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Hydrogen production by catalytic steam reforming of hydrocarbon fuels over Ni/Ce–Al₂O₃ bifunctional catalysts: Effects of SrO addition

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ABSTRACT

Steam reforming reactions of hydrocarbon fuels were investigated in a fixed bed tubular reactor over nickel supported on Ce–Al₂O₃ (NCA) bifunctional catalysts promoted with different content of SrO (NCA/x%SrO), in order to obtain high H₂ yield with minimum deactivation by carbon deposition. Physicochemical characteristics of the catalysts were detected by using automatic adsorption instrument, X-ray diffraction, Temperature programmed reduction/desorption, Raman spectroscopy, and Scanning/transmission electron microscope-energy dispersive spectrometer. It was found that the catalytic activities over series NCA/x%SrO catalysts were obviously improved compared with CA catalyst at the range of 550 °C–800 °C, meanwhile the amount of carbon deposition was significantly decreased with the addition of SrO promoter. In addition, the promotion effect became more stable when the introduction of SrO, which indicated that SrO played an essential role in the catalytic action. The regeneration experiments over the same NCA/5%SrO catalyst were performed three times, and the reforming activities were quite close to the results of fresh ones. The valuable information indicated in this work is that based on the specific properties of NCA/x%SrO, three kinds of metal particles can be introduced into Al₂O₃ by different way, which should be an effective approach to maintain both catalytic activities, thermal stability and anti-carbon ability.

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Introduction

World energy production is mainly dominated by fossil fuels, and petroleum as the most versatile fossil fuel possesses the advantages of high energy density and convenient

transportation [1–4]. However, the limited reserves and the severe environmental pollution attributed to the overuse of fossil fuels have caused the extensive concern from both academia and industry to substitute the fossil fuels with renewable clean fuels [5,6]. In this case, H₂ emerges as a clean raw material and energy carrier, can be used directly in

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transport and stationary power generation or by means of a hydrogenated intermediate that can be transformed in situ into H_2 by reforming for use in hydrogen fuel cells [7–9].

Currently the use of hydrogen gas as an energy carrier is faced with several technical problems [10–12]. It is difficult and expensive to store hydrogen at high-energy density levels on account of low density. Reforming high-energy density fuels, such as methanol, ethanol, gasoline, jet fuel, or diesel; can overcome the problems by the production of hydrogen on-site or on-board [13,14]. The reforming of hydrocarbon fuels for hydrogen can be carried out by several different approaches including steam reforming, partial oxidation reforming, and autothermal reforming [15–17]. Catalytic steam reforming is an efficient process that yields high H_2 concentrations. A number of studies have been reported on the investigation of low-carbon hydrocarbons (<C4) steam reforming over Ni-alumina catalysts on account of the cost efficiency, good availability and high activity [18–24]. However, despite displaying remarkable catalytic properties in low-carbon hydrocarbons steam reforming, there are two major challenges of using Ni-alumina catalysts in high-carbon hydrocarbons (for example, gasoline, jet fuel, or diesel). The first one is that the alumina support lacks an adequate thermal stability which provokes the sintering of supported metals; the second one is that the alumina support has the drawback of inducing the deactivation of catalysts caused by carbon deposition [25,26].

To overcome these limits, various techniques have been introduced to improve the thermal stability of alumina, minimize the negative effect of its acid character [27–29]. Wang et al. [27] summarized the H_2 yield and total conversion of gasoline (mixtures of hydrocarbons) over a series of nickel-palladium-cerium supported upon alumina catalysts, and demonstrated that the molar compositions for H_2 , CO, CO_2 and CH_4 were about ranging between 65 and 68, 14–18, 12–17 and 2–7%, respectively. Fauteux-Lefebvre et al. [28] investigated the diesel steam reforming over a nickel-alumina spinel catalyst for more than 15 h at steam-to-carbon ratios lower than 2. Constant diesel conversion and high hydrogen concentrations were obtained. Korabelnikov et al. [30,31] studied steam reforming of heptane and decane over nickel-alumina and modified nickel-alumina catalysts, respectively. The results showed that catalytic steam reforming reaction can obtain higher H_2 yield. However, how to avoid carbon deposition as well as enhance the stability of catalyst is still a great challenge that needs to be solved urgently.

