Naphthalene Steam Reforming over Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ (x = 0, 0.10, 0.20 and 0.25) Mixed Oxide Catalysts

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Abstract

In this study, the catalytic activity of Ni supported on $Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ (x = 0, 0.10, 0.20 and 0.25) catalysts prepared by urea hydrolysis and incipient wetness impregnation is investigated via steam reforming reaction of naphthalene as a model biomass tar compound. Experiments were carried out in a fixed bed reactor at 700 °C and atmospheric pressure using a molar ratio of steam/carbon (S/C) equal to 2. The catalysts also were characterized by various techniques, such as surface area, temperature-programmed reduction (TPR), X-ray diffraction (XRD) and temperature-programmed oxidation (TPO). In comparison with Ni/α-Al_2O_3, the catalytic performance data showed that nickel supported on mixed oxide catalysts exhibit high activities and stabilities for the steam reforming of naphthalene and high resistance toward carbon deposition. Moreover, the promotion effect of manganese doping markedly suppressed carbon deposited on the Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ catalysts. It can be suggested that the incorporation of manganese ions into ceria lattice improved the oxygen storage capacity as well as the oxygen mobility on the surface of mixed oxides, facilitating gasification of surface carbon.

Introduction

Tar formation is a major problem in biomass gasification process [1]. Condensation or formation of tar aerosols cause downstream problems in the process equipments. Moreover, this tar is also carcinogenic and possibly mutagenic substance [2]. Recently, the $Ce_{0.75}Zr_{0.25}O_2$ mixed oxide solid solutions shows a high catalytic activity, particularly for the oxidation of hydrocarbons and the removal of post-combustion pollutants [3-5]. One of the important routes to improve the catalytic performances of ceria-based mixed oxides is by doping and modification with other elements. Particular attention is being paid to manganese oxides which present good oxidation ability due to several oxidation states of manganese species [6-9]. Hence, in the present work, we aimed to study the effect of manganese doping on the structural and redox properties of mixed oxides $Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ (x = 0, 0.10, 0.20 and 0.25), and the catalytic activity of naphthalene (tar model) steam reforming over nickel supported on these mixed oxide.

Results and discussion

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From XRD spectra (Fig. 1), Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ catalysts exhibited major peaks at about 29, 33, 47, and 58° (2θ) indicating the cubic fluorite structure of CeO_2. Small peaks characteristic of NiO were observed at about 37 °, 43 ° and 62° (2θ). No peaks of zirconia and manganese oxides are observed in the XRD patterns indicating that all zirconium cations and manganese cations dissolved in the ceria lattice. These results are similar to what reported elsewhere [9, 10]. Since the ionic radius of Zr^{4+} (8.4 nm), Mn^{4+} (5.6 nm) and Mn^{3+}(6.2 nm) are smaller than that of Ce^{4+}(9.7 nm), a dissolution within CeO_2 lattice is then possible at low dopant concentrations of both Zr and Mn. However, it was evident that at high dopant of Mn (Mn/(Mn+Ce) > 0.75), the presence of Mn_2O_3 or Mn_3O_4 was observed [7, 9, 11, 12].

The TPR results of Ni supported on $Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ mixed oxide and α-Al_2O_3 catalysts are shown in Fig. 2. The reduction profiles of Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ are characterized by two peaks. The low-temperature peak at temperature of 230–350 °C which is the reduction of free NiO particles [13, 14] and another peak at higher temperature of 350–550 °C is associated with the reduction of NiO to Ni^0. It was noticed that the second reduction temperature peak of Ni/$Ce_{0.75}Mn_{0.25}O_2$ catalyst is slightly lower than that of Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ catalyst indicating a less interaction between NiO and $Ce_{0.75}Mn_{0.25}O_2$. For Ni/α-Al_2O_3 catalysts, only one broad peak was observed at 510 °C, which is attributed to agglomerated NiO.

