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CO_2 methanation on the catalyst of Ni/MCM-41 promoted with CeO_2

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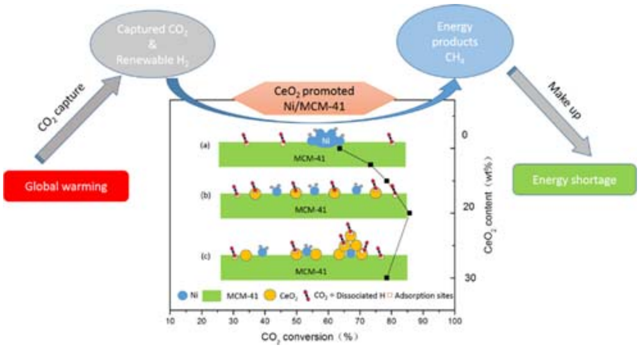
HIGHLIGHTS

- CO_2 methanation can alleviate global warming and produce alternative energy product.
- Synergetic effect among Ni active sites, CeO_2 and MCM-41 improved Ni dispersion.
- High CO_2 conversion and CH_4 selectivity were obtained on CeO_2 promoted Ni/MCM-41.
- The promoted catalyst maintain its high reactivity after 30 h in-stream test.

GRAPHICAL ABSTRACT



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ABSTRACT

CO_2 as a raw feed combined with renewable hydrogen for the production of useful chemicals and alternative energy products is one of the solutions to environmental and energy problems. In this study, a series of Ni-xCeO_2/MCM-41 catalysts with a nickel content of 20 wt% were prepared through deposition precipitation method for CO_2 methanation. Different characterization methods, including BET, XRD, TEM, SEM, H_2-TPR and H_2-TPD were applied to help explore the influence mechanism of CeO_2 on Ni/MCM-41 in CO_2 methanation. It was found that all CeO_2-promoted catalysts exhibited enhanced catalytic activity when compared to Ni/MCM-41. The catalyst modified with 20 wt% CeO_2 showed the best catalytic performance, with CO_2 conversion and CH_4 selectivity of 85.6% and 99.8%, respectively, at the temperature of 380 °C under atmospheric pressure. The synergetic effects among Ni^0 active sites, the promoter and the support, including nickel dispersion improvement and increased CO_2 adsorption sites due to the addition of CeO_2, were considered as important factors for high reactivity of the promoted catalysts. The stability test showed that the promoted catalyst maintained its high reactivity after 30 h.

1. Introduction

Global warming has caused serious impact on the environment in recent years, especially obvious on climate change (Fernandez-Duque et al., 2017). The increasing greenhouse gas emission is the leading cause of global warming. Among the greenhouse gases, CO_2 contributes over 60% to global warming due to its huge emission amount which is over 30 Gt a year (Ketzer et al., 2017; Wang et al., 2017). Nowadays, continuous efforts have been made to reduce the atmospheric CO_2 concentration through carbon capture and storage. Considering that it is abundantly available, inexpensive, non-toxic and non-hazardous, the captured CO_2 as a raw feed combined with renewable hydrogen (Sun et al., 2013) for the production of useful chemicals and alternative energy products has received extensive attention for its significant contribution to alleviating the stress of environment and making up for the shortage of energy. CO_2 methanation technology, which was firstly put forward by Paul Sabatier in 1902, can generate methane under

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atmospheric pressure, and became one of the most practical and effective technologies in utilizing CO_2 (Aresta and Dibenedetto, 2007). The Gibbs free energy change of CO_2 methanation reaction is $-114\ kJ\cdot mol^{-1}$. It remains the most advantages with regard to thermodynamics, since the reaction is considerably more competitive than other reactions which form hydrocarbons or alcohols (Inui and Takeguchi, 1991).

$$CO_2(g) + 4H_2(g) = CH_4(g) + 2H_2O(g)\ \Delta G^{\theta}_{298K} = -114\ \text{kJ}\cdot\text{mol}^{-1} \quad (1)$$

This reaction has great significance for its potential in commercial application. Even the National Aeronautics Space Administration (NASA) is also interested in applications of the Sabatier reaction in future manned space colonization on Mars (Kester, 1974). However, a major challenge that hinders the conversion of CO_2 is the lack of a high active catalyst which can be able to perform effectively under low temperature with good stability. Both noble metal (Rh, Ru, Pt and Pd) and non-noble metal (Fe, Co and Ni) catalysts have been investigated in the past few years. Nickel catalyst was reported as a good replacement for noble metal (Wang et al., 2013b). Compared with Rh and Ru, Ni has a great potential in the development of functional catalyst for its cheaper price (Liu et al., 2010; Wang et al., 2014a). However, it still remains as a major challenge for the industrial application of Ni based catalysts because of the rapid deactivation caused by sintering of active nickel species and coke deposition (Chen et al., 2017).

