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Steam reforming of methane to hydrogen over Ni-based metal monolith catalysts

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ABSTRACT

A series of Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts with different Ni contents (5 wt%, 10 wt% and 15 wt%) as well as 10% Ni/$Ce_xZr_{1-x}O_2$/SBA-15/Al_2O_3/FeCrAl ($x = 0$, 0.5 and 1) metal monolith catalysts with $Ce_xZr_{1-x}O_2$ of 1.7 wt% were prepared and characterized by X-ray diffraction (XRD) and temperature-programmed reduction (TPR). The catalytic activity and stability of these catalysts for steam reforming of methane (SRM) were evaluated in a continuous flow microreactor. The results showed that Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts with Ni loading above 10 wt% had good catalytic activities under atmospheric pressure. For 10% Ni/$Ce_xZr_{1-x}O_2$/SBA-15/Al_2O_3/FeCrAl ($x = 0$, 0.5 and 1) metal monolith catalysts, CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ as promoters can improve the activity and stability of metal monolith catalysts, while the addition of ZrO_2 can lead to the decrease of catalytic activity and stability. The 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst exhibited excellent activity and stability at 800 °C for 110 h on stream. The activity of 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst gradually decreased at 800 °C after 60 h on stream. The reason for this phenomenon is probably the formation of $NiAl_2O_4$ on the surface of catalyst.

1. Introduction

Steam reforming of methane (SRM) is currently the most cost-effective and highly developed method for production of hydrogen, since natural gas used in this process is abundantly available at relatively low cost and high H_2/CO ratios are desired for hydrogen production [1–3]. The commonly used catalysts for SRM are Al_2O_3-supported Ni-based catalysts. However, this kind of catalysts has been found to deactivate easily due to coking and sintering of Ni metal, and moreover, the formation of spinel and inactive $NiAl_2O_4$ phase in the reaction could accelerate the deactivation [1]. It is known that CeO_2 is an effective promoter for Ni-based catalysts in reforming reactions due to its oxygen exchange capacity [4]. The addition of ZrO_2 to CeO_2 improves the oxygen storage capacity of CeO_2, the redox property and the thermal resistance [5–9]. Roh et al. [10] also reported that the interaction between Ni and Ce-ZrO_2 has a beneficial effect on preventing formation of inactive $NiAl_2O_4$.

Some studies suggested that suitable supports could improve the performance of metal catalysts [11–14]. The activity and stability of Ni-based catalysts are dependent on the dispersion of Ni metal, since nickel crystals will sinter quickly above 600 °C [12]. Using the materials with high surface area as catalyst supports may prevent sintering and enhance the stability of catalysts. Mesoporous molecular sieve SBA-15 [15] is an ideal material for loading metal particles due to its high surface area, large pore volume and uniform pore size distribution. Metal particles can be confined in the pore channel of SBA-15, which can partially prevent the sintering process. Also, compared with other mesoporous silicas, such as MCM-41 and MCM-48, SBA-15 has better thermal and hydrothermal stability due to its thick pore wall. Our previous study [13] found that the Ni/SBA-15 and Ni/$Ce_xZr_{1-x}O_2$/SBA-15 ($x = 0$–1) catalysts had good catalytic activities of SRM, and 10 wt% Ni/SBA-15 catalyst exhibited excellent stability at 800 °C for 740 h on stream.

