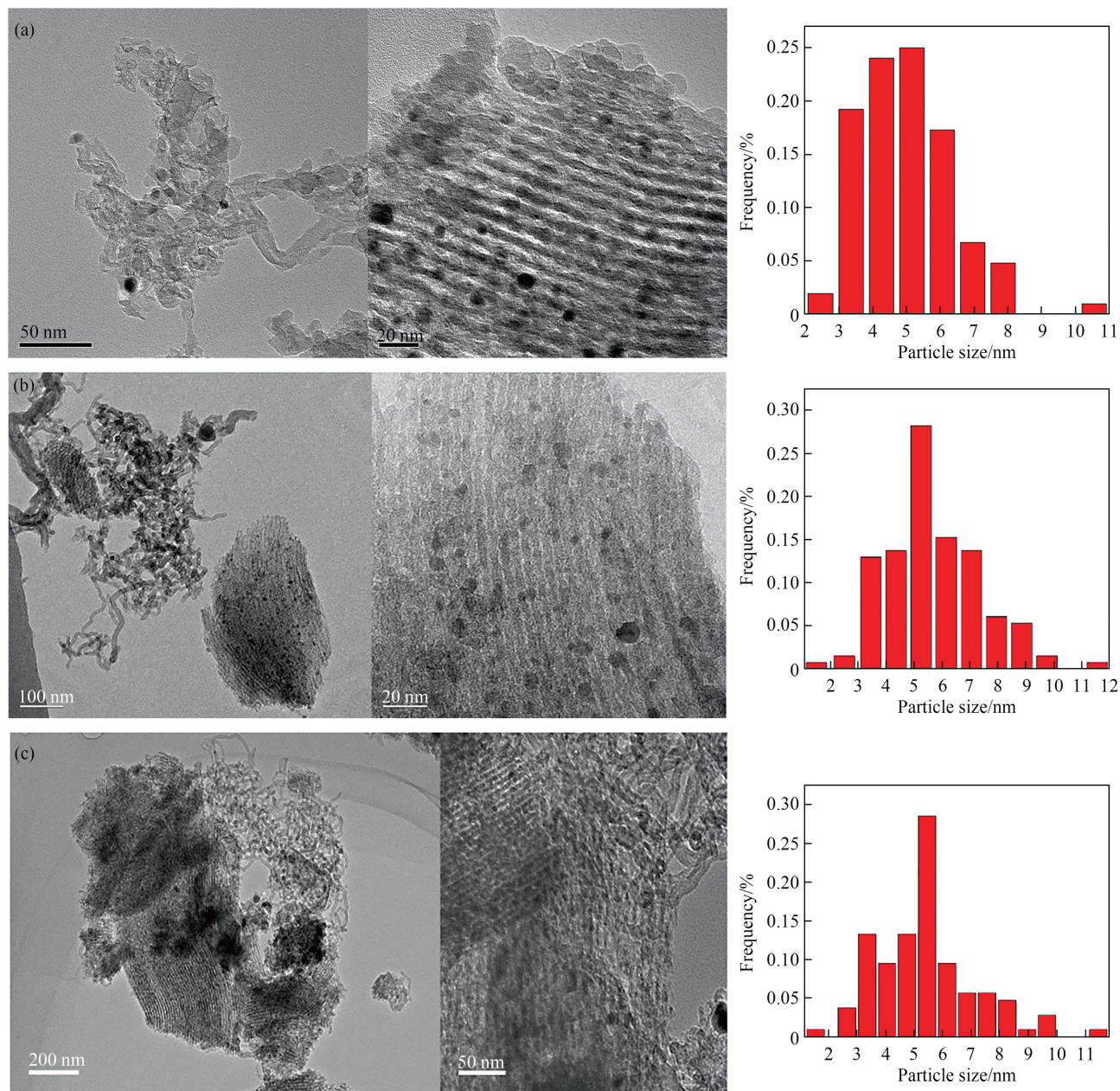


Fig. 6. TEM images and particle distribution of spent catalysts. (a: 8Ni0Ce; b: 8Ni2Ce; c: 8Ni4Ce).

of smaller Ni particles with stronger interaction with support [26]. They could be distinguished with approximate size to the smaller Ni particles (external diameter about 10 nm), implying the base growth on these smaller particles just like shown in Fig. 6. This kind coke had almost no impact on Ni activity, but could block the mesochannels and lead to the drop of BET surface area, especially for the 8Ni2Ce (Table 1) [65]. The G band coke was considered as the carbon deposited on the surface of metal and formed a shell to covered the Ni active sites to deactivate the catalyst [26]. From Fig. 9, it was also found that the ratio of I_D/I_G for 8Ni2Ce reduced, indicating the carbon on metal surface relatively increased. But, owing to the minimum total carbon deposited (4.5% mass loss in Fig. 8), this part of shell coke was still less. In addition, the active sites, especially that at the interface of Ni-CeO₂ over 8Ni2Ce maybe the most due to the morphology of highly dispersed CeO₂ surrounding the smaller nickel particles and the

biggest BET surface area (still the biggest BET surface area of 359 m²·g⁻¹ after 6.5 h stability test shown in Table 1), thereby it had the highest capacity for both kind of coke and kept its good stability.

