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Mn and Mg dual promoters modified Ni/α-Al_2O_3 catalysts for high temperature syngas methanation

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ABSTRACT

Mn and Mg doped Ni/α-Al_2O_3 catalysts were prepared by impregnation method for high temperature syngas methanation. The catalysts were characterized by N_2 adsorption-desorption, XRD, HRTEM, H_2-TPR, CO-TPD, CO_2-TPD, CO pulse chemisorption and XPS. Compared to single promoter doped catalysts, dual promoters doped catalysts exhibited better high temperature activity. In particular, an optimal catalyst with Mn, Mg content of 2 wt% (2Mn2Mg) achieved almost 100% CO conversion and 97.5% CH_4 selectivity at 500 °C, 2.0 MPa, and a WHSV of 12,000 $mL{\cdot}g^{-1}{\cdot}h^{-1}$, and showed good stability in stability test. Mn and Mg species could help to form a moderated interaction between NiO with support in co-impregnation process, which inhibited Ni agglomeration in high temperature, improved the Ni dispersion, and enhanced the CO/CO_2 adsorption capacity. Meanwhile, the Ni electron cloud density increased by electron transfer from promoters, which facilitated the dissociation of CO on the catalyst surfaces. In addition, the impregnation sequence and promoters loading was also investigated.

1. Introduction

With environmental deterioration and improvements in environmental protection consciousness, clean and efficient utilization of fossil fuels has become more significant. Compared with other fossil fuels, methane is regarded as a clean fuel with high calorific value, combustion efficiency and lower emissions [1]. However, there is a huge shortage of natural gas around the world. Methanation has attracted much attention from both academia and industry since its discovery in 1902. Gasification of coal to syngas and further conversion to synthetic natural gas via the methanation reaction has become an effective approach for meeting increasing demands for natural gas [2–4]. The strongly exothermic property of syngas methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$, $\Delta H_{298K} = -206.16$ KJ/mol), inevitably leads to regional overheating in the catalyst bed, causing catalyst deactivation by carbon deposition and sintering [5–7]. Therefore, it remains a great challenge to develop methanation catalysts with high activity and good resistance against carbon deposition and sintering at high temperatures.

Many metals have been investigated for methanation reaction, such as Ni, Co, Fe, Rh and Ru. Ni is widely regarded as the optimal choice for its relatively high activity and low cost. Ni- based catalysts supported on various oxides, such as Al_2O_3 [8,9], SiO_2 [10], CeO_2 [11] and TiO_2 [12,13], have been investigated. Among these oxides, aluminum oxide has been extensively used in industrial applications. However, traditional Ni/γ-Al_2O_3 catalysts are vulnerable to deactivation due to the aggregation of small Ni particles at high temperature (300–600 °C) [14,15]. Therefore, it appears necessary to inhibit Ni particle aggregation in syngas methanation catalysts to achieve a high CO conversion and CH_4 selectivity at high temperature.

Unlike γ-Al_2O_3, α-Al_2O_3 support has the superiority of being chemically stable, acid-free and surface inert, which might contribute to the thermal stability of methanation catalysts under harsh conditions [16–18]. However, Ni/α-Al_2O_3 catalysts still have the disadvantage of weak interactions between the active metal and support, which might allow Ni particles agglomerate easily at high temperatures, and thus lower the catalyst's high temperature stability.

The disadvantages of Ni/α-Al_2O_3 catalysts can be overcome by the addition of appropriate promoters. In a previous investigation, MnO_x has been found to be able to generate more oxygen vacancies, promote CO_2 dissociation, and generate surface oxygen intermediates that can react with carbon deposits, reducing carbon deposition on Ni particles during CO methanation [19,20]. MgO has been found to be an effective promoter for improving resistance to carbon deposition and minimize Ni particle sintering [21–24].

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To date, few reports have presented Mn and Mg as dual promoters doped into Ni/α-Al_2O_3 to produce methanation catalysts. In this study, Mn and Mg doped Ni/α-Al_2O_3 catalysts were prepared by an impregnation method for high temperature syngas methanation. These catalysts were characterized by N_2 adsorption- desorption, XRD, HRTEM, H_2-TPR, CO-TPD, CO_2-TPD, CO pulse chemisorption and XPS. Moreover, effects of the impregnation sequence and promoter loading on the physical–chemical properties and catalytic performance of the catalysts were also investigated.

2. Experimental

2.1. Catalyst preparation

All chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd., China, and commercial α-Al_2O_3 purchased from Shandong Aluminum Industry Co. Ltd., China. Before impregnation, the support was calcined in air at 550 °C for 3 h.

The Ni/α-Al_2O_3 catalyst with a consistent Ni loading of 20 wt%, was prepared by a sequenced impregnation and co-impregnation method. A typical process was as follows: $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in deionized water with vigorous stirring and kept at 60 °C for 1 h to form a solution. The α-Al_2O_3 powder (80–100 mesh) was added into the mixed solution for impregnation at 60 °C overnight, and dried in 110 °C for 12 h. The product was next calcined by heating 2 °C/min to 550 °C in air and held for 6 h. $Mg(NO_3)_2{\cdot}6H_2O$ and $Mn(NO_3)_2{\cdot}6H_2O$ were then dissolved in deionized water, mixed with the Ni/α-Al_2O_3 catalyst, and the above steps repeated. The catalysts were denoted as *x*Mn*y*Mg, where *x* and *y* represented the promoter loading (wt%).

To investigate the influence of the impregnation sequences, three different catalysts with the same Ni, Mn and Mg content (20, 2, 2 wt%, respectively) were produced using different sequences: (i) Mn and Mg were co-impregnated on Ni/α-Al_2O_3, (ii) Mg was impregnated on Mn doped Ni/α-Al_2O_3, and (iii) Mn was impregnated on Mg doped Ni/α-Al_2O_3. The prepared catalysts were denoted as 2Mn2Mg, 2Mg-2Mn and 2Mn-2Mg.