Monolith structured catalysts, especially metal monolith catalysts using FeCrAl alloy foils as catalyst supports, have received much attention in recent years [16,17]. Compared with conventional fixed-bed reactors loaded with catalyst pellets, metal monolith catalytic reactors have several advantages, such as lower pressure drops, a smaller size and lower temperature gradients in the reactors [18–20]. Chattopadhyay and coworkers [1] evaluated the performances of Ni-Rh/Al_2O_3-CeO_2-ZrO_2, Ni-Rh/λ-Al_2O_3 and Ni-Pd/λ-Al_2O_3 catalysts which were tested as powders and supported on metal foil for steam reforming of natural gas, and demonstrated the potential for the use of metal structured support to achieve commercially relevant hydrogen production targets at lower residence times. Zhou et al. [21] investigated the reactivity of plate-type metal-monolithic anodic alumina supported nickel catalysts in the SRM reactions. In our

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previous study [22], by combining the advantages of mesoporous molecular sieve SBA-15 and metal monolith catalysts, a series of Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts were prepared and showed good catalytic activity and stability for methane reforming with CO_2. In this paper, we prepared a series of Ni/SBA-15/Al_2O_3/FeCrAl and 10% Ni/$Ce_xZr_{1-x}O_2$/SBA-15/Al_2O_3/FeCrAl (x = 0, 0.5 and 1) metal monolith catalysts and evaluated their catalytic activity and stability for SRM.

2. Experimental

2.1. Catalyst preparation

SBA-15 was synthesized using the literature method [23]. Typically, a homogenous mixture composed of Pluronic P123 triblock copolymers (EO_{20}–PO_{70}–EO_{20}) and tetraethyl orthosilicate (TEOS) in hydrochloric acid was stirred at 40 °C for 22 h, and further treated at 100 °C for 24 h. The resultant solid was filtered, washed, dried and finally calcined at 550 °C for 6 h.

Ni/SBA-15 catalysts were prepared by impregnating appropriate amounts of a $Ni(NO_3)_2$ solution to SBA-15, then drying at 100 °C and calcining at 550 °C for 6 h in air. The nickel loading was from 5 wt% to 15 wt%. The Ni/$Ce_xZr_{1-x}O_2$/SBA-15 (x = 0, 0.5 and 1) catalysts were prepared by successive impregnation method. First, appropriate amount of solution with required amounts of $Ce(NO_3)_2$ and/or $Zr(NO_3)_2$ was impregnated to SBA-15, then dried at 100 °C and calcined at 550 °C for 6 h. The resulting $Ce_xZr_{1-x}O_2$/SBA-15 (x = 0, 0.5 and 1) samples were further impregnated with a $Ni(NO_3)_2$ solution, then dried at 100 °C and calcined at 500 °C for 5 h. The nickel loading was 10 wt% and the total content of $Ce_xZr_{1-x}O_2$ was 1.7 wt%. Ni/SBA-15 or Ni/$Ce_xZr_{1-x}O_2$/SBA-15 (x = 0, 0.5 and 1) slurry was prepared using our previous method [22,24]. First, the obtained sample powder was mixed with a sol made from SB powder (pseudo-boehmite). Then, the proper amount of nitric acid was added into the mixture. This mixture was vigorously stirred at a rate of 300 rpm for 10 h, and finally the Ni/SBA-15 or Ni/$Ce_xZr_{1-x}O_2$/SBA-15 (x = 0, 0.5 and 1) slurry was obtained.

The monolith supports (Al_2O_3/FeCrAl) were prepared according to our previous method [22,24,25]. The monolith supports were dipped into the slurry prepared above, withdrawn at a constant speed of 3 cm min^{-1}, dried at room temperature in air and thereafter at 120 °C for 3 h, and then calcined at 500 °C for 4 h. Finally, the Ni/SBA-15/Al_2O_3/FeCrAl and 10% Ni/$Ce_xZr_{1-x}O_2$/SBA-15/Al_2O_3/FeCrAl (x = 0, 0.5 and 1) monolith catalysts were obtained, in which the contents of Ni/SBA-15 and Al_2O_3 were about 15–20 wt% and 10 wt%, respectively.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of metal monolith catalysts were obtained on a Rigaku D/Max 2500 VB2+/PC diffractometer using Cu Kα radiation operating at 200 mA and 40 kV. Temperature-programmed reduction (TPR) experiments were performed using Thermo Electron Corporation TPD/R/O 1100 series Catalytic Surfaces Analyzer equipped with a TC detector. Samples were heated under 10 vol% O_2/He with a temperature ramping of 10 °C min^{-1} to 300 °C, then cooled to room temperature in flowing N_2, and finally reduced with 5 vol% H_2/N_2 mixture by heating to 900 °C at 20 °C min^{-1}. Water produced by the reduction of the sample was condensed in a cold trap before reaching the detector. The metal monolithic catalysts were used directly as the specimens for TPR.

