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Promotion effect between Ni and Co aerogel catalysts in CH_4 reforming with CO_2 and O_2

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ABSTRACT

Ni-MgO/Al_2O_3 (Ni-A) and Co-MgO/Al_2O_3 (Co-A) aerogel catalysts are mechanically mixed with different weight ratios and their catalytic performances in CH_4 reforming with CO_2 and O_2 are investigated. The catalyst mixtures showed higher CH_4 conversions than those theoretical values predicted from the mixture law, indicating an interesting promotion effect between them. The catalysts are characterized by XRD, BET, SEM, TG/DTG and Raman spectrum techniques. It is disclosed that the reduced Co-A can be easily oxidized during the reaction, but Ni-A can prevent its oxidation during the reaction, which enables Co-A in the mixture to maintain its catalytic reforming ability. CH_4 conversion is raised dramatically for ~50% as comparing the catalysts mixtures with Co-A. On the other hand, the amount of carbon can be decreased by ~17 wt.% with the increase of Co-A's weight ratio in the mixture. Meanwhile, carbon species on the spent catalysts turn from inactive graphite to active carbon species. This could be attributed to the strong affinity of Co-A for oxygen species and the decreased active metal particle size in the mixtures.

1. Introduction

Rapid growing in population and industrialization has led to large consumption of fossil fuels, which created increasing emission of greenhouse gases (GHG) to the environment. CH_4 and CO_2 constitute a major part of the GHG [1] and have the key contributions in environmental problems such as global warming, sea level rising and ocean acidification, etc. [2]. Various measures were proposed for GHG mitigation, reforming offers many environmental benefits: converting GHG to useful chemicals and fuels, utilization of biogas or nature gas reserves with high CO_2 contents [3]. Among different reforming technologies, CH_4 reforming with CO_2 and O_2 (oxy-CO_2 reforming) is a more energy efficient and safe manner to utilize CH_4 and CO_2 resources by coupling CH_4-CO_2 reforming and CH_4 partial oxidation [4], which exhibits properties attracting intensive research interests in the past decades: firstly, heat required by the endothermic CO_2 reforming can be supplied internally, secondly, major green house effect contributors (CH_4 and CO_2) are converted simultaneously to valuable syngas [5]. Moreover, other than the H_2 rich syngas (H_2/CO = 3) produced by CH_4 steam reforming, H_2/CO ratio of the syngas from oxy-CO_2 reforming process can be adjusted flexibly between 1 and 2 by changing the reactant ratio [6], which is more favorable for the production of oxygenated chemicals or hydrocarbons via Fischer-Tropsch process.

The selection of catalyst is of vital importance to CH_4 oxy-reforming technology and should be considered from catalytic (i.e. activity and stability) and economical aspects [7]. Noble metals, Ni and Co are the most commonly studied active metals. Noble metals (Pt [8], Rh [9], Pd, etc.) are especially suitable for CH_4 oxy-reforming since endothermic reforming reaction and exothermic oxidation can be effectively coupled, which contributes to high CH_4 conversion and inhabitation of hot spots [10]. But the application of noble metal based catalysts is limited due to their high price and unavailability. Other than the noble metals, Ni and Co are highly active but much cheaper. However, Ni-based catalysts undergo severe coke deposition during the reaction, which deactivates the catalysts by blocking the active sites [11]. Various substrates or promoters were used to improve the coke resistance of Ni-based catalysts [12]. Alkaline earth metal oxides or lanthanides, e.g. Ca, La, Ce, etc, were adopted due to their ability not only to increase the active metal dispersion [13], but also to enhance the adsorption

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and activation of CO_2 [14]. On the other hand, Co-based catalysts also showed good catalytic performances for CH_4 reforming, which attracted great research interests concerning the improvement to its composition [15], synthesis procedure [16] and reactor [17]. Nevertheless, Co-based catalysts can be oxidized easily with O_2 in the reactants, limiting their use in the oxy-reforming reactions [18].

Recently, Ni-Co bimetallic catalysts are extensively studied for their superior performances. Zhang et al. prepared Ni-Me (Me = Co, Fe, Cu, or Mn) bimetallic catalysts using a co-precipitation method. They found that the Ni-Co bimetallic catalyst exhibited a better performance than those of other Ni-Me combinations, and a long-term stable performance of 250 h was reached with little carbon deposition, which was ascribed to the synergy between Ni and Co [19]. Yahyavi et al. synthesized Ni-Co/Al_2O_3-MgO nano-catalysts using an ultrasound-assisted impregnation method. Better textual properties and higher active metal dispersion were obtained, leading to the good performance for CH_4-CO_2 reforming [20]. It was also reported that the coke resistance of the Ni-Co bimetallic catalyst would be raised by decreasing its active metal content, since active metal particle size below the "critical size" for carbon accumulation can be obtained [21].

The importance of Co/Ni ratio on the performances of Co-Ni bimetallic catalysts was stressed [22]. Takanabe et al. found that bimetallic Co-Ni/TiO_2 catalysts with Co/Ni ratios lower than 9:1 could suppress the oxidation of active metal, while the catalysts with Co/Ni ratios lower than 2:8 underwent carbon deposition in CH_4-CO_2 reforming [23]. Choudhary et al. studied the influence of Co/Ni ratio on the performance of the $Co_xNi_{1-x}O$ (x = 0–0.5) supported on MgO precoated SA-5205 in CH_4 steam and oxy-steam reforming. They found the influence of Co/Ni ratio on the activity and selectivity was strong in CH_4 steam reforming, but small in the oxy-steam reforming process [24]. Chen et al. reported that metal-support interaction of the Co-Ni bimetallic aerogel catalyst increased with the increase of Co/Ni ratio, which influenced its activity and stability in methane oxy-CO_2 reforming [25].

