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Research article

Low-temperature CO_2 reforming of methane on Zr-promoted Ni/SiO_2 catalyst

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ABSTRACT

Ni–Zr/SiO_2 catalyst was prepared using the impregnation method and was employed for the dry reforming of methane. The Ni species ensured a superior dispersion of the Zr species, promoting the formation of low temperature active center for the target reaction, while the introduction of promoter Zr changed the nature of the active center. At high temperature, the *Ea* values corresponding to CH_4 and CO_2 on Ni–Zr/SiO_2 catalyst were much lower than those on Ni/SiO_2 catalyst. In addition to facilitate the activation of the C–H bond in CH_4, the Zr promoter on Ni–Zr/SiO_2 catalyst also facilitated the formation of CO_{ads} and O_{ads} species at low temperatures, and accelerated the formation–decomposition of intermediate formates. These factors including the synergetic effect of Ni and Zr species led to the enhancement of the activation of both CH_4 and CO_2 at low temperatures, with 2.0% initial conversion of both CH_4 and CO_2 (at 1 h) achieved at 400 °C.

1. Introduction

Carbon dioxide reforming of methane (dry reforming of methane, DRM) could not only reduce the emissions of the two greenhouse gases (CH_4 and CO_2) but also produce synthesis gas with a low H_2/CO ratio, which could be used to produce a wide spectrum of hydrocarbons and alcohols via the use of catalysts [1–4]. Methane is the main ingredient in natural gas, however, the activation of methane remains difficult because of its strong C–H bond [5–8]. The efficient upgrading of methane has gained importance as petroleum oil reserves diminish [7,9,10]. CO_2 is the most abundant waste produced by human activities. Its utilization in redox reaction requires high energy substances or electroreductive process [11]. Therefore, the use of CO_2 for methane reforming is an interesting application [1–4,9,11]. Supported Ni-based catalysts are the most promising potential catalysts for the DRM because of their high activity, low cost and extensive availability [2–4,8]. The CO_2 reforming of methane is an endothermic reaction, and all related previous studies have been focused on the DRM at high temperatures. Although much effort has been devoted to investigating the reforming process over Ni-based catalysts at high temperature, to the best of our knowledge, the development of catalysts for the reforming of methane at low temperature (below 600 °C) has been scarce. Because high-temperature DRM causes sintering leading to deactivation of the catalyst and high operating costs of the process, low-temperature activation of CH_4 and CO_2 has attracted feverish research efforts as the global predicament of dwindling resources grows increasingly dire. Therefore, the development of catalytic DRM at low temperatures is expectable.

Here, we show that Ni–Zr/SiO_2 catalyst exhibits high activation ability for both CH_4 and CO_2 at low temperatures (approximately 400 °C). The effect of Zr promoter on the Ni–Zr/SiO_2 catalyst for the CO_2 reforming of CH_4 is also discussed.

2. Experimental section

2.1. Catalyst preparation

The catalysts were prepared by the impregnation method which was the same as that reported in the previous work [12]. Briefly, the SiO_2 support (20–40 mesh) was impregnated with an aqueous solution containing an appropriate amount of $Ni(NO_3)_2$ or $Ni(NO_3)_2$ and $Zr(NO_3)_4$ for 24 h at 20 °C without stirring, and then the excess solvent was removed by heating at 80 °C in water bath. After that, the samples were dried at 110 °C for 4 h and finally calcined at 800 °C for 5 h in air, yielding respectively the Ni/SiO_2 or Ni–Zr/SiO_2 catalyst.

2.2. Catalytic reaction

The CH_4 temperature-programmed decomposition (CH_4-TPDe) was carried out using a fixed-bed quartz equipped with an online mass analysis system (HPR-20QIC). Typically, 0.25 g catalyst was initially reduced in H_2 at 800 °C for 1 h. After being cooled under Ar atmosphere, the sample was then tested from 60 °C to 800 °C at 10 °C/min under diluted CH_4

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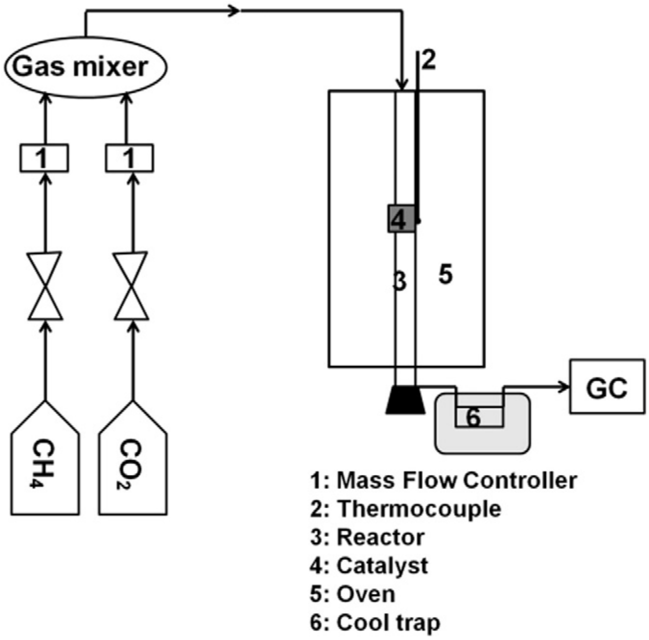

Scheme 1. Schematic diagram of the activity test setup.

