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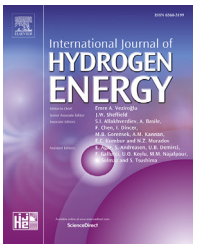

Sponge Ni catalyst with high activity in CO_2 methanation

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ABSTRACT

CO_2 methanation over sponge Ni was investigated. When CO_2 methanation was carried out using sponge Ni without any pretreatment, the sponge Ni exhibited a CO_2 conversion of 83% at 250 °C under a high space velocity (0.11 $mol_{CO2}\ g_{cat}^{-1}\ h^{-1}$). We think that the sponge Ni is a promising new catalyst for CO_2 methanation because it showed the high activity even under the high GHSV, and we can design a small plug flow reactor compared to a conventional reactor, resulting in a low manufacturing cost for the reactor. The high activity can be derived from the great number of crystal defects of *fcc*-Ni in the sponge Ni. On the other hand, with high-temperature pretreatment, the sponge Ni lost its activity in CO_2 methanation as well as the surface defect sites. Thus, the activity loss can be explained by the disappearance of the surface defect sites by the high-temperature pretreatment.

Introduction

Since Sabatier and Senderens reported CO_2 methanation in 1902 [1], the subject of methanation has been widely researched [2–5]. The origin of CO methanation is the purification of syngas for ammonia synthesis. During the oil crisis in the 1970s, the coal-to-syngas processes started to adopt the methanation technologies. Additionally, biomass conversion into syngas has also been investigated, and the first plant started operation in 2008 with a pilot-scale capacity of 1 MW of syngas [6].

Since the 1980s, CO_2 methanation has been important in the production of substitute syngas [7]. Nowadays, the CO_2 methanation process is gaining new attention because of an increasing demand for the storage of excess electricity. If hydrogen is supplied *via* water electrolysis, CO_2 methanation allows for the chemical storage of electricity (power-to-gas). If the cost of the hydrogen production can be lowered, this attempt will succeed admirably. Recently many CO_2 methanation plants have reached pilot scale. For instance a demonstration plant with 6 MW have been in operation since 2013 by Audi E-Gas project [8].

Methanation of CO_2 (Eq. (1)) is a linear combination of reverse water gas shift (RWGS) reaction (Eq. (2)) and CO methanation (Eq. (3)), while there still exists an argument about the reaction mechanism for CO_2 methanation over heterogeneous catalysts. It is generally admitted that CO_2 is converted to CO *via* a reverse water gas shift (RWGS) reaction and the thus-formed CO is methanated [9,10]. Recently Roger et al. [11] and Wang et al. [12] have proposed a different mechanism: CO_2 is subsequently hydrogenated to formate, –

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CH_2OH, $-CH_3$, and then CH_4. They considered that CO is a byproduct of CO_2 methanation, not an intermediate for CO_2 methanation. In either case, due to the exothermic nature of CO_2 methanation, a high-temperature operation limits the CO_2 conversion [13]. However, chemical reactions are kinetically limited at low temperature. Hence, a central issue of the reaction is the enhancement of the CO_2 methanation rate at low temperatures. As will be seen in Table 2, most of the reported catalysts were not sufficiently active in CO_2 methanation at 250 °C.

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g) \quad \Delta_r H^0_{298K} = -165 \text{ kJ mol}^{-1} \tag{1}$$

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g) \quad \Delta_r H^0_{298K} = 41 \text{ kJ mol}^{-1} \tag{2}$$

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \quad \Delta_r H^0_{298K} = -206 \text{ kJ mol}^{-1} \tag{3}$$

The methanation of CO_2 has mainly been investigated using Ni [14–19] and noble metals such as Ru [20–23] and Rh [24] as active species on various metal oxides. Ni catalysts are commonly used for the methanation because of their low cost and high activity. This reaction is strongly affected by the nature of the support material as well as the active species, such as CeO_2 [14,17,22], Y_2O_3 [25], ZrO_2 [26–28], $Ce_xZr_{1-x}O_2$ [11,12,16,29], and so on. According to Kikuchi's work, Ni/CeO_2 catalysts showed higher CO_2 conversion close to the equilibrium conversion at temperatures above 350 °C compared to those of Ni/α-Al_2O_3, Ni/MgO, and Ni/TiO_2 [14]. This is because the CeO_2 on the catalyst played a major role in CO_2 adsorption and active metal dispersion [14,22]. Recently, several researchers have found the high activity of Ni–Al hydrotalcite-like catalysts in CO_2 methanation [30–32]. When the hydrotalcite was calcined, its dehydration, dehydroxylation, and loss of compensating anions occurred, which created special acidic and basic sites on it [33]. Additionally, as an advantage of the hydrotalcite catalysts, highly-loaded Ni-based catalysts were prepared, leading to a high surface area of Ni. When a NiO/Al_2O_3 catalyst with high Ni loading up to 60 wt% was prepared *via* hydrotalcite-like compounds, it possessed well-dispersed NiO particles of 3–7 nm [34].

