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Deactivation of Ni catalysts during methane autothermal reforming with CO_2 and O_2 in a fluidized-bed reactor

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Abstract

A series of different-sized Ni catalysts (4.5–45.0 nm) were prepared and used for methane autothermal reforming with CO_2 and O_2 in a fluidized-bed reactor. It was found that the activity and stability of Ni catalysts depend strongly on the particle size and the operating space velocity. Small sized Ni is more active and stable at space velocity $<54{,}000\ h^{-1}$. Characterizations disclosed that methane decomposition rate decreases with the enlarging Ni particle size, and some of the surface carbons (derived from methane decomposition) are inactive in CO_2 atmosphere. As the methane decomposition rate slows on larger Ni particles and at higher space velocity to ensure complete conversion of the oxygen, surface Ni will be gradually oxidized by remaining O_2, leading to Ni deactivation.

Keywords: Methane; Reforming; Ni catalyst; Deactivation; Space velocity

1. Introduction

The transformation of methane and carbon dioxide, the cheapest carbon-containing materials and the most problematic greenhouse gases, into more valuable compounds has long attracted the attention of researchers. Among published results, the catalytic CO_2 reforming of CH_4 to synthesis gas [Eq. (1)] has been investigated comprehensively over the past few years, as has been well summarized in recent reviews [1–5]. The synthesis gas generated from CO_2 reforming of CH_4 has a low H_2/CO ratio and thus is suitable for the Fischer–Tropsch synthesis of higher hydrocarbons and for the synthesis of oxygenate products. Rostrup–Nielsen's group [6,7] and Ruckenstein's group [1,5,8] have made significant contributions to improving the understanding of steam and CO_2 reforming over Ni catalysts in both experimental research and theoretical studies:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H_{298K} = 247\ \text{kJ/mol}. \qquad (1)$$

Most of the group VIII metals are more or less active toward this reaction, and Ni has been popularly explored for its high activity and low price [1–5,9]. Due to the inherent inertness of methane and CO_2, high temperature (typically, 800–900 °C) is needed to achieve a meaningful yield. Under such severe conditions, carbon deposition and/or sintering of the metal particles occur on the surface of the catalyst, and sintering further accelerates carbon deposition because large metal ensembles stimulate coke formation [8].

Another drawback is that CO_2 reforming of methane is a highly endothermic reaction (247 kJ/mol). The addition of oxygen to the reforming reactants is an effective method of supplying heat, because partial oxidation of methane to synthesis gas is an exothermic reaction [Eq. (2)]. This combined CO_2 reforming and partial oxidation of methane, also called methane autothermal reforming [MATR], has drawn significant interest in recent years in alternative routes for the conversion of methane to synthesis gas [Eq. (3)] [10–16]:

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2, \quad \Delta H_{298K} = -38\ \text{kJ/mol}, \qquad (2)$$

$$CH_4 + xCO_2 + ((1-x)/2)O_2 \rightarrow CO + 2H_2, \quad \Delta H_{298K} = (285x - 38)\ \text{kJ/mol} \quad (0 < x < 1). \qquad (3)$$

In published papers, it is suggested that MATR is carried out in two separate reaction zones in the fixed-bed reactor—in the first zone, part methane is combusted into CO_2 and steam to en-

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sure the complete conversion of the oxygen in feed, producing a hot (>1300 °C) stream, and in the second zone, the unconverted methane is reformed to synthesis gas by CO_2 and steam. A significant temperature gradient in the catalyst bed formed, which ultimately resulted in the thermal sintering and deactivation of catalyst [10,17,18]. It is of great practical interest to overcome this limitation of the MATR process in fixed-bed reactor.

Tomishige [11–13] and Zheng [15,19,20] reported their studies on the MATR process in a fluidized-bed reactor, and they suggested that the high rates of heat transfer and high stability of operation be obtained. Fluidization has a favorable effect on the inhibition of carbon deposition, which is probably because the catalyst particles are circulated between the oxidizing zone and reducing zone and carbon gasification proceeds readily in the oxidizing zone. Moreover, catalyst can maintain a suitable level of reducibility during fluidization that enhances the conversion of methane [11–13,15,19,20].

Recently, we have found that the activity and stability of Ni catalysts during the MATR in fluidized-bed reactor depend strongly on the particle size of Ni and the operating space velocity. Larger-sized Ni catalysts (average Ni particle size >16 nm) are inactive at higher space velocity (90,000 h^{-1}) and deactivate rapidly (at low space velocity, 18,000 h^{-1}). Whereas small-sized ones (average Ni particle <9.5 nm) are more active and stable at the space velocity <54,000 h^{-1}. Characterizations of the spent catalysts have found that neither carbon deposition nor metal sintering would form on the deactivated catalysts. That is, the deactivation mechanism of Ni catalysts during the MATR process in a fluidized-bed reactor cannot be explained by those achievements of CO_2 reforming of methane. More fundamental studies are still needed to reveal the deactivation mechanism of Ni catalyst in the MATR process in the fluidized-bed reactor. The aim of this work is to correlate the particle size of Ni and the operating space velocity with its catalytic performance and deactivation. For this purpose, MATR at different space velocities, methane decomposition (in both continuous and pulsed methane flow) and the reactivity of carbon deposited during methane decomposition toward CO_2 and O_2 were determined on different-sized Ni catalysts.