Other than synergy between active metals of Ni-Co bimetallic catalysts, similar effects were also found between two mechanically mixed catalysts. Mechanically mixing is a facile way to combine two different types of catalysts. Properties of the mixed catalysts may enable the application of external enhancement, e.g. microwave [26], magnetic field [27], etc. to the reaction. Fidalgo et al. disclosed the synergetic effect between heterogeneous mixed activated carbon and industrial Ni/Al_2O_3 catalyst, which facilitated the application of microwave heating in dry reforming [28]. However, an opposite result was reported by Ferreira et al. that mechanically mixing the nickel and lanthanide oxides together deteriorated the activity and selectivity of each metal oxides, even though a promotion effect was found when they were in the bimetallic form [29]. This indicated that the catalytic behavior of the mechanically mixed catalysts could be different from that of the bimetallic ones.

Ni and Co-based aerogel catalysts were applied for CH_4 reforming due to their high activities and stable performances [30]. It was reported that synergetic effect was found between the active metals of the Co-Ni bimetallic aerogel catalyst [25]. Nevertheless, catalytic performance of the heterogeneous mechanically mixed Ni and Co aerogel catalysts in methane oxy-CO_2 reforming was not reported, especially, the effect of weight ratio on the catalytic performances need to be clarified. In this paper, catalytic performances of the heterogeneous mixtures of Ni and Co aerogel catalysts with different weight ratios in CH_4 oxy-CO_2 reforming were investigated. The catalysts were characterized by X-ray diffraction, SEM, TG/DTG, etc. Based on the results, the promotion effect between these two catalysts was discussed.

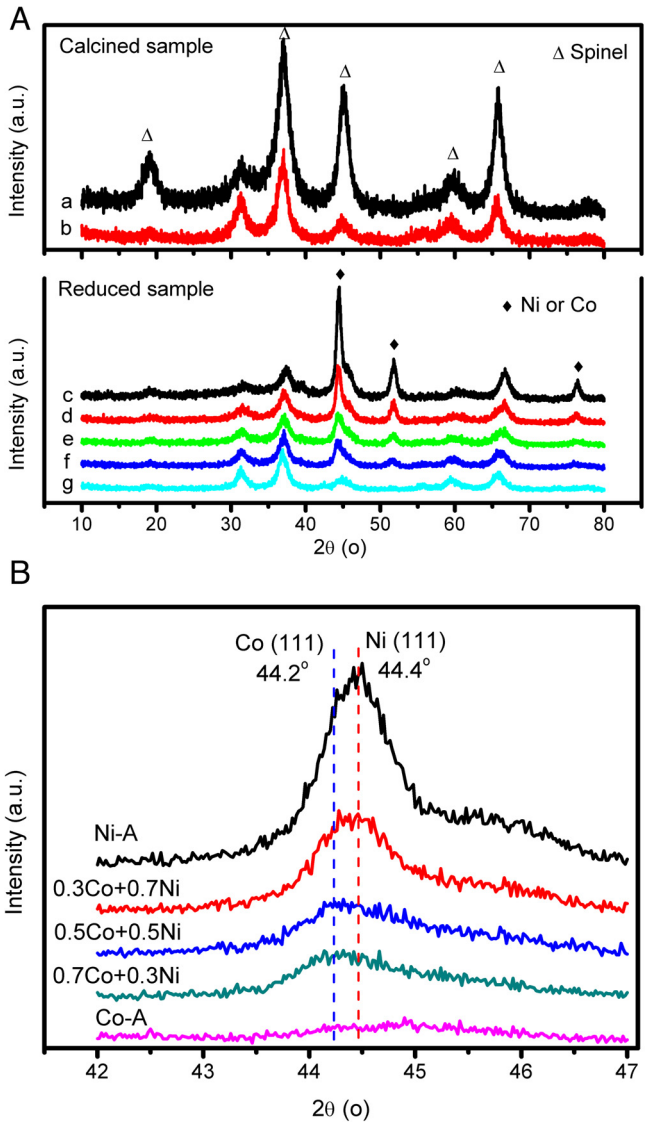

Fig. 1. XRD patterns of the calcined and reduced catalysts. A. 10°–80°, (a) Ni-A, (b) Co-A, (c) Ni-A, (d) 0.3Co + 0.7Ni, (e) 0.5Co + 0.5Ni, (f) 0.7Co + 0.3Ni, (g) Co-A; B. 42°–47°.

2. Experimental section

2.1. Catalyst preparation

The Ni/MgO-Al_2O_3 aerogel catalyst was synthesized using the raw materials of $Al(NO_3)_3{\cdot}9H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $NH_3{\cdot}H_2O$ (chemical grade, Beijing Yili Fine Chem. Co., Ltd., China). The preparation procedure has been reported in detail previously [27] and will only be briefly described here. Al $(NO_3)_3{\cdot}9H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ were dissolved in deionized water to form a starting solution (denoted as solution A). A 2.5 wt.% $NH_3{\cdot}H_2O$ solution was then added dropwise to solution A with continuous and vigorous stirring at room temperature until the pH value reached 7.5 to form a hydrogel. Subsequently, $Ni(NO_3)_2$ solution was added dropwise to the hydrogel, and then the pH value was adjusted to 9. Next, the resultant hydrogel was aged for 2 h at room temperature. After being thoroughly washed with distilled water and absolute ethanol for several times, the as-prepared gel was then treated in an autoclave for 1 h in the supercritical condition of ethanol (260 °C and 8.0 MPa). After releasing ethanol vapor at 260 °C, the resultant powder was cooled