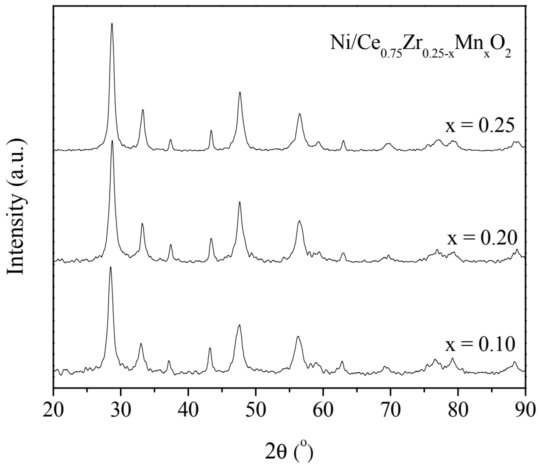

Fig. 1. X-ray diffraction patterns for Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ mixed oxide catalysts.

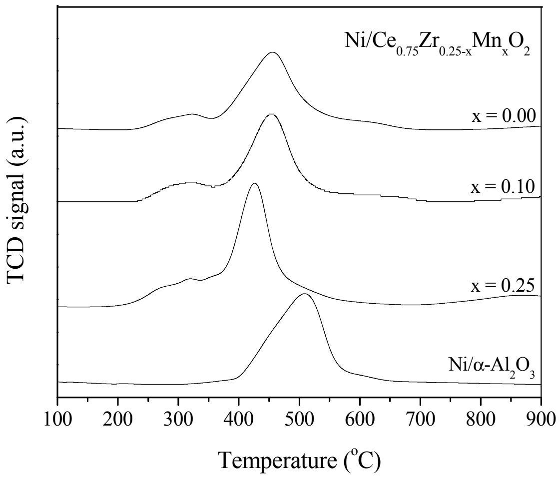

Fig. 2. H_2-TPR profiles of the Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ mixed oxide and Ni/α-Al_2O_3 catalysts.

The BET surface areas of Ni supported on $Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ mixed oxide catalysts are in the range of 62–77 m^2 g^{-1} and the average pore diameters of these catalysts are 6.3–7.9 nm. It should be noted that BET surface area of the samples slightly decreases with increasing Mn content, except Ni/$Ce_{0.75}Mn_{0.25}O_2$. This is related to the formation of the large MnO_x particles whose surface area is much smaller [12, 15].

The catalytic activities and stabilities of Ni supported on $Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ mixed oxide catalysts for steam reforming of naphthalene were studied and compared with those of Ni/α-Al_2O_3 catalyst. It was found that naphthalene conversions by Ni/$Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ (x = 0, 0.10, 0.20, 0.25) mixed oxide catalysts are completed for at least 6 hrs time on streams, while the rapid deactivation was observed for Ni/α-Al_2O_3 catalyst after 2 hrs. This indicated that nickel supported on mixed oxide catalysts are active and more stable for steam reforming of naphthalene. This might be due to the reducibility and oxidation ability of mixed oxide supports; promoting the oxidation of carbon precursors.

Table 1 summarizes the products selectivities, hydrogen yield and H_2/CO molar ratio during naphthalene steam reforming. It was found that the steam reforming products are mainly CO, CO_2 and H_2 for $Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ (x = 0.10, 0.20 and 0.25) and the H_2/CO ratio is about 2.40 ± 0.12. On the other hand, the main products of naphthalene steam reforming over $Ni/Ce_{0.75}Zr_{0.25}O_2$ are CO, CO_2, H_2 and a trace of CH_4 with the H_2/CO ratio is about 1.84 ± 0.05, indicating carbon formation. In addition, an increase in CO_2 selectivities by introducing of Mn to CeO_2-ZrO_2 mixed oxide was also observed suggesting that the water gas shift (WGS) reaction is possibly taken place over $Ni/Ce_{0.75}Zr_{0.25\ x}Mn_xO_2$ (x = 0.10, 0.20 and 0.25).

