Improvement of catalytic stability for CO_2 reforming of methane by copper promoted Ni-based catalyst derived from layered-double hydroxides

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ABSTRACT

Copper-promoted nickel-based metal nanoparticles (NPs) with high dispersion and good thermal stability were derived from layered-double hydroxides (LDHs) precursors that were facilely developed by a co-precipitation strategy. The copper-promoted Ni-based metal NPs catalysts were investigated for methane reforming with carbon dioxide to hydrogen and syngas. A series of characterization techniques including XRD, N_2 adsorption and desorption, H_2-TPR, XPS, CO_2-TPD, TEM, TGA and in situ CH_4-TPSR were utilized to determine the structure-function relationship for the obtained catalysts. The copper addition accelerated the catalyst reducibility as well as the methane activation, and made the Ni species form smaller NPs during both preparation and reaction by restricting the aggregation. However, with higher copper loading, the derived catalysts were less active during methane reforming with CO_2 to syngas. It was confirmed that the catalyst with 1 wt% Cu additive gave the higher catalytic activity and remained stable during long time reaction with excellent resistance to coking and to sintering. Furthermore, the mean size of metal NPs changed minimally from 6.6 to 7.9 nm even after 80 h of time on stream at temperature as high as 700 °C for this optimized catalyst. Therefore, this high dispersed anti-coking copper-promoted nickel catalyst derived from LDHs precursor could be prospective catalyst candidate for the efficient heterogeneous catalysis of sustainable CO_2 conversion.

1. Introduction

Carbon dioxide together with methane takes up the majority in greenhouse gases, and the increased emission of which caused to the global warming by the well-known "greenhouse effect". As a cheap carbon source, the conversions of CO_2 into valuable fuels and chemicals have attracted more and more attention [1,2]. In such a practical background, the researches on methane reforming with carbon dioxide therefore make their exclusively important sense in environmental and energy area. As expressed by the equation $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ ($\Delta H_{298\,K} = 247$ kJ/mol), the both major greenhouse gases CO_2 and CH_4 are simultaneously consumed in this process, and the generated syngas (with a theoretical H_2/CO ratio of 1) could be directly used to produce hydrocarbons by Fischer–Tropsch synthesis and oxygenated chemicals such as dimethyl ether [3,4]. Ni based catalysts have been extensively investigated because of its good ability in cleavage of C–H and C–O bonds. Furthermore, lower cost and higher availability of Ni compared to noble metal also make it widely applied in the preparation of methane dry reforming catalysts [5–8]. However, the great challenges for Ni based catalysts focus on their fast deactivation owing to the thermal sintering of Ni particles and the excessive carbon deposition during the severe reduction and reaction process [9,10]. Although the introduction of precious metal such as Ru, Rh and Pt into the catalysts as either active sites or promoter could improve the activity and catalytic stability [11–14], the high cost of catalyst would be the main aspect limiting their application in large scale.

Intensive studies have confirmed that the well dispersed Ni nanoparticles (NPs) with appropriate particle size were helpful to suppress the aggregation of active sites and to restrict the carbon deposition [15,16]. In view of this, the catalyst composition and the preparation method could be further optimized

based on the reported results to achieve the highly efficient and stable samples under the cruel reaction conditions [17,18]. Layered-double hydroxides (LDHs), usually with a formula like $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n}\cdot mH_2O$, have a typical morphology with hexagonal platelets. It could be used as catalyst or catalyst precursor as the composition is easy to control by changing the type of divalent (M^{2+}) and trivalent (M^{3+}) cations [19–21]. The M^{2+} and M^{3+} cations are uniformly distributed within the hydroxide layers in the flakes of LDHs, without clusters of like cations, such a feature make it possible to obtain well dispersed layered double oxides (LDO) through thermal treatment at high temperature [22]. Ni based catalysts prepared by synthesizing LDH as precursor have also attracted considerable interests for methane dry reforming reaction, in despite of the catalytic activity was improved compared to the Ni contained samples prepared by conventional method like impregnation, but there still was great room to improve the ability in anti-sintering and anti-coking [22,23]. It has been reported that the introduction of Cu into the Ni based catalyst originated from LDHs can effectively improve the activity and coke resistance for the catalytic steam reforming of biomass tar [24] and ethanol [25]. Moreover, when Cu was added into Ni/Al₂O₃ [26] and Ni/SiO₂ [27] systems, the resulting samples showed obvious improvement in enhancing the catalytic stability and in inhibiting the coke formation during methane dry reforming reaction.

In this work, the Ni-containing LDO catalyst modified with different amounts of Cu were prepared by the calcination and reduction of $Ni/Cu/Mg/Al/CO_3^{2-}$ LDHs. The relationship between the catalyst structure and the catalytic performance of these samples, such as the interaction of Cu with Ni and the coke deposition during the reaction, were discussed in the methane reforming with carbon dioxide.