2.3. Catalyst test

The catalytic activities of the metal monolith catalysts were carried out in a fixed-bed continuous flow microreactor at 700–850 °C under atmospheric pressure. The tests were performed with cylindrical monolith catalysts, which were made up of several cylinders in different diameter and 60 mm in length. Prior to each catalytic measurement, the catalyst was reduced in H_2 at 750 °C for 3 h. The reactant gas steam ($GHSV = 1.8 \times 10^4\ ml\ g_{cat}^{-1}\ h^{-1}$) consisted of CH_4 and H_2O with a molar ratio of 1:2. The flow rates of the gas components were maintained with a mass-flow controller. Water was fed with a syringe pump into an evaporator installed at the inlet of the reactor. A cold trap at the outlet of the reactor was used to condense any water from the reactants. The products were on-line analyzed by gas chromatography with a TC detector (Beijing East & West Electronics Institute, GC-4000A). The reaction temperature was controlled with a K-type thermocouple placed in the vicinity of the catalyst bed. The stability tests of the samples were carried out in the same reactor at 800 °C under the above test conditions.

3. Results and discussion

3.1. Catalyst activity and stability

The catalytic activities of the metal monolith catalysts are shown in Fig. 1. As observed, for all metal monolith catalysts, the CH_4 conversion increased with the temperature. For Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts, the CH_4 conversion increased when Ni content increased from 5 wt% to 10 wt%. Compared with 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst, the CH_4 conversion remained almost constant for 15% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst, indicating that these two catalysts have better activities of SRM. For 10% Ni/$Ce_xZr_{1-x}O_2$/SBA-15/Al_2O_3/FeCrAl (x = 0, 0.5 and 1) metal monolith catalysts, the addition of CeO_2 or $Ce_{0.5}Zr_{0.5}O_2$ improved the catalytic activity, whereas the addition of ZrO_2 lowered CH_4 conversion. The 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst had the best catalytic activity for SRM.

Fig. 2 shows the stability of 10% Ni/SBA-15/Al_2O_3/FeCrAl (a), 10% Ni/CeO_2/SBA-15/Al_2O_3/FeCrAl (b), 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl (c) and 10% Ni/ZrO_2/SBA-15/Al_2O_3/FeCrAl (d) metal monolith catalysts for SRM. For the 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst, the CH_4 conversion showed no significant decrease over 60 h on stream and gradually decreased after 60 h of reaction. With the increase of reaction time, the CO selectivity slightly decreased and the molar ratio of H_2 to CO slowly increased from about 4.0 to 4.5. For 10% Ni/CeO_2/SBA-15/Al_2O_3/FeCrAl metal

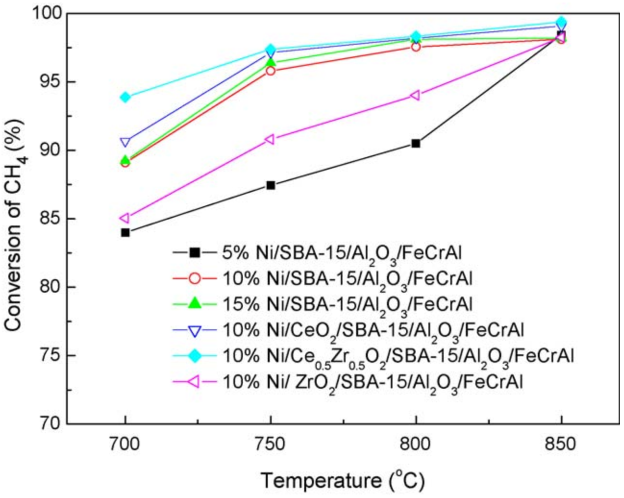

Fig. 1. CH_4 conversion over metal monolith catalysts. *Reaction conditions*: $GHSV = 1.8 \times 10^4\ ml\ g_{cat}^{-1}\ h^{-1}$, $V(H_2O)/V(CH_4) = 2$.

