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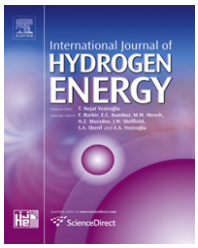

Properties of Ni/Y_2O_3 and its catalytic performance in methane conversion to syngas

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ABSTRACT

Ni/Y_2O_3, with Y_2O_3 support prepared by the conventional precipitation method, was prepared by an impregnation method. The physicochemical properties of Y_2O_3 and Ni/Y_2O_3 were characterized by BET, CO_2-TPD, NH_3-TPD, TPR, XRF and TGA, and compared with those of γ-Al_2O_3 and Ni/γ-Al_2O_3, respectively. The catalytic performance of Ni/Y_2O_3 in the reaction of partial oxidation of methane (POM) to syngas was evaluated and compared with that of Ni/γ-Al_2O_3 catalyst, too. The results showed that, Y_2O_3 was a basic support with few acidic sites while γ-Al_2O_3 was an acidic support. NiO particles supported on Y_2O_3 were more easily to be reduced than those supported on γ-Al_2O_3. In the partial oxidation of methane, Ni/Y_2O_3 catalyst showed high catalytic activity and exhibited better catalytic stability than Ni/γ-Al_2O_3. After POM reaction at 700 °C for 550 h, methane conversion decreased little and only 2.2 wt% carbon was deposited on Ni/Y_2O_3 catalyst. Ni/Y_2O_3 was stable in POM even after a series of reaction temperature variations within the temperature range of 400 ~ 800 °C.

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1. Introduction

Catalytic conversion of methane to syngas (and also to hydrogen gas) is an important route for the effective utilization of natural gas [1–4]. Generally, there are three ways for the conversion of methane to syngas, including the steam reforming of methane (SRM), the carbon dioxide reforming of methane (CRM) and the partial oxidation of methane (POM). SRM is a traditional industrial route, whereas CRM and POM are potential technical routes and have attracted more and more attentions in the recent 20 ~ 30 years. Particularly, POM has overwhelmed SRM due to its obvious advantages, such as high energy efficiency [5], suitable H_2/CO ratio for methanol synthesis and Fischer–Tropsch processes.

In the partial oxidation of methane, compared with noble metal-based catalysts, such as Rh, Ru, Ir, Pd, Pt [6–10], Ni-based catalysts have been widely studied because of their good catalytic performances as well as the low costs. However, Ni-based catalysts are suffered from deactivation due to carbon deposition in POM [11,12]. Lots of methods have been employed to improve their abilities to resist carbon deposition. Reports showed that the acidic-basic properties of Ni-based catalysts could affect the amount of carbon deposited. Choudhary et al. [13,14] discovered that, no obvious carbon was deposited on Ni/CaO after 15 h reaction in POM. Miao et al. [15] modified Ni/Al_2O_3 catalyst with Li_2O and La_2O_3, and the obtained $LiNiLaO_x/Al_2O_3$ exhibited improved ability to resist carbon deposition during the 50 h life-test in POM. Similar results were also obtained on ZrO_2, MgO and La_2O_3, which were also used as the supports of Ni-based catalysts in POM [16–18]. Except oxide supports, non-oxide supports, such as SiC and Si_3N_4, were also employed in POM. Shang et al. [19]

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studied the catalytic performance of nitrified Ni/SiC in the partial oxidation of methane, and the results showed that, compared with Ni/SiC, less carbon was deposited on the nitrified Ni/SiC. Ni/Si_3N_4 also exhibited good catalytic performance in POM [20], and almost no carbon was deposited. However, it is not the truth that, the more basic of catalysts, the more able to resist carbon deposition, because methane coupling reaction might occur on catalysts with the supports of strong basicity [21]. Therefore, searching suitable supports for POM is still an important issue.

Y_2O_3, an important metal oxide, has been applied in a wide range of areas because of its optical, thermal and chemical stabilities [22–24]. In the recent years, Y_2O_3 has also been applied in some catalytic reactions. Yao et al. [25] showed that the addition of a small quantity of Y_2O_3 and K_2O to Ag/Al_2O_3 could adjust the electronic density of adjacent silver atoms and produce proper adsorbed oxygen species, and the conversion of propylene and the selectivity to propylene oxide were high on the obtained $Ag–Y_2O_3–K_2O/Al_2O_3$ catalyst in the reaction of epoxidation of propylene. Costa et al. [26] studied Pd/CeO_2 and Pd/Y_2O_3 in the partial oxidation of ethanol, and it was found that the selectivity to CO was higher over Pd/Y_2O_3 catalyst, since Pd/Y_2O_3 catalyst favored the transformation of ethoxy species to acetate whereas Pd/CeO_2 catalyst facilitated the further oxidization of CO to CO_2. Wu et al. [27] employed different Rh supported catalysts in the steam reforming of ethanol (SRE), and the order of catalytic activity was: $Rh/Y_2O_3 > Rh/CeO_2 > Rh/La_2O_3 > Rh/Al_2O_3$. The activity of Rh/Y_2O_3 in SRE was promoted due to the surface oxygen vacancies of Y_2O_3. Yttria stabilized zirconia (YSZ) was also used as supports in the steam reforming of ethanol [28], the selective reduction of NO [29], the carbon dioxide reforming of methane [30] and the partial oxidation of methane [31].

