doi:10.1246/cl.2010.692

Zirconium-substituted Hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ for Carbon Dioxide Reforming of Methane

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A study on zirconium-modified hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ ($x = 0$, 0.02, 0.04, 0.06, 0.08, and 0.10) for CO_2 reforming of CH_4 was carried out. The modifier zirconium improved the catalytic activity, especially the conversions of CH_4 and CO_2 reached 93.4% and 97.7% over $La_{0.8}Zr_{0.04}NiAl_{11}O_{19-\delta}$. Both the XPS and TPR data indicated the presence of Ni^{3+} and Ni^{2+}. It was found that the Ni^{3+}/Ni^{2+} ratio depended upon the amount of the Zr, which facilitated the formation of highly dispersed active Ni^0 species.

In recent years, the reforming of methane using carbon dioxide has received considerable attention from both industrial and environmental aspects. This reaction converts the two major greenhouse gases (CH_4 and CO_2) into synthesis gas with a lower H_2/CO ratio.[1,2] Noble metals (Ru, Rh, Pd, Pt, Ir, etc) have been successfully employed as highly active catalysts for CO_2 reforming of CH_4.[3–7] However, the high cost and limited availability of noble metals have stimulated research for cheaper metals such as ferrous metals (Fe, Co, and Ni) as worthwhile alternatives.[8–12] Supported Ni-based catalysts are known as typical catalysts for this reaction. However, carbon deposition and sintering of the metallic nickel often occur, causing deactivation and blockage of the catalysts. Therefore, it is important to improve the state of supported Ni catalysts in order to overcome these disadvantages.

Some researchers have reported a series of Ni-based hexaaluminates as a new generation of catalysts for the title reaction, in which the active component Ni ions are inlaid into the hexaaluminate lattices to substitute a portion of the Al ions.[13–15] Interaction between Ni particles and the hexaaluminates can stabilize small Ni crystallites and decrease carbon deposition. Every hexaaluminate compound crystallizes in either β-Al_2O_3 or magnetoplumbite structure. Both of these structures consist of alternative stacking of a spinel block and a mirror plane, and the structure of hexaaluminates depends on the charge and radius of the large modification cations in the mirror plane layer.[16,17] But there are no reports on the influence of the valence state of nickel on the catalytic properties of the hexaaluminates for the title reaction.

In this study, the Zr-modified hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ were successfully prepared and characterized by XRD, XPS, TPR, and DTA-TG in order to investigate the influence of the amount of Zr ions and the influence of the Ni^{3+}/Ni^{2+} ratio on their structures and the catalytic properties for this reaction. Possible explanations for the obtained results are given.

The hexaaluminate catalysts $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ ($x = 0$, 0.02, 0.04, 0.06, 0.08, and 0.10) used in this research were prepared as follows: $La(NO_3)_3{\cdot}6H_2O$, $Zr(NO_3)_4{\cdot}5H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in distilled water with a molar ratio of 0.8:x:1:11. Then the aqueous solutions were slowly added to a poly(ethylene glycol)–isopropyl alcohol solution under magnetic stirring. The mixture was evaporated to dryness at 80 °C and then stored in an oven to remove poly(ethylene glycol) and decompose the nitrates. After being ground into fine powder, the samples were calcined at 400 °C for 2 h, followed by calcination at 1250 °C for 5 h.

XRD patterns were recorded on a Shimadzu XD-3A diffractometer equipped with Ni-filtered Cu Kα radiation. The amount of carbon deposited on the catalysts was determined by oxidation conducted using a thermogravimetric analyzer (TGA; Perkin-Elmer TGA7). The binding energy of ions on the surface of the catalysts was measured by X-ray photoelectron spectroscopy (XPS; V.G. ESCA Mark II) using Al Kα radiation. The reducibility of the hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ was characterized by temperature-programmed reduction (TPR). 0.1 g of catalyst was embedded in a quartz tube with an inner diameter of 4 mm in each run. Before reduction, the sample was purged and then the reactor was heated from room temperature to 1200 °C at a heating rate of 7 °C min^{-1} in a 5% H_2/Ar gas flow at a rate of 30 mL min^{-1}. Nickel dispersion on the reduced catalysts was measured by oxygen chemisorption and the titration of absorbed oxygen with hydrogen (HOT) at 500 °C and pulse of 0.2 mL (5% H_2/Ar).[18]

The reaction was carried out at atmospheric pressure at 800 °C in a tubular fixed-bed quartz reactor with an inner diameter of 8 mm. A thermocouple was placed in the center of the catalyst bed to monitor the reaction temperature. The reactant mixture consisted of CH_4 and CO_2 at a molar ratio of 1:1 and flow rate of 30 mL min^{-1}. 0.3 g of catalyst was embedded in each run. Prior to conducting the catalytic reaction, the catalyst was reduced in situ at 900 °C in a flow of 10% H_2/Ar gas for 40 min.