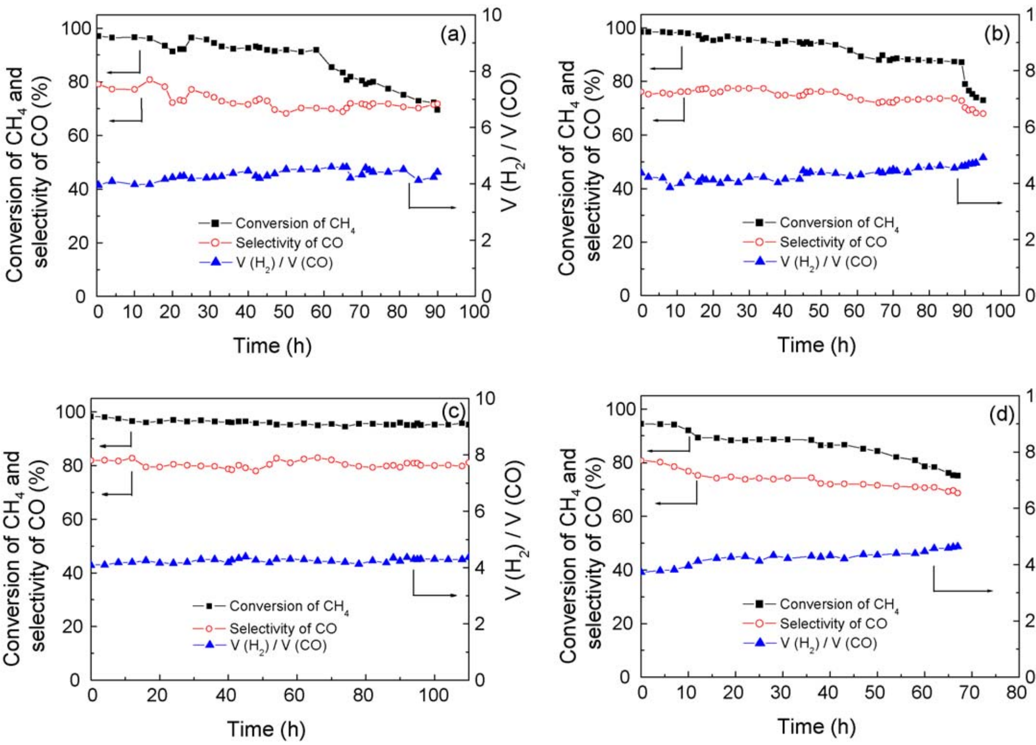

Fig. 2. Stability of metal monolith catalysts for SRM. (a) 10% Ni/SBA-15/Al_2O_3/FeCrAl; (b) 10% Ni/CeO_2/SBA-15/Al_2O_3/FeCrAl; (c) 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl; (d) 10% Ni/ZrO_2/SBA-15/Al_2O_3/FeCrAl. *Reaction conditions*: $T = 800\ ^{\circ}C$, GHSV $= 1.8 \times 10^4$ ml g_{cat}^{-1} h^{-1}, $V(H_2O)/V(CH_4) = 2$.

