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Hydrogen production via methanol steam reforming over Ni-based catalysts: Influences of Lanthanum (La) addition and supports

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ABSTRACT

The effect of the addition of Lanthanum (La), the different loading of nickel oxide and various supports on the catalytic performance of Ni-based catalysts was investigated for methanol steam reforming to produce hydrogen. TEM, N₂ adsorption-desorption, XRD, and TPR were used to characterize the catalysts. Separated NiO particles, La–Ni or La–Ni–Al mixed oxides as well as NiAl₂O₄ spinel were detected. The results showed that the addition of lanthanum into Ni-based catalyst decreased the steamed temperature and the selectivity of CO. This change was closely associated with separated NiO particles with the smaller size and higher dispersion as well as the different interaction between NiO particles and support upon the modification of lanthanum. It was also found that the moderate loading of nickel facilitates the catalytic performance for methanol steam reforming due to the generation of separated NiO species with moderate particle size. Moreover, the different interaction strength between nickel species and support could give rise to the difference in the catalytic performance of active Ni species, depending on the support. The Al₂O₃ supported catalyst exhibits better conversion of CH₃OH, higher hydrogen selectivity and lower CO selectivity than those of SiO₂ and MgO supported catalysts.

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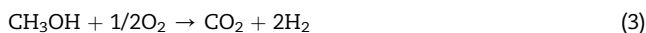
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Introduction

Owing to the increasing depletion of fossil fuels (coal, petroleum and natural gas) together with seriously environmental problems, the utilization of renewable and clean energies has received great attention [1,2]. Hydrogen (H_2) has been considered to be one of the most promising energy alternatives due to the advantages of carbon free, relatively high energy density as well as little impact on surroundings [3,4], which has been extensively employed to generate electricity via the energy system of proton exchange membrane fuel cell (PEMFC) for vehicles and portable applications. However, the storage, transportation and distribution of hydrogen are still a challenge [5,6]. In various liquid fuels and biomass, methanol (CH_3OH) is one of the most interesting alternative to produce H_2 onboard [2,7,8], which can be transformed to hydrogen-rich gas through thermal decomposition (1), partial oxidation (2) or steam reforming (3). Among them, steam reforming of methanol with low reforming temperature and low concentration of CO has an important superiority from process heat recovery and system simplification point of view.



A large number of catalysts for methanol (CH_3OH) steam reforming have been reported in the previous literature, including Cu-based catalysts, Pd-based catalysts and Ni-based catalysts, etc. [9,10]. Cu-based catalysts are known as be the traditional materials with pyrophoric characteristics but suffer deactivation by sintering with elevated temperature [2,9]. Pd-based catalysts are considered as the most active catalysts for the reforming of CH_3OH , while the exorbitant price and special pretreatment limit the large scale application [10]. Ni-based catalysts are deemed to be a promising industrial catalysts owing to the high catalytic activity, wide availability and the economical cost [1,11]. Nevertheless, it also suffers deactivation due to coke deposition when exposed to hydrocarbon fuels in long term applications [12]. Many efforts have been focused on developing the new nickel composite systems to prohibit carbon formation and lower the reformed temperature.

The rare earth element (lanthanum, La, etc.) acts as the common additive and has extensively applied into Ce-based materials for the elimination of CO, hydrocarbons, and NO_x [13,14]. It can act as the base sites that are considered to effectively eliminate the coke deposition. On the other hand, the incorporation of rare earth into ceria-zirconia lattice could enhance the oxygen storage capacity and improves the interaction between active species and support [14]. Recently, the effect of some rare earth (La, Pr, Ce, Rh) on the Ni-based catalysts were performed for ethanol steam reforming, methane reforming with carbon dioxide [12,15,16]. Galetti and

co-workers found that the modifying of Pr decreased the average size of Ni particle and the amount of carbon, leading to higher catalyst stability for ethanol steam reforming [12]. In the study about the effect of lanthanum on Ni/Mo/SBA-15 catalyst for methane reforming, Huang et al. reported that the addition of lanthanum led to the increased interaction between Ni and Mo–La, which enhanced the dispersion of nickel and resisted the sintering of nickel [17]. Although a large amount of literature has researched the effect of lanthanum (one of main representative elements) on the Ni-based catalysts for ethanol steam reforming, methane reforming with carbon dioxide, the characterization of the interaction of lanthanum species with nickel oxide or aluminum oxide need to be deep studied due to the well-dispersed lanthanum species, especially for methanol steam reforming. More important, the usage of La-modified Ni-based catalysts for methanol steam reforming is of significant interest due to the enhanced catalytic activity and stability. Moreover, support is one of key factor that can control the dispersion of active nickel species and the interaction between active phase and additives. It was reported that the interaction of nickel precursors and Al_2O_3 could lead to formation of the spinel $NiAl_2O_4$ phase [16,18]. This species could increase the Lewis acid sites (LAS) of weak strength, giving rising to the decrease of coke formation and higher catalyst stability. Considering the above-mentioned information, the effect of the addition of lanthanum, the loading of nickel species and various different supports on the Ni-based catalysts for methanol steam reforming were discussed in this paper.

Methodology

Catalyst preparation

La–Ni/ Al_2O_3 catalysts were synthesized by co-incipient wetness impregnation method using $La(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ as the source of lanthanum and nickel, respectively. After impregnation, the samples were kept overnight at the room temperature and subsequently dried at 100 °C for 12 h. At last, the dried samples calcined in air at 700 °C for 4 h. The content of lanthanum species was constant 10 wt%. The initial mass ratios of nickel species were varied from 5%, 7.5%, 10%, 12.5%, which were denoted as 10La–5Ni/ Al_2O_3 , 10La–7.5Ni/ Al_2O_3 , 10La–10Ni/ Al_2O_3 , 10La–12.5Ni/ Al_2O_3 , respectively. For comparison supposes, 10Ni/ Al_2O_3 without the addition of lanthanum was also prepared by incipient wetness impregnation with the weight ratio of 10%. In order to investigate the effect of support, SiO_2 and MgO were used as the support to replace the Al_2O_3 , which were denoted as 10La–10Ni/ SiO_2 and 10La–10Ni/MgO.

Catalyst characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were carried out using a JEM 2100 microscope, the corresponding particle size distribution of nickel species was evaluated from measuring 100 individual particles by using the software of

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