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Highly carbon-resistant Ni–Co/SiO_2 catalysts derived from phyllosilicates for dry reforming of methane

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ABSTRACT

This paper describes synthesis and characterization of Ni and Ni-Co alloy supported over SiO_2 derived from phyllosilicates. A series of 10 wt% Ni-Co phyllosilicate supported over SiO_2 with different Ni/Co ratio is successfully prepared by hydrothermal method where urea is used to release ammonia gradually providing a basic environment. TPR results show that adding of Co enhances the metal-support interaction. After H_2 reduction at high temperature, small and uniform Ni-Co alloy particles are well supported over silica. These catalysts are tested for dry reforming of methane (DRM) at 750 °C. The catalytic performance is highly affected by Ni/Co ratio: 10Ni and 7Ni3Co show high and stable activity for 100 h, whereas 5Ni5Co, 3Ni7Co and 10Co exhibit severe deactivation due to oxidation of metal sites. A harsher test has shown that adding of Co with a proper amount indeed can help to suppress metal sintering and carbon formation.

1. Introduction

In the current scenario of increasing energy demand, hydrogen is regarded as a new and green source of energy, and has attracted much research attention [1]. One way of producing hydrogen is via reforming reactions of hydrocarbons. Among reforming reactions, dry reforming of methane (DRM) is regarded as one of the most attractive options in energy and environmental research because it not only reduces and recycles the greenhouse gases (methane and carbon dioxide), but also produces syngas which can be used directly as fuel or feedstocks for chemical industry [2–4].

DRM is a highly endothermic reaction, as shown in [Eq. (1)], usually conducted at high temperature (700 ~ 900 °C):

$$CO_2 + CH_4 \rightleftharpoons 2H_2 + 2CO \quad \Delta H^\circ_{298} = 247\ \text{kJ mol}^{-1} \tag{1}$$

Due to low cost and wide availability, Ni-based catalysts are more attractive for industrial utilization [5]. However, Ni-based catalysts suffer from heavy carbon deposition which would cover the active sites resulting in catalytic deactivation and may even block the reactor. In the DRM atmosphere, carbon formation usually originates from methane cracking [Eq. (2)] and Boudouard reaction [Eq. (3)]:

$$CH_4 \rightarrow C_{ads} + 2H_2 \quad \Delta H^\circ_{298} = 75\ \text{kJ mol}^{-1} \tag{2}$$

$$2CO \rightarrow C_{ads} + CO_2 \quad \Delta H^\circ_{298} = -172\ \text{kJ mol}^{-1} \tag{3}$$

Hence, it is crucial to make Ni-based catalysts resistant to carbon formation, and a lot of efforts have been made to achieve this target. Several effective strategies have already developed to increase the carbon-resistance of Ni- based catalysts. One of them is formation of specific structures such as perovskite [6–8], spinel [9,10] and double-layered hydroxides [11,12]. Phyllosilicate material as catalysts has been studied a lot recently due to its unique layered structure: nickel ions (or other metals like Co, Cu, and Fe etc.) are incorporated and sandwiched between sheets of silica. Sivaiah and Valange [13] developed nickel phyllosilicate by treating sodium silicate and nickel chloride with hydrothermal method. After reduction at 700 °C, the remaining unreduced phyllosilicate structure acted as a support for Ni metal particles. This catalyst showed a very high activity and excellent carbon-resistance for DRM. Later, researchers have tried to support phyllosilicate over silica usually via ammonia evaporation method. Zhang and Gong [14] used this method to prepare 20% Ni/SiO_2 and it turned out to be an excellent catalyst for steam reforming of ethanol with high carbon-resistance. Yang and Lin [15] also used this method and succeeded to support nickel phyllosilicate on silica nanospheres (5% Ni/SiO2). They tested it for partial oxidation of methane (POM) and it showed a high stability for 50 h. Binary metal phyllosilicate has been reported as well; Ni–Cu phyllosilicate supported on silica has been prepared and tested for DRM [16] as

