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Full Length Article

Bi-functional composite oxides M(Na, K)-Ni/La-Al_2O_3 catalysts for steam reforming of *n*-decane

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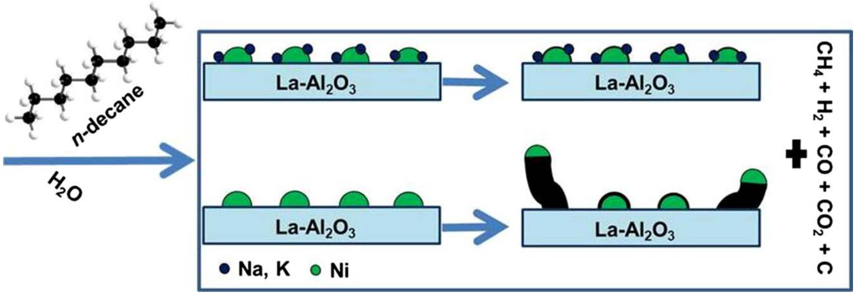
GRAPHICAL ABSTRACT



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ABSTRACT

n-Decane steam reforming towards hydrogen has been researched in a fixed-bed reactor containing spherical particle of Ni supported La-Al_2O_3 catalyst. The as-prepared Ni/La-Al_2O_3 catalyst was modified by the alkaline promoters M(Na, K) in order to inhibit carbon deposition. The physicochemical properties of these catalysts were characterized by Nitrogen physisorption, X-ray diffraction, X-ray photoelectron spectroscopy, Infrared spectroscopy, Temperature programmed reduction/desorption, Scanning electron microscopy-energy dispersive X-ray spectroscopy. The results showed that the addition of alkaline modifiers had a slightly impact on the surface area, crystallinity and morphology of Ni/La-Al_2O_3 catalyst, but improved the activity and stability, as well as reduced the rate of carbon deposition formation and thereby increased the working life of the catalysts. Meaningfully, K was shown an excellent catalytic performance in inhibiting carbon deposition, and the presence of K-modifier prevented metal sintering and controlled Ni particle size and dispersion, strengthened the metal-support interaction, and decreased the acidity of catalysts.

1. Introduction

Nowdays, a growing consensus of the world is the global warming phenomenon that mainly results from the overuse of fossil fuels. The development of green energy sources as an alternative has became an important task to alleviate the energy crisis [1–4]. Hydrogen is a great candidate for traditional fossil fuels since zero pollution [5–8]. Unfortunately, hydrogen gas with low density is difficult and expensive to store [9–11]. In this context, many researchers focus on the catalytic hydrogen production via steam reforming of high-energy density fuels, such as ethanol, gasoline, jet fuel, or diesel [12–15].

n-Decane is a kind of rich hydrogen carrier with high-energy

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density, is suitable for generating hydrogen by steam reforming due to its high hydrogen yield [16–18]. However, *n*-decane steam reforming is a complex process compared with low-carbon hydrocarbons (such as alcohols, ethers) reforming reactions. Catalysts deactivation mainly caused by carbon deposition is more easily occurred during steam reforming reaction, especially at higher temperatures [19–21]. Therefore, the catalysts used in *n*-decane steam reforming reaction are put forward higher requirements.

According to the literatures [22–31], various catalysts have been used in hydrocarbons steam reforming. Noble metal-based catalysts, such as Pt, Ru and Rh, which can effectively break C—C bonds have been paid more attention in the past few years [22–24]. The nickel-based catalysts also have the high C—C bonds breaking activity for steam reforming reactions, and the relatively lower cost compared with noble metals. Therefore, nickel-based catalysts seem to be an excellent alternative. More and more researcher reported about hydrocarbons steam reforming over Ni-alumina catalysts [25–31]. However, catalysts deactivation caused by the thermal sintering and carbon deposition over Ni-based catalysts during *n*-decane steam reforming reaction is still a appreciable problem [19,20]. As a consequence, the task of developing a excellent catalyst with remarkable catalytic activity, stability, anti-coking and anti-sintering properties remains a major challenge. Previous study [41] shows that Ni/La-Al_2O_3 (NLA) catalyst owns excellent catalytic activity (100% *n*-decane conversion), good thermal stability and larger surface area ($> 140.0\ m^2/g$). But the anti-coking ability effect of NLA catalyst is not obvious.

Many studies have been conducted to inhibit carbon deposition formation during hydrocarbons steam reforming process. According to the literatures [32–36], the presence of basic additives or promoters (e.g. Li, Na, K, Mg) on supported nickel catalysts can enhance the resistivity toward carbon deposition. Haddenet al. [37] proved that the K promoted the adsorption ability of water under steam reforming reaction. The main effect of alkali dopants is suppression of carbon deposition with improved stability favoring water adsorption or neutralizing acid sites of the catalyst. However, the addition of these additives have a negative effect on catalytic activity due to the blocking of the more reactive Ni sites [38,39]. One of the reasons origins from the difficulties in determination of the location, dispersion and chemical state of the promotors on the catalyst surface, a part of the promoter is in an intimate contact with nickel, whereas the other part is distributed over the alumina support [40]. Under the circumstances, how to introduce alkali promoters to develop excellent catalysts, which can reduce the rate of carbon deposition formation under the condition of having a slightly impact on the activity and stability, is an extremely critical task.