4. Conclusions

In conclusion, highly dispersed CeO₂ and Ni nanoparticles was obtained over SBA-15 supporting catalysts by the promoting of ceria prepared with the aid of sucrose and successfully applied in the steam reforming of JP10 (C₁₀H₁₆). The investigation in characterization confirmed that addition of appropriate amount ceria with the aid of sucrose not only made the majority of Ni particles confined in the mesochannel of SBA-15 but made the highly dispersed CeO₂ surrounding the smaller nickel particles (average size of 3.8 nm) to form much more interface between them. The inter-

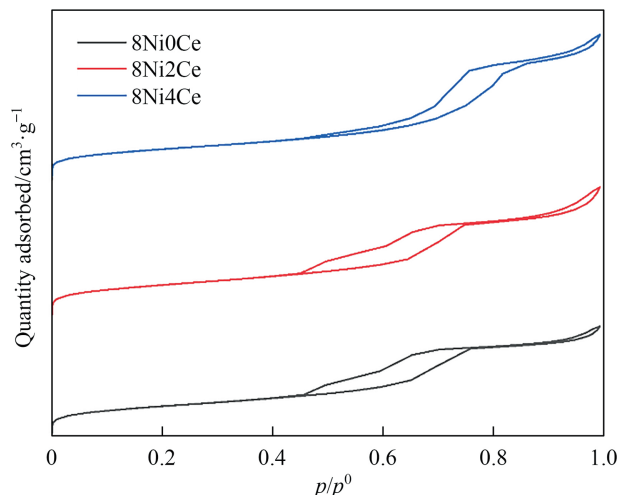


Fig. 7. N₂ adsorption-desorption isotherms of spent catalysts.

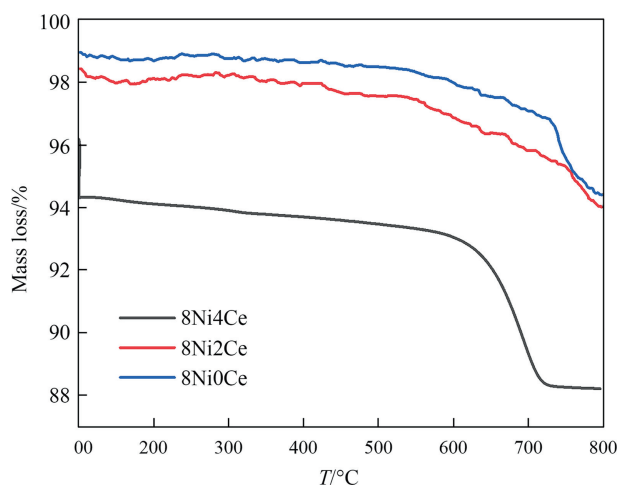


Fig. 8. TG profiles for the spent samples.

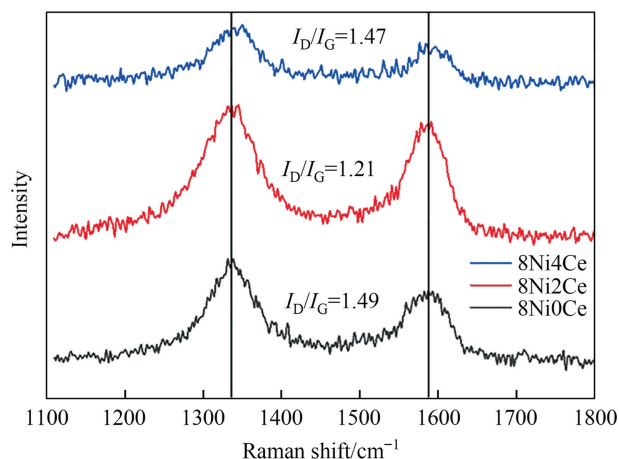


Fig. 9. Raman spectra of spent catalysts.

face enhanced the cooperation effect and accelerated the turnover frequency (TOF) to compensate the reduced surface metal area. TPR result indicated that the much large amount Ni-O-Ce solid solution was formed, which lead to stronger interaction between Ni and ceria and much more oxygen vacancies due to the lattice distortion by the incorporation of Ni into the CeO₂ lattice to inhibit the sintering of Ni particles, facilitate the water-gas-shift reaction and suppress the carbon deposition effectively. The highly dispersed CeO₂ also led to more Ce³⁺ cations and thus the more oxygen vacancies. All these good properties ensured higher stability of 8Ni2Ce over time on stream of 6.5 h with conversion higher than 95% for the steam reforming of JP10 and much less carbon deposition (mass loss less than 4.5% by TG).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

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