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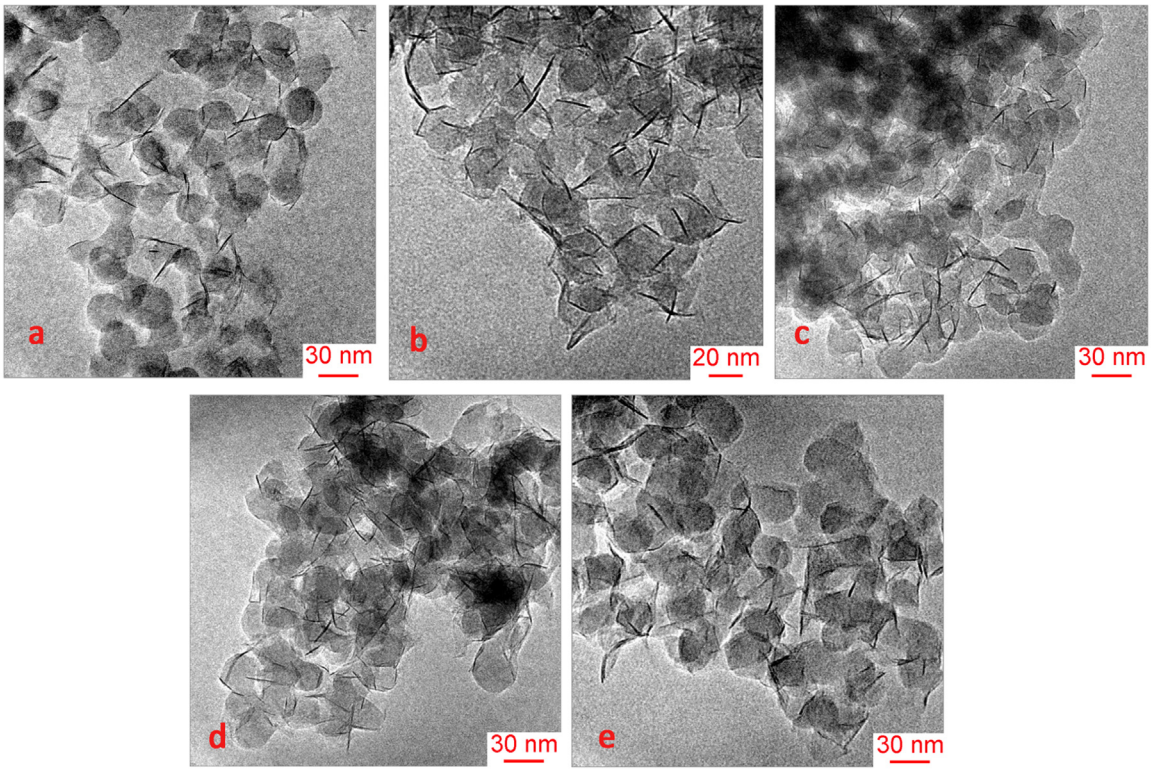

Fig. 1. TEM images of fresh catalysts: (a) 10Ni (b) 7Ni3Co (c) 5Ni5Co (d) 3Ni7Co (e) 10Co.

well as steam reforming of toluene [17]. The formation of Ni-Cu alloy helped to enhance the carbon-resistance.

Another practical way to increase carbon-resistance is formation of alloy. Ni-Co alloy supported on various materials has been investigated continuously, such like Ni–Co/TiO_2 [18,19], Ni–Co/CeO_2 [20], Ni–Co/ZrO_2 [21], Ni–Co/MgO [22,23], Ni–Co/La_2O_3 [24], Ni–Co/Al_2O_3-La_2O_3 [25], Ni–Co/Al_2O_3–MgO [26] and so on (seen in Table S1). It can be obviously concluded that formation of Ni–Co alloy helps to inhibit carbon deposition for reforming reactions, but the optimal Ni/Co ratio varies with support materials, probably due to the different metal-support interaction.

Herein, we are interested to investigate the catalytic performance of Ni–Co alloy supported over silica derived from phyllosilicates for DRM. A series of 10 wt% Ni–Co phyllosilicate with different Ni/Co ratio is successfully prepared by hydrothermal method with the assistance of urea. Both 10Ni and 7Ni3Co showed high and stable activity for 100 h long DRM test at 750 °C. A test at harsher conditions has shown that adding of Co in a small amount indeed helps to suppress metal sintering and carbon formation.

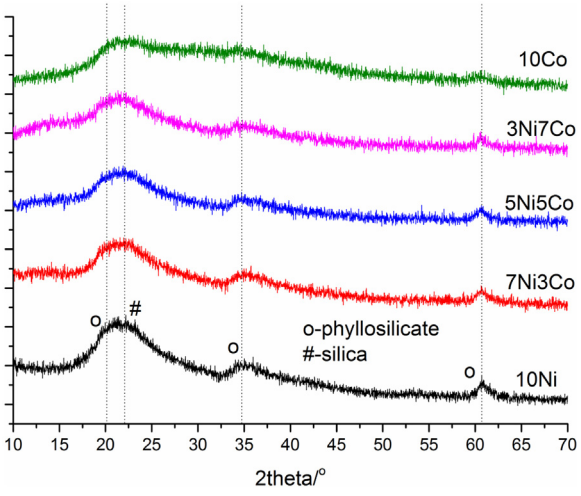

Fig. 2. XRD patterns of fresh catalysts.

2. Experimental

2.1. Preparations of catalysts

Ni-Co phyllosilicates supported over silica was prepared by hydrothermal method. All the chemicals were purchased from Sigma without any pretreatment before use. Certain amount of Ni$(NO_3)_2{\cdot}6H_2O$ and Co$(NO_3)_2{\cdot}6H_2O$ with 5 g urea was weighted and dissolved in 80 ml DI water with continuous stirring for 10 min. 1.4 ml colloidal silica (LUDOX, 50 wt%) was then added in, followed by stirring for 30 min. The solution was put in an autoclave which was sealed well and kept in a 190 °C oven for 24 h. The precipitate was collected by centrifugation and washed with water and ethanol. After drying at 80 °C, the sample was calcined at 700 °C for 4 h. The total metal weight loading was designed to be 10%. The catalyst is denoted as xNiyCo, where x means the weight percent of nickel and y is that of cobalt, i.e. 7Ni3Co means sample with 7 wt% nickel and 3 wt% cobalt.

2.2. Characterization of catalysts

JEOL TEM was employed to investigate the morphology of fresh, reduced and spent Ni–Co phyllosilicate catalysts. Powders were put into ethanol, sonicated for several minutes and dropped onto copper grids to make a TEM sample. Ni and Co weight percentage was measured with JEOL SEM-EDX.

XRD patterns were scanned with Bruker D8 Advance X-ray diffractometer (Cu Kα radiation with a wavelength λ of