The work investigated the effect of adding alkali promoters to Ni supported on La-Al_2O_3 catalysts. The catalysts are prepared by using co-precipitation technique in combination with two step impregnation method. The purpose of this work is screening the suitable catalysts for steam reforming process in order to maximize *n*-decane conversion and H_2 yield, and minimize the formation of byproducts and carbon deposition.

2. Experimental

2.1. Preparation of La-Al_2O_3 support and M-Ni/La-Al_2O_3 catalysts

La-Al_2O_3 composite oxides support (3.0 wt% La) was prepared by co-precipitation method, and the details were described in our previous works [41–43].

Monometallic Ni reference catalyst (Ni/La-Al_2O_3, 6 wt% Ni) was prepared by incipient-wetness impregnation method. The sample was impregnated for 2 h with aqueous solutions of $Ni(NO_3)_2{\cdot}6H_2O$, subsequently dried at 120 °C for 2 h, and finally calcined in air at 800 °C for 4 h.

M-Ni bimetallic catalysts (M-Ni/La-Al_2O_3, M=Na or K, 5.0 wt%) were prepared by wet impregnation of the calcined Ni/La-Al_2O_3 catalyst with aqueous solutions of the corresponding metal precursors ($NaNO_3$, KNO_3), and then the catalysts were dried at 120 °C, calcined at 800 °C in air for 4 h. Finally, the Ni/La-Al_2O_3 and M-Ni/La-Al_2O_3 catalysts were made into columnar particles, and marked as NLA, Na-NLA, and K-NLA, respectively. All the catalysts were pretreated at 450 °C in a gas mixture of H_2 (5%) and Ar for 60 min.

2.2. 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 CuKα radiation. X-ray photoelectron spectroscopy was performed using an XSAM-800 spectrometer (KRATOS Co., UK) with MgKα excitation under a high voltage (13 kV) and current (20 mA), calibrated internally by the carbon C_{1s} binding energy at 284.8 eV. IR spectroscopy was also applied to study the chemical structure of catalysts. The infrared spectra of the samples were obtained at wavelengths ranging from 400 to 4000 cm^{-1}.

The surface acidity of all the catalysts were tested by using TP-5076 TPD experimental device. The sample (ca.100 mg) was heated to 400 °C in a flow of N_2, kept for 45 min, and then cooled to room temperature. The gas flow was then switched to NH_3 (2%) in N_2 (flowrate 20 mL/min). The surface acidity was carried out from room temperature to 700 °C. Furthermore, 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.

In addition, field emission scanning electron microscopy (FEI, Quanta 600FEG, USA) was used to characterize the micro-morphological of carbon deposition, and an Oxford-IE-250 energy dispersive spectrometer (EDS) was coupled with FESEM to analyze the element composition of selected points or areas.

2.3. Catalytic activity evaluation

To evaluate catalytic activity of the catalysts, steam reforming of *n*-decane was chosen as the probe reaction. Steam reforming experimental apparatus consists of a liquid reactants feeding unit, a tubular fixed-bed quart reactor (12 mm i.d.) loaded with 3.0 g catalyst, heating systems, the condenser, and a analysis unit [41,42], and the schematic diagram was shown in Fig. 1. A mixture vapors of *n*-decane and water was fed in the reactor after preheating and uniform mixing. The mole ratios of steam/*n*-decane was kept at 3, 7 respectively by adjusting the flow rates of reactants, and the total flow were 5.0 mL/min. The temperature of the preheaters were both kept at 350 °C, and the temperature of reactor was set at 600, 650, 700 °C, 750 °C or 800 °C respectively for evaluating the catalysts activity. The time on stream at each temperature point was 10 min.

Gas phase products were analyzed by two on-line gas chromatographs: (1) GC-2010, (SHIMADZU Co., Ltd.), equipped with a HP-Al/S separation capillary column and flame ionization detectors for analyzing CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, C4; (2) SP-2100A, (Beijing Beifen-Ruili analytical instruments Co., Ltd.), was used to separate H_2, CO and CO_2 with a TDX-01 packed column and a thermal conductivity detector. The amount of solid deposition covering the catalysts during an experiment was measured by temperature programmed oxidation (TPO). The used catalysts were heated to 700 °C (8 °C/min) in a flow of air. The evolution of CO and CO_2 was monitored by the on-line CO_2 gas analyzer

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