The stability of the hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ at 800 °C was investigated. The catalytic results are illustrated in Figures 1a and 1b. Both the catalytic activity and long-term stability show the following sequence: $x = 0 < x = 0.10 < x = 0.02 < x = 0.08 < x = 0.06 < x = 0.04$. It is shown that the conversion and stability of CH_4 and CO_2 tend to increase with increasing x up to $x = 0.04$, then decrease with increasing x up to $x = 0.10$. For different x values ($x = 0$, 0.02, 0.04, 0.06, 0.08, and 0.10), the amount of carbon deposition is 12.7, 6.33, 2.48, 3.79, 4.28, and 8.62 wt % (for 17 h), respectively. Therefore, the $La_{0.8}Zr_{0.04}NiAl_{11}O_{19-\delta}$ catalyst shows the best catalytic activity and the lowest amount of carbon deposition. The conversions of CH_4 and CO_2 over it reached 93.4% and 97.7%, respectively. And the catalytic performance is obviously better than some other Ni-based catalysts.[11] So, it is concluded that Zr is an available modifier to these hexaaluminates and that the $La_{0.8}Zr_{0.04}NiAl_{11}O_{19-\delta}$ is the best one in this series of catalysts for CO_2 reforming of CH_4.

The XRD patterns of the $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ before reduction are given in Figure 2. It is noted that the samples

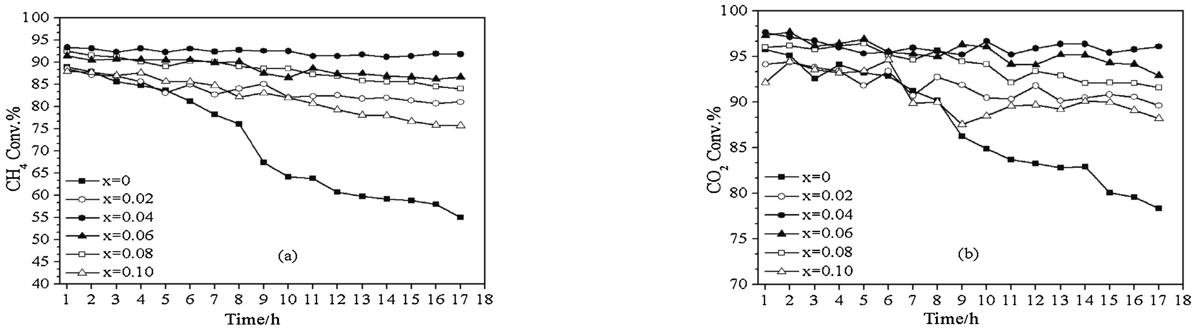

Figure 1. Catalytic activity and stability of the hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ at 800 °C (a) CH_4 conversion, (b) CO_2 conversion. $CH_4:CO_2 = 1:1$, GHSV = 9000 h^{-1}.

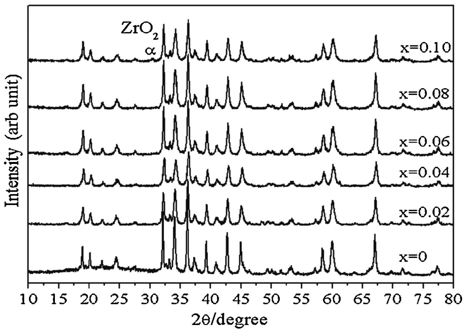

Figure 2. XRD patterns of $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ before reduction.

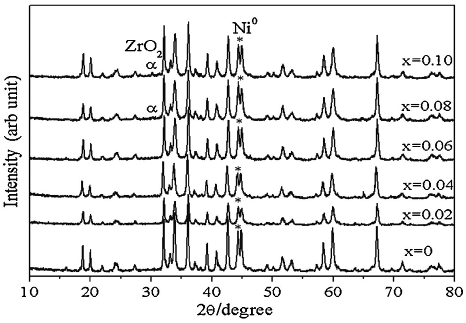

Figure 3. XRD patterns of $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ after TPR experiment.

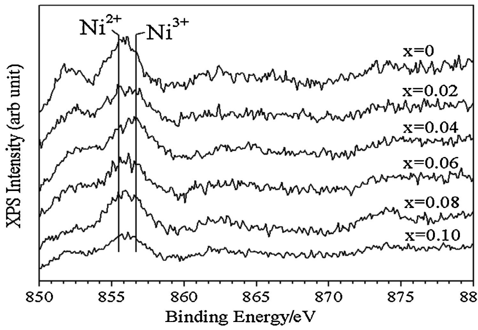

Figure 4. XPS spectra of Ni ions on the surface of hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ before reduction.

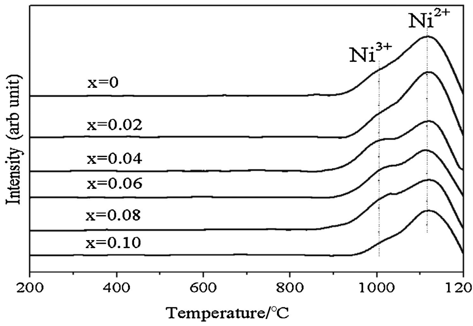

Figure 5. TPR profiles of hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$.

exhibit the same crystalline structure, meaning that all of them are hexaaluminate structures (PDF-36-1316) except $La_{0.8}Zr_{0.10}NiAl_{11}O_{19-\delta}$ which contains a peak at 30°, and this peak is attributed to the ZrO_2 (PDF-49-1746).

