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$La_{1-x}K_xFe_{0.7}Ni_{0.3}O_3$ catalyst for ethanol steam reforming—The effect of K-doping

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ABSTRACT

Coking is the critical problem for catalysts for steam reforming of ethanol (SRE). Several techniques have been reported for improving the ability to prevent coking of catalysts, such as adding alkaline to balance the acidic sites on the support, using support which can generate oxygen vacancies and using bimetallic catalysts. In this work, we try to improve the ability to prevent coking of this kind of catalyst by doping additives to modify the active component, which has not been attracted attention for SRE catalysts yet. $La_{1-x}K_xFe_{0.7}Ni_{0.3}O_3$ ($x = 0$, 0.05, 0.1) with perovskite structure was prepared by citric acid complexation method, and after reduction K-doped $Ni/LaFeO_3$ catalysts were obtained. The catalytic performance including the ability to prevent coking and sintering over the catalysts were investigated. The catalysts were characterized by using X-ray diffraction, transmission electron microscopy, thermal analysis techniques and X-ray photoelectron spectroscopy analysis. The results indicate that the K-doped catalysts are very active, highly selective to hydrogen, as well very stable for SRE reaction. The doping of potassium can also restrain the sintering of nickel. The doping of K improved the ability to prevent coking of the catalyst markedly, which is attributed to the electron donation effect of potassium to nickel and this donation effect can promote the ability for breaking C—C bond on the metal nickel sites.

1. Introduction

The environmental problems associated with the intensive use of fossil fuels are increasingly demanding the development of sustainable energy systems. Besides solar source, tidal energy and wind energy, hydrogen is another potential renewable energy and it only burns into water which is harmonious to the environment. Furthermore, hydrogen fueled cells have high energy efficiency. Among various fuel sources for hydrogen production, ethanol has attracted much attention, owing to its easy handling, wide distribution around the world, safe transportation and storage, low toxicity and high volumetric energy density [1,2]. Especially ethanol can be fermented from bio-materials which from photosynthesis, and the bio-ethanol contains water, thus reforming of ethanol with water to produce hydrogen can avoid partially the separation of water from the ethanol.

The reported catalysts for steam reforming of ethanol (SRE) include oxide catalysts, base metal catalysts mainly Ni-based catalysts, Co-based catalysts and Cu-based catalysts and noble metal catalysts. The catalytic performance of the oxide catalysts are relatively poor, since they are easy to be deactivated due to carbon deposition. Co and Ni-based catalysts show better performance than Cu-based catalysts because of their higher activity for breaking C—C and C—H bond. But the sintering of metal particles and carbon deposition are still the major problems [3,4]. Besides the high price, noble metal catalysts are also inclined to be deactivated by carbon deposition or sintering of the active metal nanoparticles, although they show good catalytic activity and selectivity.

There are two kinds of carbon deposition which are coke and graphitized carbon such as nanotubes (CNTs). The former is generated from polymerization of organics (like ethylene), the latter is formed from Boudouard reaction ($2CO = CO_2 + C$) or the decomposition of methane ($CH_4 = C + 2H_2$). It is known that the CNTs cause lighter deactivation, for that the formed CNTs generally stretch away from the active nano metal particles, while the coke usually wraps up the active site of metal thus leads to serious deactivation [5,6].

To overcome the problem of carbon deposition, several technical routes have been reported. Since the dehydration reaction of

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ethanol tends to occur on the acidic supports which will result in coking, one of the routes is to use alkaline additives to modify the acidic support. For example, Ca modified Ni/ZrO_2 exhibits much higher stability than that of Ni/ZrO_2 [7]. Another solution is to use supports which can generate oxygen vacancies, such as ceria, to eliminate the carbon deposited. For example, Co/CeO_2 shows good ability to prevent the formation of carbon deposition, for that oxygen species can be activated on the oxygen vacancies of ceria and react with the deposited carbon [8]. The third promising solution reported recently is bimetal catalyst. For instance, coke deposition was much less on bimetallic catalyst of Cu-Ni than on the monometal of Cu or Ni, the cooperation of Cu and Ni can help to remove the coke [9]. By the way, the sintering of active component also leads to the increasing of carbon deposition. Coking is a polymerization reaction which needs more coordination number or bigger active group of the active metal atoms. So, the high dispersion of the active metal nano particles is very important for improving the ability to prevent coking [10,11].