2. Experimental

2.1. Catalyst preparation and characterizations

Ni catalysts sized from 4.5 to 45.0 nm were prepared via direct impregnation of $[Ni(en)_3]^{2+}$ (en, ethylenediamine), $[Ni(EDTA)]^{2-}$ (EDTA; ethylenediaminetetraacetic acid), nickel(II) acetylacetonate dihydrate (99+%), nickel(II) acetate, and $Ni(NO_3)_2{\cdot}6H_2O$ onto a spherical SiO_2 support (special product for fluidized reactor, $S_{BET} = 330\ m^2\ g^{-1}$, average diameter 0.25–0.38 mm, Qingdao, China). Nickel(II) acetylacetonate dihydrate (99+%), nickel(II) acetate, and $Ni(NO_3)_2{\cdot}6H_2O$ were purchased from Acros Organics (Beijing Branch, China). $[Ni(en)_3]^{2+}$ and $[Ni(EDTA)]^{2-}$ were prepared as described previously [21–23]. The loading amount of Ni was controlled at 5 wt% of the support. The precursors were dried at 80 °C in vacuum and calcined at 800 °C in stagnant air for 4 h.

The morphologies of these catalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD was obtained in D8 Advance (Bruker, Germany) equipment using nickel-filtered Cu$K\alpha$ radiation at 40 kV and 40 mA. Diffraction data were recorded using continuous scanning at a rate of 0.02°/s, step 0.02°. Average Ni particle size was calculated according to Scherrer–Warren equation. TEM images were obtained using an accelerating voltage of 200 kV (TEM, JEOL-2020F). Samples were first ground to powder, reduced in hydrogen, and dispersed on Cu grids in tetrachloromethane under supersonic-wave shaking.

2.2. MATR on different-sized Ni catalysts

MATR was carried out in a quartz fluidized-bed reactor (id = 12 mm). As noted previously [24], the minimum fluidization velocity (ω_{mf}) and the maximum fluidization velocity (ω_t) could be calculated as

$$\omega_{mf} = \frac{d_p^2(r_s - r_g)g}{1650\mu_g}\ (\mathrm{m/s}) \tag{4}$$

and

$$\omega_t = \frac{d_p^2(r_s - r_g)g}{18\mu_g}\ (\mathrm{m/s}), \tag{5}$$

where d_p and r_s are the diameter and the density of catalyst, and μ_g and r_g are the viscosity and density of the reactant mixture. In this experiment ($d_p = 0.25$–0.38 mm, $r_s = 470$–$500\ kg/m^3$, $r_g = 0.32\ kg/m^3$ and $\mu_g = 37.5\ \mu Pa/s$), the total feed gas flow rate must be controlled between 78 and 3070 ml/min to ensure the efficient fluidization of catalysts particles in the reactor at 700 °C.

CH_4 (99.99%), CO_2 (99.9%), and O_2 (99.9%) were introduced into the reactor controlled by three sets of mass flow controller (Brooks 5850E) at a molar ratio of CH_4:CO_2:O_2 = 10:4:3. Catalyst is first reduced in H_2 at 700 °C for 1 h. The effluent gas was cooled in an ice-water trap and analyzed using an online gas chromatograph (Shimadzu, GC-8A) with a packed column (TDX-01) and a thermal conductivity detector. All spent catalysts were further characterized by XRD and TG-DTA (PE-TGA7) at 50–900 °C in air flow.

2.3. The reactivity of surface carbons on different-sized Ni catalysts

The reactivity of surface carbons toward CO_2 and O_2 was investigated via coking reaction (CH_4 temperature-programmed decomposition [CH_4-TPDe]) and followed temperature-programmed oxidation with CO_2 (CO_2-TPO) and O_2-TPO. Before these experiments, catalysts were first reduced in H_2 flow at 700 °C for 1 h, then cooled to 50 °C in Ar. CH_4-TPDe was performed in 10% CH_4/Ar (50 ml/min) from 50 to 800 °C at a ramp of 15 °C/min and held at 800 °C for 20 min. Then the catalyst bed was cooled to 50 °C in Ar, and CO_2-TPO was performed in 10% CO_2/Ar (50 ml/min) from 50 to 800 °C at a ramp of 15 °C/min. Finally, after the catalyst bed was cooled to 50 °C in Ar, consecutive O_2-TPO was carried out in a flow