Figure 3 shows the XRD patterns of the hexaaluminates $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ after TPR experiment. A peak of metallic $Ni^0(111)$ at 44.5° can be clearly seen in the patterns of the samples. Besides, there is no difference in the structure of catalyst between before and after TPR, indicating that a large fraction of metallic Ni^0 exsit on the hexaaluminate phase to form individual metallic phase, which is the active component for the reaction. However, the ZrO_2 peak still exists over the $La_{0.8}Zr_{0.10}NiAl_{11}O_{19-\delta}$, and it begins to emerge over the $La_{0.8}Zr_{0.08}NiAl_{11}O_{19-\delta}$ after TPR experiment. It is deduced that all the modifier Zr ions are inlayed into the hexaaluminate lattices and reach the saturation point when $x = 0.04$. When $x > 0.04$, a part of Zr ions cannot be embedded into the hexaaluminate lattices, so they assemble on the surface of the catalysts in the form of ZrO_2 and cover the active sites. When $x > 0.06$, the amount of the ZrO_2 is high enough to be tested by XRD after TPR.

As shown in Figure 4, the XPS spectra of all the samples are fitted to two components at 855.5 and 856.7 eV. The Ni $2p_{3/2}$ peak, which appears at around 855.5 eV is characteristic of Ni^{2+}/Ni^{3+} ions in an oxygen environment.[19,20] As this peak comes only from Ni^{2+} ions, it can be concluded that the surface of all the samples contains a certain of Ni^{2+} proportion together with Ni^{3+} ions. While the peak at 856.7 eV is contributed to Ni^{3+}.[21]

TPR and XPS are complimentary techniques when used to identify the oxidation states of a reducible metal oxide.[22] The TPR profiles of the $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ catalysts are presented in Figure 5. For the samples, two H_2-consumption peaks (1005 and

Table 1. Ni^{3+}/Ni^{2+} ratio and the Ni dispersion for reduced $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ catalysts

Catalysts (x)	Ni^{3+}/Ni^{2+}	Dispersion/%
0	0.53	8.3
0.02	0.89	10.4
0.04	2.90	26.5
0.06	1.61	14.3
0.08	0.98	14.0
0.10	0.72	10.2

1118 °C) are observed. The peak at lower temperature (1005 °C) is due to reduction of Ni^{3+} to Ni^{2+},[22] and the peak at the higher temperature (1118 °C) is associated, in some report,[23,24] to reduction of Ni^{2+} into metallic Ni^0. This reveals that the valence state of nickel is +3 and +2, which supports the XPS result.

The spectral Ni^{3+}/Ni^{2+} area ratios obtained from the main lines at 855.5 and 856.7 eV vary according to the x value. The Ni^{3+}/Ni^{2+} ratios and the Ni dispersion of the reduced $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ catalysts are compiled in Table 1. It is clear that both the Ni^{3+}/Ni^{2+} ratios and the Ni dispersion tend to increase with increasing x up to $x = 0.04$, then decrease with increasing x up to $x = 0.10$. This is consistent with the catalytic activity trend of the $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ catalyst for CO_2 reforming of CH_4. Groppi[25] suggested that the hexaaluminates consists of alternative stacking of a spinel block and a mirror plane. It is indicated that the Ni ions are shared between octahedral and tetrahedral sites of the spinel blocks and that the Ni in the octahedral sites can more easily be reduced than that in the tetrahedral sites.[26,27] At the same time Marco et al.[28] pointed out that the Ni^{3+} ions in spinel-related structure occupy octahedral sites. It is concluded that the Ni^{3+} of the octahedral sites can be reduced to the more active Ni^0. Therefore, the Ni^{3+}/Ni^{2+} ratio determines the Ni^0 dispersion of the $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ catalysts. And Ni^0 is the site of catalytic activity for the topic reaction.

Carbon dioxide reforming of methane is studied over hexaaluminate $La_{0.8}Zr_xNiAl_{11}O_{19-\delta}$ ($x = 0$, 0.02, 0.04, 0.06, 0.08, and 0.10) catalysts. The partial substitution of La by Zr leads to a modification of the catalytic performance. The $La_{0.8}Zr_{0.04}NiAl_{11}O_{19-\delta}$ shows the best catalytic stability, and the lowest amount of carbon deposition. A close correlation is observed between substitution degree (x) and the Ni^{3+}/Ni^{2+} ratios, which determines the Ni^0 dispersion. In fact, the Ni^{3+} ions in the octahedral sites can easily be reduced to active Ni^0 from the crystal structure of hexaaluminates. That is, the more Ni^{3+} ions, the more active Ni^0. Therefore, the zirconium is an effective modifier in the hexaaluminates for this topic reaction.

The authors gratefully acknowledge the support of this work from NNSF China (No. 20673047).

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