2.2. Catalyst characterization

Nitrogen adsorption-desorption isotherms were measured by an ASAP 2020 (Micrometrics, USA). Prior to testing, a sample was degassed under vacuum at 350 °C for 4 h to remove impurities. Specific surface areas were calculated using the Brunauer-Emmet-Teller (BET) method within the relative pressure (p/p_0) range of 0.1–0.3. Total pore volume and average pore diameter were evaluated using the standard Barrett–Joyner–Halenda treatment.

Powder X-ray diffraction (XRD) patterns were measured by a Rigaku Model D/MAX2550 VB/PC measurement using Cu Kα radiation (λ = 1.54056 Å) operated at 50 kV and 100 mA. XRD patterns were recorded with a scanning angle (2θ) range of 10°–80° at a rate of 2°/min.

H_2-TPR, CO-TPD and CO_2-TPD were all measured by an AutoChemII 2920 (Micromeritics, USA). Prior to H_2-TPR, 0.1 g sample loaded in a quartz U-tube was pretreated heated at 350 °C in Ar for 1 h. Then the sample was cooled to room temperature and heated to 1000 °C at 10 °C/min in 10 vol% H_2/Ar with a gas flow of 30 mL/min. For CO-TPD (CO_2-TPD), 0.2 g sample was reduced at 600 °C in H_2 for 2 h. Then the samples cooled to room temperature and saturated with CO (CO_2). After removing physically adsorbed CO (CO_2) by Ar flushing for 1 h, the sample was heated to 600 °C at 10 °C/min in Ar with a gas flow of 30 mL/min. The H_2/CO/CO_2 consumption was monitored using a thermal conductivity detector (TCD).

CO pulse chemisorption was measured by an AutoChemII 2920 (Micromeritics, USA) to investigate the dispersion in the reduced catalyst. 0.1 g sample was reduced at 700 °C for 2 h in H_2, then cooled to room temperature in He, 10% CO/He pulse adsorption was performed at 50 °C for 20 times.

HRTEM and elemental mapping were performed by a transmission electron microscope apparatus (JEOL JEM-2100, Japan) with an accelerating voltage of 200 kV, and fitted with an energy dispersive X-ray detector (EDX, Oxford-INCA). Sample powders were dispersed in ethanol at room temperature for 30 min by ultrasonic and then dipped onto a copper grid.

The Ni binding energy was analyzed by the X-ray photoelectron spectroscopy (XPS) measurement by an ESCALAB 250Xi system (Thermo Fisher Scientific, UK) with Al Kα radiation ($h\nu$ = 1486.6 eV). Binding energies were calibrated using the C *1 s* at 284.6 eV.

2.3. Catalytic evaluation

Syngas methanation reactions were carried out in fixed bed reactor with a stainless steel tube (50 cm length; 10 mm inner diameter). Typically 0.5 g catalyst (80–100 mesh) diluted with suitable amount of inert Al_2O_3 was placed in a uniform temperature zone. The catalysts were heated to 700 °C at a heating rate of 2 °C/min, and then reduced in situ with hydrogen for 2 h. After reduction, the catalyst was cooled to 500 °C with nitrogen. When the temperature was stable, the syngas (15.0 CO, 10.0 CO_2, 70.0 H_2, and 5.0 vol% N_2) was fed into the reactor. The high-temperature catalytic activity of catalysts was conducted at 500–700 °C, 2.0 MPa and a weight hourly space velocity (WHLV) 12,000 $mL{\cdot}g^{-1}{\cdot}h^{-1}$, and stability tests conducted at 600 °C, 2.0 MPa and a WHLV of 12,000 $mL{\cdot}g^{-1}{\cdot}h^{-1}$.

Gas compositions were analyzed using a gas chromatograph (Agilent 7890A) with one flame ionization detector (FID) and two thermal conductivity detectors (TCD). The FID equipped with a HP-POLT 'S' Al_2O_3 column used to analyze CH_4 and $C_{2–6}$ alkenes and olefins, a TCD equipped with two Porapak-Q columns and one 5A molecular sieve column to analyze CO, N_2 and CO_2, and the other TCD equipped with one Porapak-Q column and one 5A molecular sieve column was used to analyze $H_{2.}$

The CO, CO_2 conversion and CH_4 selectivity and yield were calculated using the following formulas.

CO conversation:

$$XCO = \frac{NCO,\text{ in} - NCO\text{,out}}{NCO\text{,in}} \tag{1}$$

CO_2 conversation:

$$XCO2 = \frac{NCO2,\text{ in} - NCO2\text{,out}}{NCO2\text{,in}} \tag{2}$$

CH_4 selectivity:

$$SCH4 = \frac{NCH4,\text{ out} - NCH4\text{,in}}{(NCO,\text{in}-NCO,\text{out}) + (NCO2,\text{in}-NCO2,\text{out})} \tag{3}$$

CH_4 yield:

$$YCH4 = \frac{NCH4,\text{ out} - NCH4\text{,in}}{NCO,\text{ in} + NCO2\text{,in}} \tag{4}$$

where, N_{in} or N_{out} refers to the flow rate (mol/h) at inlet or outlet.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Textural properties of catalysts and support

The textural properties of calcined catalysts and support were measured by nitrogen adsorption-desorption, with the BET surface area of samples summarized in Table 1. The BET surface area of α-Al_2O_3 was only 5.3 $m^2{\cdot}g^{-1}$, which was probably due to tunnel collapses in the support, which occurred during high temperature calcination. BET surface areas of calcined catalysts range from 6.0 to 9.0 $m^2{\cdot}g^{-1}$, and