(the flow-rate of CH_4 and Ar was 5 and 30 mL/min, respectively) atmosphere and keep 30 min. The CH_4 ($m/e = 16$), H_2 ($m/e = 2$), CO ($m/e = 28$), and H_2O ($m/e = 18$) produced were recorded as a function of temperature.

Similar to the CH_4-TPDe, the temperature-programmed reaction (TPRe) was performed over the reduced catalysts. 0.25 g sample was tested from 60 °C to 800 °C at 10 °C/min under the reactant mixture atmosphere ($CH_4/CO_2 = 1$, $F = 60$ mL/min). The H_2 ($m/e = 2$), CO ($m/e = 28$), CO_2 ($m/e = 44$), CH_4 ($m/e = 16$), and H_2O ($m/e = 18$) were recorded as a function of temperature.

The catalytic activity test was carried out in a fixed-bed continuous flow micro-quartz-tube reactor at atmospheric pressure (See Scheme 1), which was the same as that reported in our previous work [12].

2.3. Catalyst characterization

Transmission Electron Microscopy Mapping (TEM Mapping) of the samples was obtained on an FEI company Tecnai G2 20 Twin instrument equipped with an EDX spectrometer operated at an acceleration voltage of 200 kV (recording time approx. 30 min).

Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) were recorded on a FTIR (Nicolet 6700) spectrometer equipped with a high-sensitive MCT detector cooled by liquid nitrogen. The DRIFTS cell (Harrick) was fitted with CaF_2 windows and a heating cartridge that allowed the samples being heated to 460 °C. The reduced samples were activated in helium at 460 °C for 1 h, and then cooled to 50 °C under helium of 20 mL/min. The spectra were collected after treated in the flow of CH_4 and/or CO_2 (diluted by helium). All spectra were measured at the respective temperatures with continuous flow of gas reactants, with a resolution of 4 cm^{-1}.

3. Results

The Ni and Zr distribution mapping of DEX analysis for the fresh catalyst is illustrated in Fig. 1. The turquoise and green points (or areas) represented signals of Ni and Zr elements, respectively. In our previous studies, the introduction of Zr was observed to enhance the reducibility of the Ni–Zr/SiO_2 catalyst [12]. Whereas the mapping of EDX results suggested that the presence of Ni facilitated the dispersion of surface Zr species (Fig. 1A and D). Besides, the introduction of Zr partly covered Ni species or enhanced the dispersion of the Ni species (Fig. 1B and C).

A comparative temperature-programmed DRM reaction (TPRe) was implemented (Fig. 2). Because of the same variation tendency of the H_2 and CO (as well as that of CH_4 and CO_2), Fig. 2 just showed the variation profiles of H_2, CH_4 and H_2O. As shown in Fig. 2A, on Zr/SiO_2, the DRM reaction was not observed in the whole TPRe process, even at 800 °C

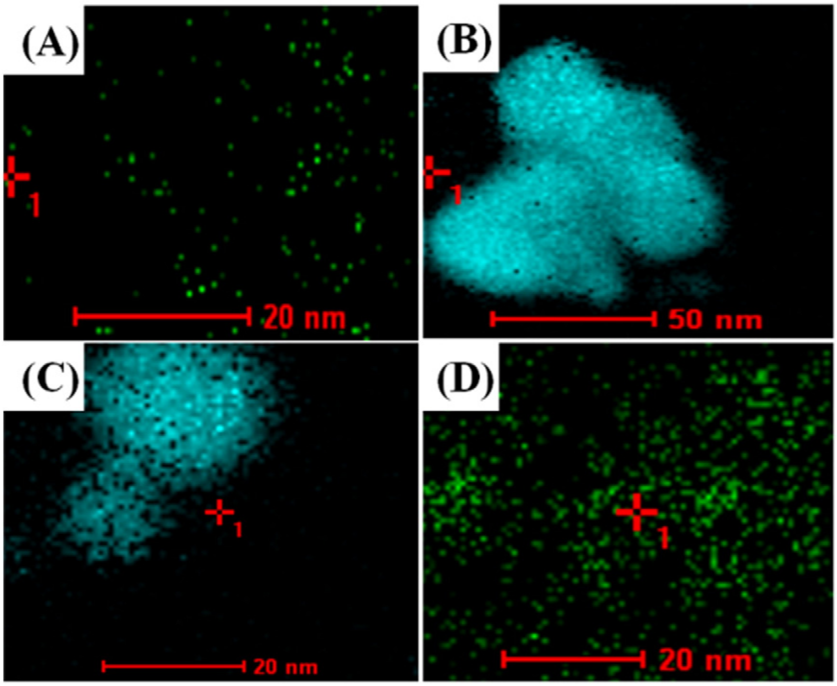

Fig. 1. The STEM mapping of EDX analysis of (A) Zr for Zr/SiO_2, (B) Ni for Ni/SiO_2, (C) Ni for Ni–Zr/SiO_2 and (D) Zr for Ni–Zr/SiO_2 catalysts.