2. Experimental

2.1. Catalyst preparation

The LDH catalyst precursors were synthesized using the co-precipitation method. A certain amount of Ni^{2+}, Cu^{2+}, Mg^{2+}, and Al^{3+} nitrates were dissolved in deionized water to form a 0.4 M aqueous solution with the molar ratio of Mg/Al equal to 2.5/1. The solution was added slowly (dropwise) to a 0.15 M sodium carbonate solution at 60 °C under strong agitation. During the co-precipitation, the suspension was kept at pH 10.0 by adding 1.0 M NaOH solution. Then, the suspension was stirred continuously at 60 °C for 1 h and aged at the same temperature for 18 h. Subsequently, the precipitate was washed with deionized water, and then the LDHs was obtained after drying at 110 °C for 12 h. The mixed oxides derived from the LDHs by calcination at 500 °C for 8 h were designated as NiCuZ-LDO and the corresponding LDH precursors were denoted as NiCuZ-LDH, where Z was the wt% value of copper content in the mixed oxides. The Cu content for the mixed oxides was 0 wt%, 1 wt%, 5 wt% and 10 wt%, respectively. In addition, the nickel amount was fixed at 10 wt% in all the mixed oxides.

2.2. Characterization

The X-ray diffraction (XRD) analysis was performed using an X-ray diffraction apparatus (Philips X'pert PRO) with Cu $K\alpha$ (45 kV, 50 mA) radiation.

The X-ray photoelectron spectra (XPS) were achieved on the XSAM800 spectrometer with an Al $K\alpha$ ($h\nu = 1486.6$ eV) X-ray source and the binding energies were amended by using C (1 s) at 284.6 eV.

Temperature-programmed reduction (TPR) experiments were carried out in a tubular reactor charged with 100 mg. The temperature of the reactor was raised linearly from 100 °C to 800 °C in a 5% H_2/N_2 mixture gas flow of 30 mL/min, with a 10°C/min ramping rate by a temperature controller. The amount of hydrogen consumed was analyzed on-line by a SC-200 gas chromatograph with a thermal conductivity detector (TCD).

The temperature-programmed desorption of carbon dioxide (CO_2–TPD) was used to measure the basic properties of samples. Before the CO_2–TPD, 50 mg catalyst was reduced in situ in a 10% H_2/N_2 mixture gas flow of 30 mL/min, with a 10°C/min ramping rate from 100 °C to 800 °C. The catalysts were treated at 300 °C for 60 min in an argon flow, then, it was saturated with carbon dioxide for 60 min at 50 °C. Then, the samples were purged with argon to remove weakly adsorbed CO_2 for 60 min, and then were heated from room temperature to 800 °C with a ramping rate of 10 °C/min. The desorbed CO_2 ($m/z = 44$) was detected on-line by a Hiden QIC-20 mass spectrometer.

The thermogravimetric analysis was performed with a TGA Q500 thermogravimetric analyzer. The samples were heated under air atmosphere from room temperature to 800 °C at a heating rate of 10 °C/min.

The temperature-programmed surface reaction (TPSR) of CH_4 was carried out in a fixed-bed reactor. The catalyst was reduced under hydrogen flow at 700 °C for 60 min before experiment. The reactant gas CH_4 was switched in with a flow rate of 30 mL/min, and the temperature of the reactor was raised from 50 °C to 800 °C at the rate of 10 °C/min by a temperature controller. The products of the experiment were detected on-line by a Hiden QIC-20 mass spectrometer.

Scanning electron microscopy (SEM) analyses of the samples were made through a JEOL JSM-7500F apparatus with the applied voltage of 10 kV.

The morphologies of the catalysts were determined visually using a JEOL JEM 2010 transmission electron micro-scope (TEM) operated at 120.0 kV.

2.3. Catalytic methane reforming with carbon dioxide

The catalytic activity measurements for methane reforming with carbon dioxide were carried out in a fixed-bed tubular quartz flow reactor (6 mm i.d.) under atmospheric pressure. 100 mg of catalyst was placed in the center of the reactor. The molar ratio of CH_4/CO_2 was 1/1, and GHSV was 24,000 mL/(h g$_{cat}$). The catalysts were reduced in situ with pure H_2 at 700 °C for 1 h before the measurement. The effluent gases from the reactor were analyzed on-line using a GC-1690 model gas chromatograph fitted with a TDX-01 column and a thermal conductivity detector (TCD). The conversion of CH_4 (X_{CH4}) and that of CO_2 (X_{CO2}), the yield of CO (Y_{CO}) and syngas ratio were calculated using Eqs. (1)–(4):

$$X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \tag{1}$$

$$X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\% \tag{2}$$

$$Y_{CO} = \frac{F_{CO,out}}{F_{CH_4,in} + F_{CO_2,in}} \times 100\% \tag{3}$$

$$\text{Ratio of } H_2/CO = \frac{F_{H_2,out}}{F_{CO,out}} \tag{4}$$

Where $F_{i,in/out}$ was the flow rate of each component in the feed or effluent.