Perovskite-type oxide (PTO) can be written as ABO_3, in which the ions in A and B sites can be partially replaced by other metal ions. $Ln_{1-x}A_xBO_{3+d}$ (Ln = La, Pr, Nd; A = Ca, Sr, Ba) with perovskite structure has attracted considerable interest, which can be used as catalysts or as materials for cathodes and oxygen ions conduction in solid oxide fuel cells [12]. There are a few reports on using PTO as catalyst for SRE. Noronha [13] used $LaNiO_3$ as precursor for SRE, and they found that catalyst deactivation occurred due to the deposition of carbon on the surface of the catalyst. Urasaki [14] evaluated 50 wt%Co supported on a PTO of $La_{1-x}Sr_xBO_3$ (B = Al, Cr, Mn, Fe, x = 0–0.2) at 823 K and found that Co/$LaAlO_3$ showed the higher catalytic activity and stability than that of Co supported on $LaCrO_3$, $LaFeO_3$ and $LaMnO_3$. Chen [15] investigated $La_xCa_{1-x}Fe_{0.7}Ni_{0.3}O_3$ for SRE and showed very good catalytic performance.

$LaFeO_3$ with perovskite structure possesses high stability in the reaction atmosphere of SRE. Metal nickel particles reduced from $LaFe_{1-x}Ni_xO_3$ should be highly dispersed. Secondly, nickel ion can act as the ion in the perovskite lattice, thus metal nickel nano particles on it should tend to interact with the support, which is beneficial for the ability to prevent sintering. Thirdly, $LaFeO_3$ can generate oxygen vacancies which can help to eliminate the carbon deposited. Owing to these characters of $LaFeO_3$, previously, we found Ni/$LaFeO_3$ reduced from $LaFe_{1-x}Ni_xO_3$ showed very good catalytic performance for SRE [16]. Yet, carbon deposition on Ni/$LaFeO_3$ was also observed for SRE, which would result in deactivation of the catalyst.

By modifying the active component, a catalytic reaction can be adjusted and the carbon deposition is a catalytic reaction. Doping additives is an effective way to modify the active component. However, to improve the ability to prevent coking for SRE catalysts, modifying the active component by doping additives has not been attracted attention.

Based on the considerations stated above, $La_{1-x}K_xFe_{0.7}Ni_{0.3}O_3$ with PTO structure was prepared and used as catalyst for SRE reaction. After reduction, $La_{1-x}K_xFe_{0.7}Ni_{0.3}O_3$ was changed to K_2O-Ni/$LaFeO_3$, where potassium was acted as the additive. The new catalyst exhibited excellent catalytic performance for SRE. The K-doping effect and the catalytic performance including carbon deposition on this catalyst were studied in this work.

2. Experimental

2.1. Catalysts preparation

$La_{1-x}K_xFe_{0.7}Ni_{0.3}O_3$ (x = 0, 0.05 and 0.1) were prepared by one step citrate complexation method similar to the literature [17]. Nitrates of nickel, iron, lanthanum and potassium with a proper molar ratio were dissolved in deionized water. Then citrate acid (with 20% excess of the total moles of the cations) and polyglycol (with 20% mole amount of the citrate acid) were added into the solution. The obtained solution was stirred for 5 h and then was concentrated by vaporization at 85 °C until the formation of a spongy solid. The solid was dried further at 120 °C for 24 h. The resultant material was calcined at 350 and 650 °C for 3 h and 5 h, respectively at a rising speed of 2 °C min^{-1}. The catalysts were signed as K-0, K-0.05 and K-0.1 for $LaFe_{0.7}Ni_{0.3}O_3$, $La_{0.95}K_{0.05}Fe_{0.7}Ni_{0.3}O_3$ and $La_{0.9}K_{0.1}Fe_{0.7}Ni_{0.3}O_3$, respectively.