Table 1. Naphthalene steam reforming over $Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ mixed oxide catalysts reaction temperature = 700 °C; time on stream = 6 hrs; S/C = 2.0)

Catalyst	S_CO (%)	S_CO_2 (%)	S_CH_4 (%)	Y_H_2 (%)	H_2/CO
$Ni/Ce_{0.75}Zr_{0.25}O_2$	97.60±0.88	2.25±0.10	0.15±0.05	72.89±1.75	1.84±0.05
$Ni/Ce_{0.75}Zr_{0.15}Mn_{0.10}O_2$	79.97±1.42	20.02±0.57	0	75.36±1.77	2.28±0.09
$Ni/Ce_{0.75}Zr_{0.10}Mn_{0.15}O_2$	74.27±1.53	25.73±0.93	0	76.33±1.17	2.37±0.12
$Ni/Ce_{0.75}Mn_{0.25}O_2$	75.54±1.21	24.46±0.92	0	76.27±1.13	2.56±0.07

The carbon formation over the spent catalysts was investigated. The TPO spectra suggested two types of carbon of the same nature for Ni/α-Al_2O_3 and $Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ catalysts. The first one oxidized at lower temperature ~325 °C which can be attributed to carbidic carbon and the second one oxidized at ~680 °C corresponding to filamentous carbon [16, 17]. It was found that the amounts of carbon formed on Ni/α-Al_2O_3 and $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts are about 63.4 and 26.7 mg g_{cat}^{-1}, respectively. While $Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ (x = 0.10, 0.20, 0.25) catalysts yielded much lower amounts of carbon formed (1.1 ± 0.3 mg g_{cat}^{-1}) than Ni/α-Al_2O_3 and $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts. It can be pointed out that the total amounts of carbon decreased when manganese is added into the ceria-zirconia system.

Conclusions

In conclusion, $Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ catalysts were found to be active for naphthalene steam reforming. It was found that the catalysts achieved the 100% conversion for at least 6 hrs during the course of the experiments with no sign of deactivation, unlike α-Al_2O_3, which showed the deactivation after 2 hrs times on stream. Carbon formation was found to decrease with an increase in Mn content as well as the absence of filamentous carbon. It is believed that an improvement in redox properties with the presence of Mn suppresses carbon formation.

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References

1. D. Sutton, B. Kelleher, J.R.H. Ross, Fuel Process. Technol. 73 (2001) 155.
2. Z. Abu El-Rub, E.A. Bramer, G. Brem, Ind. Eng. Chem. Res. 43 (2004) 6911.
3. M. Thammachart, V. Meeyoo, T. Rirksomboon, S. Osuwan, Catal. Today 68 (2001) 53.
4. S. Pengpanich, V. Meeyoo, T. Rirksomboon, K. Bunyakiat, Appl. Catal. A: Gen. 234 (2002) 221.
5. S. Pengpanich, V. Meeyoo, T. Rirksomboon, J. Schwank, Appl. Catal. A: Gen. 302 (2006) 133.
6. S. Imamura, M. Shono, N. Okamoto, A. Hamada, S. Ishida, Appl. Catal. A: Gen. 142 (1996) 279.
7. X. Wu, Q. Liang, D. Weng, J. Rare Earths 24 (2006) 549.
8. X. Wang, Q. Kang, D. Li, Catal. Comm. 9 (2008) 2158.
9. M. Machida, M. Uto, D. Kurogi, T. Kijima, Chem. Mater. 12 (2000) 3158.
10. G. Qi, R.T. Yang, R. Chang, Appl. Catal. B: Environ. 51 (2004) 93.
11. G. Qi, R.T. Yang, J. Phys. Chem. B 108 (2004) 15738.
12. G. Blanco, M.A. Cauqui. J.J. Delgado, A. Galtayries, J.A. Pérez-Omil, J.M. Rodríguez Izquierdo, Surf. Interf. Anal. 36 (2004) 752.
13. H. Roh, K. Jun, W. Dong, J. Chang, S. Park, Y. Joe, J. Mol. Catal. A 181 (2002) 137.
14. S. Pengpanich, V. Meeyoo, T. Rirksomboon, K. Bunyakiat, Catal. Today 93-95 (2004) 95.
15. X. Wu, Q. Liang, D. Weng, J. Fan, R. Ran, Catal. Today 126 (2007) 430.
16. J.C. Vargas, S. Lib, A.-C. Roger, A. Kiennemann, Catal. Today 107-108 (2005) 417.
17. D. Swierczynski, S. Libs, C. Courson, A. Kiennemann, Appl. Catal. B: Environ. 74 (2007) 211.