In our previous studies [32,33], we have introduced the rare earth Ce or La promoters into alumina to make Ce– Al_2O_3 or La– Al_2O_3 composite oxide as the support to improve the thermal stability and specific surface areas of Ni-alumina catalysts. Based on these data, the catalytic activity and stability over Ni/Ce– Al_2O_3 catalysts were evidently heightened, moreover, the Ni/Ce– Al_2O_3 catalyst exhibited higher H_2 yield and showed 100% fuel conversion at 750 °C. But, the effect of carbon-resistant is not obvious and the amount of carbon deposition should be further decreased. One approach to develop carbon-resistant catalysts is to add a second catalytic species. In literatures [34–36], alkaline earth metals are usually added into Ni-alumina catalysts as promoters to optimize the carbon-resistant effect of the catalysts for fuel reforming. However, the simultaneous addition of these additives can

help to avoid carbon deposition as well as enhance their stability, but at the expense of a reduction of their activity due to the blocking of the more reactive Ni sites [37,38]. Under the circumstances, how to introduce alkaline earth and ceria species synchronously into Ni-alumina to develop bifunctional catalysts for remitting the above two problems (activity, stability and anti-carbon ability) is an extremely critical task.

In the present study, the activity, stability and anti-carbon ability of the series NCA/x%SrO catalysts were evaluated for the steam reforming of hydrocarbons with different structures. By introducing Sr and Ce species by different way, the structure and surface morphology of these catalysts could be tuned, along with their activity, stability and anti-carbon ability. This work provided some fundamental suggestions for the catalytic reforming mechanism of hydrocarbons, and catalysts optimization for the catalytic steam reforming of hydrocarbons.

Experimental section

Ce– Al_2O_3 composite oxides and Ni/Ce– Al_2O_3 /x%SrO catalysts preparation

Ce– Al_2O_3 composite oxide (10 wt.% Ce) support was prepared by coprecipitation method, and the preparation process was similar to our early works [39,40], denoting as CA. Ni(NO_3) $_2$ ·6 H_2O as the Ni precursor has been supported on the CA composite oxide by incipient-wetness impregnation method with 6 wt.% of Ni loading (6% of Ni loading performed better catalytic reforming activity), denoting as NCA. The as-prepared NCA catalyst was divided into five lots, numbered 2#, 3#, 4#, 5#, 6#; and then the 3#, 4#, 5#, 6# samples were subsequently made into columnar particles with Sr(NO_3) $_2$ solution with different concentration, the SrO content is 2.5%, 5.0%, 7.5%, 10.0% in these catalysts respectively, and whereafter the columnar catalysts were dried, roasted for 4 h at 800 °C. The NCA/x%SrO catalysts were denoted by Cat3 (NCA/2.5%SrO), Cat4 (NCA/5.0%SrO), Cat5 (NCA/7.5%SrO) and Cat6 (NCA/10%SrO), and the other one (2#) was denoted by Cat2 (NCA). The catalyst made by Ce– Al_2O_3 (CA) composite oxides was denoted by Cat1. The catalysts dosage were all 3.0 ± 0.05 g.

Catalysts characterization

Surface area (S_{BET}) and pore volume (V_p) of the fresh catalysts were obtained by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2010 instrument, and pore size distribution was determined by the Barret-Joyner-Hallenda (BJH) method. Crystalline phases of the catalysts were identified by XRD using a Rigaku Mineflex instrument operated with monochromatic $CuK\alpha$ radiation. Temperature programmed reduction (TPR- H_2) profiles of fresh catalysts under H_2 -blanket were carried out using a TP-5076 TPR instrument. Typically, a sample of ca. 100 mg is placed in a U shaped quartz tube and heated from 40 to 925 °C at 8 °C/min in a gas mixture containing H_2 and Ar. The consumption of H_2 during the reduction is monitored by a thermal conductivity detector (TCD). Prior to a TPR test, the sample is outgassed under inert gas flow at 450 °C for 1 h. Furthermore, the surface acidity of all the catalysts were tested by using TP-5076 TPD

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