monolith catalyst, during the 90 h on stream, the CH_4 conversion gradually decreased from 98.6% to 87.2%, the CO selectivity slightly decreased and the molar ratio of H_2 to CO increased from about 4.0 to 4.5. The CH_4 conversion rapidly decreased after 90 h of reaction, and at the same time, the CO selectivity decreased and the molar ratio of H_2 to CO increased from about 4.5 to 4.9. For the 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst, the CH_4 conversion remained almost unchanged at 800 °C for 110 h on stream, and the CH_4 conversion was 95.3% after 110 h reaction. The CO selectivity fluctuated in the range of 78% and 82%, and the molar ratio of H_2 to CO increased from about 4.1 to 4.3. For the 10% Ni/ZrO_2/SBA-15/Al_2O_3/FeCrAl catalyst, with the increase of reaction time, the CH_4 conversion decreased from 94.5% to 75.2%, the CO selectivity decreased from 81% to 69%, and the molar ratio of H_2 to CO increased from 3.7 to 4.6. It is clearly observed that the molar ratio of H_2 to CO increased and CO selectivity decreased with the reaction time for all metal monolith catalysts except 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl. This can be explained by water gas shift reaction ($H_2O + CO \rightarrow CO_2 + H_2$) [26]. The decrease of CH_4 conversion with the reaction time promoted the process of water gas shift reaction, resulting in the increase of the molar ratio of H_2 to CO and the decrease of CO selectivity. The 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst had the best stability for SRM. It demonstrated that the addition of CeO_2 or $Ce_{0.5}Zr_{0.5}O_2$ can improve the stability of metal monolith catalyst. It is well recognized that CeO_2 can reversibly release and restore a large amount of oxygen atoms which can react with surface hydrocarbon species resulting in the decrease of coke formation [4]. So, the addition of CeO_2 can improve the stability of catalyst for SRM. For $Ce_{0.5}Zr_{0.5}O_2$, the addition of Zr to CeO_2 can improve thermal resistance, redox property and oxygen storage capacity of CeO_2 [8]. Also, due to the insertion of Zr into the CeO_2 framework, the O_2-sublattices are distorted resulting in a higher mobility of oxygen [4,10]. These lead to the highest stability of 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst.

3.2. XRD

The XRD patterns of Ni/SBA-15/Al_2O_3/FeCrAl (a–c) and 10% Ni/$Ce_xZr_{1-x}O_2$/SBA-15/Al_2O_3/FeCrAl (x = 0, 0.5 and 1) (d–f) as well as the used 10% Ni/SBA-15/Al_2O_3/FeCrAl (g) metal monolith catalysts are shown in Fig. 3. It can be seen that there are characteristic peaks attributed to α-Al_2O_3 in the patterns of 5% Ni/SBA-15/Al_2O_3/FeCrAl and 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts. The α-Al_2O_3 is formed on the FeCrAl surface as a result of oxidation of aluminum by heat treatment [22]. The formation of the α-Al_2O_3 layer can improve the combination ability between the Al_2O_3 wash

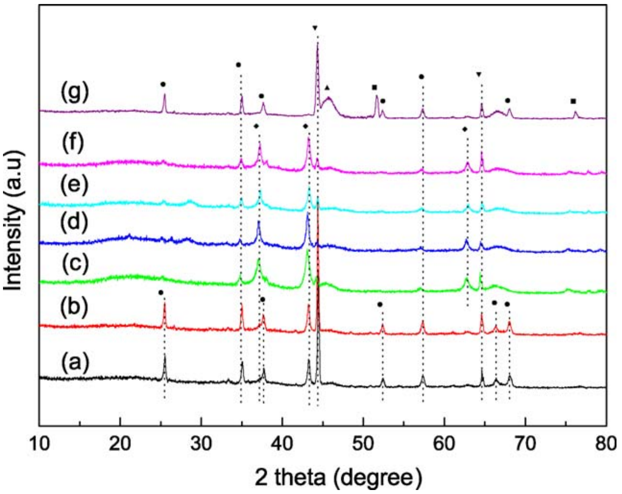

Fig. 3. XRD patterns of metal monolith catalysts. (a) 5% Ni/SBA-15/Al_2O_3/FeCrAl; (b) 10% Ni/SBA-15/Al_2O_3/FeCrAl; (c) 15% Ni/SBA-15/Al_2O_3/FeCrAl; (d) 10% Ni/CeO_2/SBA-15/Al_2O_3/FeCrAl; (e) 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl; (f) 10% Ni/ZrO_2/SBA-15/Al_2O_3/FeCrAl; (g) 10% Ni/SBA-15/Al_2O_3/FeCrAl (after reaction). *Phases*: α-Al_2O_3 (●); FeCr (▼); NiO (◆); Ni (■); $NiAl_2O_4$ (▲).