Using porous supports such as Al_2O_3, SiO_2, TiO_2, ZrO_2 and biochar which generally offer large surface areas and multiple pores, is an effective way to improve Ni dispersion and suppress the aggregation of nickel particles (Wang et al., 2014b; Wang and Gong, 2011; Zhu et al., 2015). In addition, zeolites have drawn more and more interest in recent years due to their specific pore structures and framework (Lu and Kawamoto, 2013; Wang et al., 2015). For the first time since the MCM-41 mesoporous materials reported in 1992, the MCM-41 catalyst loaded with metal has received extensive attention. MCM-41 is a new type of nanostructure materials, with large specific surface area and uniform large pore size which can aid the easy diffusion of reactant molecules in and out of its mesopores (Pattiya et al., 2008). Du et al. prepared Ni/MCM-41 catalyst containing 1–3 wt% Ni by in situ synthesis for the research of CO methanation, and CH_4 selectivity of 96.0% was obtained at 400 °C under atmospheric pressure (Du et al., 2007). Zhang et al. applied Ni/MCM-41 prepared by a hydrothermal synthesis method for the production of substitute natural gas from syngas methanation (Zhang et al., 2013a). During the stability test of 100 h, the CO conversion and CH_4 yield maintained around 100% and 82%, respectively. Considering its good performance in methanation, Ni/MCM-41 was found to be a good, novel and thermal stable candidate for CO_2 methanation (Liu et al., 2009). Recently, studies have found that CeO_2 as an additive could effectively promote the adsorption and the activation of CO_2 molecules on the catalysts. Because of its oxygen exchange capacity, CeO_2 reversibly released and restored a large amount of oxygen atoms (Corthals et al., 2008). Li et al. found that the addition of CeO_2 could promote the interaction between support and metal active component, so as to well control the growth of the Ni particles thus improving the catalytic performance of Ni based catalyst (Li et al., 2015). Zhou et al. also found that the catalytic performance was related to the CeO_2 content in catalysts to some extent (Zhou et al., 2014).

From the above, CeO_2 promoted Ni/MCM-41 catalyst was considered to be beneficial for CO_2 methanation. In this study, a series of Ni/MCM-41 catalysts containing different CeO_2 contents (0 wt%, 5 wt%, 10 wt%, 20 wt% and 30 wt%) were prepared by deposition-precipitation method. The effect of CeO_2 content on the catalytic performance of Ni-CeO_2/MCM-41 catalyst for CO_2 methanation was investigated, and the influence mechanism of CeO_2 on the supported nickel catalysts was also explored.

2. Experimental section

2.1. Preparation of catalysts

MCM-41 silica was purchased from Nanjing Xian Feng Corp. (Nanjing, China). It was calcined at 500 °C for 4 h to eliminate the impurities adsorbed on the surface before the preparation of the catalysts. A 20 wt% Ni/MCM-41 catalyst was prepared as the following steps: first, 4.94 g $Ni(NO_3)_2\cdot 6H_2O$ was added to 250 mL deionized water to get the uniform solution, then 4.0 g MCM-41 was added into the solution followed by stirring for 1 h at ambient temperature. Next, K_2CO_3 solution with the concentration of 0.2 mol/L was dropwise added as precipitant into the suspension until the pH value reached 9–10, followed by stirring for 2 h at 90 °C. After that, the suspension was filtered and washed by deionized water to neutral state. The obtained precipitate was dried at 110 °C overnight and calcined at 500 °C in air for 4 h.

As for the preparation of CeO_2 promoted catalyst, 5 wt% CeO_2 promoted Ni/MCM-41 was described as an example in detail. First, 4.94 g Ni $(NO_3)_2\cdot 6H_2O$ and 0.63 g Ce $(NO_3)_3\cdot 6H_2O$ were added to 250 mL deionized water to get the uniform solution, then 3.75 g MCM-41 was added into the solution followed by stirring for 1 h at ambient temperature, then the same procedure described in the preparation of Ni/MCM-41 was followed. A series of CeO_2 promoted catalysts were prepared through the same method by varying the amount of Ce $(NO_3)_3\cdot 6H_2O$ and MCM-41. All the catalysts have the same nickel content of 20 wt%. The prepared catalysts were designated as Ni-xCeO_2/MCM-41, where x represents the content of CeO_2, which is, 5 wt%, 10 wt%, 20 wt% and 30 wt%, respectively.

2.2. Characterization of catalysts

Adsorption-desorption isotherms of N_2 were recorded at −196 °C using a Quadrasorb SI apparatus. Before the measurement, the sample was degassed at 300 °C for 3 h. The specific surface area and pore size were obtained via Brunauer-Emmett-Teller (BET) method while pore volume was calculated by Barrettr-Joynerr-Halenda (BJH) model using the desorption isotherm branch. X-ray diffraction (XRD) measurements were conducted on a PANalytical X'Pert PRO X-ray diffractometer using a Cu-Kα radiation source at 40 kV and 30 mA in the 2θ scanning range of 1°–90°. The crystallite size of Ni was calculated according to the Scherrer equation based on Ni (111) surface. The surface morphologies were observed by scanning electron microscopy (SEM, FEI Model SIRION-100). The particle sizes and their distributions were determined by transmission electron microscopy (TEM, Philips-FEI, Tecnai G2F30).

Temperature-programmed reaction of hydrogen (H_2-TPR) was carried out on an AutoChem II 2920 instrument (Micromeritics Instrument Corp.). Each sample (30 mg) was pretreated by argon at 200 °C for 1 h, and then cooled down to 50 °C. The reduction was carried out with a heating rate of 10 °C/min up to 900 °C. The H_2 consumption amount was recorded with a thermal conductivity detector (TCD). The amount of reduced catalysts at active sites were measured by temperature programmed desorption of hydrogen (H_2-TPD) experiments using an AutoChem II 2920 instrument. Each sample (30 mg) was reduced with a mixed stream of 10% H_2/Ar prior to the measurements. After cooling down to 50 °C, the reduced sample was purged for 90 min under H_2/Ar atmosphere and then flushed with argon for another 90 min to remove the physically adsorbed hydrogen. The temperature was raised from 50 °C to 800 °C at a heating rate of 10 °C/min. The desorbed hydrogen was detected using a TCD. Temperature programmed desorption of CO_2 (CO_2-TPD) was also conducted on the same instrument. Prior to the experiment, each sample (100 mg) was prepared followed the same process of H_2-TPD. After cooling down to 50 °C, pure CO_2 was fed into the instrument for 30 min until the adsorption equilibrium was reached. After that, the excess adsorptive gas was purged with an Ar flow for 30 min and the catalyst was heated up to 800 °C at a heating rate of 10 °C/min.