The mole ratio of Fe/Ni = 7/3 is the optimized composition, and the reason for $x \leq 0.1$ in $La_{1-x}K_xFe_{0.7}Ni_{0.3}O_3$ is that more potassium can hardly be embedded into the PTO lattice.

2.2. Catalyst characterization

X-ray diffraction (XRD) experiments were performed on a Philips X'pert Pro automated powder diffractometer with graphite-monochromated Co-Kα (λ = 0.178901 nm) radiation in the Bragg-Brentano parafocusing geometry. The spectra were collected between 20 and 90° (2θ range), with a scanning speed of 5° min^{-1}.

Transmission electron microscopy (TEM) measurements were performed on a FEI (PHILIPS) Tecnai-G2F20 instrument equipped with Field Electronic Emitter. Samples were deposited on copper grids with a holey-carbon-film support after ultrasonic dispersion of the catalyst in water-free ethanol.

Thermal analysis including thermogravimetry (TG) and differential thermal analysis (DTA) were performed on a DTG-50/50H from Shimadzu Corporation from room temperature to 900 °C with a heating rate of 10 °C min^{-1} and in flowing air. 5.0–10.0 mg of catalyst was used. The total weight loss is determined by Eq. (1):

$$\frac{(W_1 - W_2)}{W_1} \times 100\% \qquad (1)$$

where W_1 is the weight of the reacted catalyst before TG test, and W_2 is the weight of the reacted catalyst after the TG test.

X-ray photoelectron spectroscopy analysis (XPS) was conducted on a PHI-1600 photoelectron spectrometer. The X-ray source was monochromatic Al Kα (1253.6 eV). The analysis was obtained at room temperature after the sample was outgassed in a vacuum oven. The residual pressure in the analysis chamber was about 2×10^{-10} Torr during the analysis. Charging of the sample was minimized by referencing the spectra to the C 1s line at binding energy (BE) of 284.6 eV [18] and the data were collected at a step length of 0.1 eV.

2.3. Catalytic performance tests

Catalytic performance tests were carried out on a fixed-bed quartz reactor at atmospheric pressure. 75 mg of catalyst with 40–60 mesh grain size diluted with the same size of SiO_2 particles were loaded into the reactor and the catalyst to SiO_2 ratio was 1:8 in weight. Prior to each reaction, the system was outgassed with N_2 for 10 min, and then reduced in 5 vol.% H_2-Ar at 650 °C for $LaFe_{0.7}Ni_{0.3}O_3$ and at 700 °C for $La_{0.95}K_{0.05}Fe_{0.7}Ni_{0.3}O_3$ and $La_{0.9}K_{0.1}Fe_{0.7}Ni_{0.3}O_3$ for 60 min with a flow rate of 50 ml min^{-1}. Then the temperature was lowered to 350 °C. A premixed water-ethanol solution with water to ethanol molar ratio of 3:1 was fed into the reactor through a pump which was vaporized at 140 °C. The total flow rate of the liquid of water-ethanol was 1.2 ml h^{-1}. The introduced reaction gas mixture was composed of 76 vol% N_2 and 24 vol% EtOHt + H_2O. The resultant weight hourly space velocity (WHSV) of the total gas mixture was 60,000 ml $g_{cat}{}^{-1}$ h^{-1}, if not specifically noted. For stability tests at WHSV of 240,000 ml $g_{cat}{}^{-1}$ h^{-1}, 25 mg of catalyst was used, and the