coat layer and the FeCrAl support. With the increase of Ni content as well as the addition of promoters, the intensity of these peaks markedly decreased. In addition, the peaks of FeCr ($2\theta = 44.3^\circ$ and 64.6°) have the similar trend. The characteristic peaks for NiO ($2\theta = 37.1^\circ$, 43.1° and 62.5°) were observed in all fresh metal monolith catalysts. For the Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts, the intensity of peaks due to NiO increased with the increase of Ni contents, suggesting that NiO species agglomerated on the surface of catalysts at Ni content of 5 wt% and with the increase of Ni contents the particle size of NiO increased. There were no obvious peaks attributed to CeO_2, $Ce_{0.5}Zr_{0.5}O_2$ or ZrO_2 in the patterns since the addition amount of $Ce_xZr_{1-x}O_2$ ($x = 0$, 0.5 and 1) was relatively low.

Compared with XRD patterns of the 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst before and after reaction (b and g), it was found that the intensity of characteristic peaks attributed to α-Al_2O_3 and FeCr decreased. There were no peaks ascribed to NiO in the pattern of the catalyst after reaction. The characteristic peaks of Ni appeared after reaction because of the reduction of NiO at high temperature. A broad peak of $NiAl_2O_4$ appeared indicating that the fine particles of $NiAl_2O_4$ were well dispersed on the surface of catalyst. The formation of $NiAl_2O_4$ may be due to the part of Ni species originally located on the external surface of SBA-15. They may react with Al_2O_3 to form $NiAl_2O_4$ at high temperature in the presence of steam. In our previous study [13], 10% Ni/SBA-15 powder catalyst exhibited excellent activity and stability for SRM at 800 °C over 740 h on stream. Evidently, the stability of 10% Ni/SBA-15 powder catalyst was much higher than the four metal monolith catalysts prepared in this paper. Compared with the XRD patterns of used 10% Ni/SBA-15 powder catalyst [13] and used 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst, it was found that NiO existed in the used 10% Ni/SBA-15 catalyst as the part of Ni metal was reoxidized to NiO under steam in the reactions. But the existence of NiO did not decrease the catalytic activity of catalyst [27]. For the used 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith metal catalyst, the lack of NiO peaks may be due to the formation of $NiAl_2O_4$ under steam at high temperature. It is believed that the catalyst may undergo sever deactivation due to the formation of spinel and inactive $NiAl_2O_4$ phase [1]. So, the decrease of activity for the 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst in stability test may be ascribed to the formation of $NiAl_2O_4$ phase on the surface of the catalyst during the reaction. Roh et al. [10] prepared Ni/Ce-ZrO_2/θ-Al_2O_3 catalysts and found that the interaction between Ni and Ce-ZrO_2 has a beneficial effect on preventing formation of inactive $NiAl_2O_4$. Therefore, for 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst, the formation of $NiAl_2O_4$ can be restrained by the addition of $Ce_{0.5}Zr_{0.5}O_2$, resulting in the highest catalytic activity and stability for SRM.