Santos et al. added a small amount of Y_2O_3 to Al_2O_3, and the obtained $Ni/Al_2O_3–Y_2O_3$ catalyst presented higher catalytic activity than Ni/Al_2O_3 in the methane autothermal reforming reaction (ATR) [32]. Fu et al. [33] used different oxides, including Y_2O_3, to modify Al_2O_3 support, and found that the ability to resist carbon deposition of the prepared Ni-based catalysts (measured after 1 h TOS of ATR) decreased in the following order: $Ni/CaO–Al_2O_3 > Ni/MgO–Al_2O_3 > Ni/TiO_2–Al_2O_3 > Ni/CeO_2–Al_2O_3 > Ni/La_2O_3–Al_2O_3 > Ni/Y_2O_3–Al_2O_3 > Ni/Fe_2O_3–Al_2O_3 > Ni/Al_2O_3$. Wang et al. [34] employed Y_2O_3 promoted metallic Ni catalyst in POM. The catalyst was acid treated nickel sponge and modified with Y_2O_3 by an impregnation method. The results showed that the conversion of CH_4 and the selectivities to H_2 and CO were increased on the Y_2O_3 modified Ni sponge. However, the amount of carbon deposited was not analyzed and long time life-test was not reported by Wang et al. [34]. What's more, in this case, Y_2O_3 was not used as catalyst support, instead, only a small amount of Y_2O_3 was used (the content of Y_2O_3 was in the range of 1.38 ~ 10.1%). On the other hand, Y_2O_3 was also used as a support of Ru catalyst in the partial oxidation of methane [35], and Nishimoto et al. reported that Ru/Y_2O_3 was an active catalyst in POM and no carbon was deposited after 10 h reaction. However, the physicochemical properties of Y_2O_3 were not revealed or longer time life-test was not reported either. In the previous studies of Y_2O_3 as supports, no matter Rh/Y_2O_3 in SRE, $Ni/Al_2O_3–Y_2O_3$ in ATR, or Ru/Y_2O_3 in POM, the relationship between the properties of Y_2O_3 and the catalytic performance of the relevant catalysts was not investigated intensively. However, the properties of Y_2O_3 might exert an influence on the performance of Ni/Y_2O_3 catalyst in POM. Therefore, in this paper, the physicochemical properties of Y_2O_3 and Ni/Y_2O_3, as well as the catalytic performance of Ni/Y_2O_3 catalyst in POM, were studied and compared with those of Al_2O_3 and Ni/Al_2O_3, respectively.

2. Experimental section

2.1. Catalyst preparation

Y_2O_3 was prepared by the conventional precipitation method. 200 mL $Y(NO_3)_3 \cdot 6H_2O$ aqueous solution (0.25 M) containing 0.05 mol $Y(NO_3)_3$ was added dropwise into 145 mL NH_3 aqueous solution (2.5 wt%) under the conditions of pH 10 ~ 11 and vigorous stirring. After 0.5 h of stirring, the white precipitate of $Y(OH)_3$ was aged at room temperature for 12 h. Then, the precipitate was filtered and washed thoroughly with deionized water till the pH of the filtrated mother liquor was 7. Afterward, the $Y(OH)_3$ hydrogel was dried at 110 °C for 12 h in air and then calcined at 500 °C for 5 h in air. Ni/Y_2O_3 catalyst was prepared by impregnating $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution (analytical grade reagent, provided by Shantou Xilong chemical factory) with the above obtained Y_2O_3 support at room temperature for 10 h. After water being removed by vaporization, the precursor of Ni/Y_2O_3 was then dried at 110 °C in air for 12 h and calcined at 650 °C in air for 5 h.

For comparison, $Ni/\gamma\text{-}Al_2O_3$ was also prepared with the impregnation method, and the detailed information was available in our previous paper [36].

2.2. Catalyst characterization

The specific surface areas of the catalysts and the supports were measured by N_2 adsorption-desorption with the BET method on a Micromeritics ASAP 2010 C analyzer. The crystalline phases of the Ni particles and the supports were investigated by X-ray diffraction (XRD). The reduction behaviors of the catalysts were characterized by Temperature programmed reduction (TPR). The amounts of carbon deposited on the catalysts were evaluated by thermogravimetric analysis (TGA). The acidic properties of the catalysts were measured by NH_3-temperature programmed desorption (NH_3-TPD). The actual contents of Ni on the catalysts were measured by X-ray fluorescence spectrometer (XRF). The detailed experimental procedures of BET, XRD, TPR, TGA, XRF and NH_3-TPD were consistent with those in our previous paper [36].

The basic properties of the catalysts were measured by CO_2-temperature programmed desorption (CO_2-TPD). The CO_2-TPD profiles were measured by Quantachrome adsorption instrument (Chembet-3000 TPR/TPD). The catalysts (0.1 g) were firstly treated in highly pure He (99.999%, 110 mL/min) at 500 °C for 0.5 h. After that, the catalysts were saturated with flowing highly pure CO_2 at 100 °C, and then flushed with highly pure He (110 mL/min) to remove the physically adsorbed CO_2. Finally, the desorption of CO_2 was carried out in

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