Based on the reports mentioned above, we wondered what happens to the CO_2 methanation activity for Ni-based catalysts when the Ni loading was increased as much as possible. This time we focused on sponge Ni catalysts, which are known to be active in CO and CO_2 methanation [35–37]. We succeeded in finding suitable pretreatment conditions for sponge Ni, resulting in high activity and selectivity in CO_2 methanation at 250 °C, as will be seen in Table 2. This work will surely contribute to reducing the plant area, which consequently reduces capital costs.

Experimental methods

Catalyst preparation

Sponge Ni. In this work, a commercial sponge Ni (NDHT-90, Kawaken Fine Chemicals Co., Ltd.) was used. This sponge Ni consists of Ni (>92.5 wt%), Al (<6.5 wt%), and some impurities. The sponge Ni was kept underwater at room temperature. The sponge Ni was dried in air (i) at room temperature for 48 h or (ii) at 110 °C for 24 h for use in the reaction test and its characterization. The samples dried in air at room temperature and 110 °C were denoted as **SpNi** and **SpNi(110)**, respectively.

NiO supported by CeO_2. A NiO/CeO_2 sample (Ni loading = 10 wt%, labeled as **NiO/CeO_2**) was prepared by a conventional impregnation method. The CeO_2 (Catalysis Society of Japan, JRC-CEO-1) was impregnated with an aqueous solution of nickel (II) nitrate hexahydrate (Kanto Chemical Co., Inc., >98%). The water was then removed at 80 °C under vacuum (above 100 hPa) using a rotary evaporator. The crude material was dried in air at 110 °C overnight and calcined in air at 600 °C for 3 h.

Characterization

Powder X-ray Diffraction (PXRD). The crystalline phases of the catalysts were determined by powder X-ray diffraction (Rigaku, Ultima IV) with a Cu $K\alpha$ radiation source at a voltage of 40 kV and a current of 40 mA. The crystallite size (D) was estimated from the diffraction peak using Scherrer's equation [38],

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{4}$$

where K is the shape factor (0.89), λ is the X-ray wavelength (0.154 nm), β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle.

Electron Microscopy. The morphology of **SpNi** was observed by a Schottky-emission scanning electron microscope (SE-SEM, JEOL, JSM-7001F).

Temperature programmed reduction by hydrogen. The reducibility of **SpNi** was investigated by temperature programmed reduction by H_2 (H_2-TPR) in a flow system (MicrotracBEL, BELCAT-ADVANCE). Approximately 70 mg of the samples were placed in a quartz tube and heated at 300 °C for 1 h in an Ar flow. Next, the samples were cooled to 50 °C in an Ar flow, after which the cell was purged with 4%H_2/Ar. The temperature was then raised from 50 °C to 800 °C at a heating rate of 5 °C min^{-1} under a 4%H_2/Ar flow (30 mL min^{-1}).

X-ray Absorption Spectroscopy. Using X-ray absorption spectroscopy (XAS) at the BL14B2 beamline at SPring-8, Japan, the Ni K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were measured. XAS data were collected in a quick mode every 5 min, that is to say, the Si (1 1 1) monochromator was continuously moved from 14.31° to 11.93° in 196 s. Spectra were collected in the transmission mode using ion chambers filled with an Ar/N_2 mixture on pressed pellets of fresh catalysts. The obtained spectra were corrected and normalized using the Athena and Artemins [39]. Fourier transformed data were analyzed by a curve-fitting method using theoretical phase-shift and amplitude functions derived by the FEFF8 program.

In this study, most of the catalysts were pretreated (H_2 reduction or CO_2 methanation) without exposure to air. The manner of H_2 reduction was as follows. **SpNi** was placed into a

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