3.3. Redox properties

The reducibility of the metal monolith catalysts was characterized by H_2 TPR method. TPR patterns of metal monolith catalysts are shown in Fig. 4. It can be seen that there were no reduction peaks in the pattern of SBA-15/Al_2O_3/FeCrAl sample. All Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts with different Ni contents had three reduction peaks, one major peak at 465 °C, a shoulder peak at 555 °C and a broad peak at around 735 °C. The two peaks at 465 °C and 555 °C could be assigned to large particles and small particles of NiO, respectively, and the peaks at around 735 °C could be attributed to a strong interaction between Ni^{2+} and SBA-15 support [28,29]. The area of these reduction peaks increased with the Ni contents. It indicated that the amount of large NiO particles increased with the increase of Ni loading, which was in agreement with the XRD results.

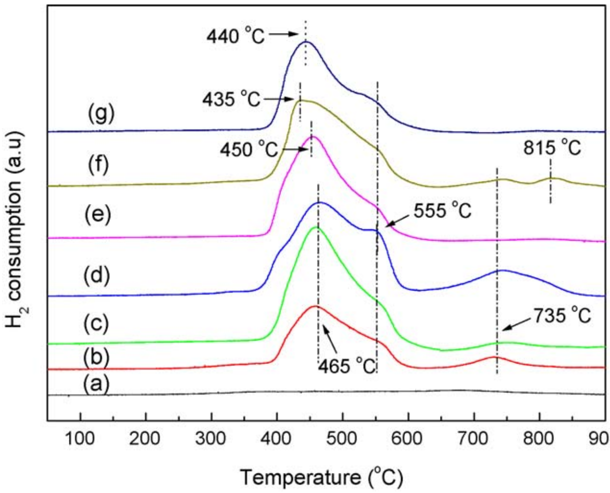

Fig. 4. TPR patterns of metal monolith catalysts. (a) SBA-15/Al_2O_3/FeCrAl; (b) 5% Ni/SBA-15/Al_2O_3/FeCrAl; (c) 10% Ni/SBA-15/Al_2O_3/FeCrAl; (d) 15% Ni/SBA-15/Al_2O_3/FeCrAl; (e) 10% Ni/CeO_2/SBA-15/Al_2O_3/FeCrAl; (f) 10% Ni/$Zr_{0.5}Ce_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl; (g) 10% Ni/ZrO_2/SBA-15/Al_2O_3/FeCrAl.

For 10% Ni/ZrO_2/SBA-15/Al_2O_3/FeCrAl and 10% Ni/CeO_2/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts, the reduction peak at 465 °C shifted to 450 °C and 440 °C, respectively, and the peak at 735 °C vanished for two catalysts. For 10% Ni/$Zr_{0.5}Ce_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalysts, the peak at 465 °C shifted to 435 °C, and the peak at 815 °C probably attributed to $Zr_{0.5}Ce_{0.5}O_2$ appeared. It suggested that the addition of $Ce_xZr_{1-x}O_2$ ($x = 0$, 0.5 and 1) could improve the redox properties of catalysts, and then influence the activity and stability of metal monolith catalysts.

4. Conclusion

The obtained Ni/SBA-15/Al_2O_3/FeCrAl with Ni contents of 10 wt% and 15 wt% as well as 10% Ni/$Ce_xZr_{1-x}O_2$/SBA-15/Al_2O_3/FeCrAl ($x = 0.5$ and 1) metal monolith catalysts have good catalytic performance for SRM, in which the CH_4 conversion was higher than 95% at 800 °C. In the stability tests, the molar ratio of H_2 to CO for all metal monolith catalysts increased with the reaction time. The CH_4 conversion of 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst began to decrease after 60 h of reaction. The addition of CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ could improve the activity and stability of catalyst. The activity of 10% Ni/CeO_2/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst markedly decreased after 90 h of reaction. The 10% Ni/$Ce_{0.5}Zr_{0.5}O_2$/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst had the best activity and stability, and the CH_4 conversion remained almost unchanged at 800 °C for 110 h on stream. The decrease of activity for the 10% Ni/SBA-15/Al_2O_3/FeCrAl metal monolith catalyst may be due to the formation of $NiAl_2O_4$ phase on the surface of the catalyst during the reaction.

Acknowledgements

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