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Carbon dioxide reforming of methane by solid state synthesis supported catalysts

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ABSTRACT

Ni catalyst supported on $MgAl_2O_4$ mixed oxide was prepared by solid state synthesis, co-precipitation and wet impregnation. The mixed oxide support was synthesized by the solid state synthesis at room temperature ($MgAl_2O_4^{solid}$) and co-precipitation method ($MgAl_2O_4^{cop}$) respectively, followed by wet impregnation for Ni loading. The catalytic performances of these samples were compared in carbon dioxide reforming of methane at 700 °C. The results showed that the catalyst $Ni/MgAl_2O_4^{solid}$ with mixed oxide support prepared by solid state synthesis greatly affected the properties and performance of the catalyst. The catalyst $Ni/MgAl_2O_4^{solid}$ showed higher CO_2 and CH_4 conversion than the $Ni/MgAl_2O_4^{cop}$ catalyst with the support prepared by conventional co-precipitation method. In addition, the BET surface area of the catalyst $Ni/MgAl_2O_4^{solid}$ was three times larger than the catalyst $Ni/MgAl_2O_4^{cop}$.

Introduction

Industrial plants particularly power plants emit huge amounts of CO_2 which causes greenhouse effect. One approach for reducing CO_2 emission is sequestration where CO_2 is captured at the source, transported to an injection site and stored in a suitable geological formation [1,2]. An attractive alternative is to use CO_2 as a raw material for producing useful end-products such as polycarbonates and synthesis gas by copolymerization of CO_2 [3,4] and carbon dioxide reforming of methane [5–10].

Researchers have been searching for a good catalyst for the reforming of methane with CO_2 in the past ten years. Noble metals such as ruthenium (Ru), platinum (Pt) and rhodium (Rh), and non-noble metals such as nickel (Ni) and cobalt (Co) have been studied extensively [5–10]. Nickel has received

increasing attention in recent years because of its cost and performance relative to other metals.

However, Ni-based catalyst deteriorates over time. Sintering occurs at a temperature of 700 °C or above and causes catalyst deactivation. Carbon formed from methane decomposition blocks the catalyst active sites. Many attempts have been made to lengthen catalyst life. The effect of supports such as Al_2O_3, ZrO_2, MgO, and mixture of Al_2O_3 and MgO has been studied [11–17]. The type, size and surface area of the support affect the catalyst activity and carbon formation. MgO is a particularly interesting support for carbon dioxide reforming of methane. With a capacity for oxygen storage, MgO can release oxygen to oxidize the carbon formed on the catalyst surface. Bimetallic catalysts such as Ni—Co supported on Al—Mg oxide [18] showed better performance than their corresponding monometallic catalysts.

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In this study, we introduced a new approach to prepare magnesium aluminate spinel, $MgAl_2O_4$, which acts as a support of catalyst. $MgAl_2O_4$ has received a great deal of attention as a technologically important material [19–21]. It has been employed in several industrial applications such as optical windows for pressure vessels; alternative materials replacing the conventional carbon anode in aluminum electrolytic cells and humidity sensors. Due to its interesting properties such as high thermal resistance, hydrophobic characteristics and good interaction with the metallic phase, magnesium aluminate spinel is widely used as a support material in different catalytic reactions including dehydrogenation [22,23] and alkane reforming [13].

Kong et al. [24] milled oxide mixture using a high energy ball mill. Other techniques have been developed for preparing oxide support. They include co-precipitation [16,18], sol–gel synthesis [25,26], hydrothermal synthesis [27] and freeze-drying [28].

In the present work, we introduced a room temperature solid state reaction using inexpensive chemicals to prepare the $MgAl_2O_4$ spinel support and Ni–$MgAl_2O_4$ catalyst. The chemicals used in the solid state reaction were the metal chloride salts which were cheaper than the nitrate salts often used in a conventional co-precipitation method. We also used conventional co-precipitation method to prepare the $MgAl_2O_4$ spinel support and Ni–$MgAl_2O_4$ catalyst for comparison. All catalysts performance was tested using a reaction of carbon dioxide reforming of methane.

Experimental

Catalyst preparation

Synthesis of support Ni catalysts by wet impregnation (Ni/$MgAl_2O_4^{solid}$ and Ni/$MgAl_2O_4^{cop}$)

Support nickel catalysts were prepared by wet impregnating the supports in an aqueous solution of 6wt.% $Ni(NO_3)_2 \cdot 6H_2O$. The impregnated samples were dried at 100 °C for 24 h after each impregnation. Then it was calcined at 850 °C for 4 h. The supports used for wet impregnation was magnesium aluminate spinel ($MgAl_2O_4$) which were prepared by co-precipitation (denoted as $MgAl_2O_4^{cop}$) and solid state reaction (denoted as $MgAl_2O_4^{solid}$) respectively.

For the $MgAl_2O_4^{cop}$ support prepared by co-precipitation, stoichiometric quantities of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in distilled deionized water (D.D.I. water). The pH value of the resulting solution was adjusted to 9 by adding an ammonia solution. The precipitate was continuously stirred for 3 h at room temperature and then aged overnight. The slurry was filtered and was washed by D.D.I. water. After the slurry was dried, it was calcined at 850 °C for 5 h.

For the $MgAl_2O_4^{solid}$ support prepared by solid state reaction, the precursors of 4.716 g $MgCl_2 \cdot 6H_2O$, 2.8 g $AlCl_3 \cdot 6H_2O$, 0.551 g $NiCl_2 \cdot 6H_2O$ and 5.187 g KCl were mixed and ground for 10 min at room temperature. Then 4.554 g KOH was added into the mixture and further ground for 20 min. The resulting slurry was washed by D.D.I. water with sonication to remove residual Cl ions, until no Cl ions were detected by $AgNO_3$ test.

The slurry was dried at 100 °C for 24 h and was calcined at 850 °C for 5 h.

Synthesis of Ni catalyst by co-precipitation Ni—$MgAl_2O_4$ (cop)

An aqueous solution containing $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (1:2:0.17) were prepared. The pH value of resulting solution was adjusted to 9 by adding an ammonia solution. The precipitate was continuously stirred for 3 h at room temperature and then aged overnight. The filtrate was washed by D.D.I. water. After the slurry was dried, it was calcined at 850 °C for 5 h.

Synthesis of Ni catalyst by solid state reaction Ni—$MgAl_2O_4$ (solid)

The precursors of 4.716 g $MgCl_2 \cdot 6H_2O$, 2.8 g $AlCl_3 \cdot 6H_2O$, 0.551 g $NiCl_2 \cdot 6H_2O$ and 5.534 g KCl were mixed and ground for 10 min at room temperature. Then 4.814 g KOH was added into the mixture and was further ground for 20 min. The resulting slurry was washed by D.D.I. water with sonication to remove residual Cl ions, until no Cl ions were detected by $AgNO_3$ test. The slurry was dried at 100 °C for 24 h and was calcined at 850 °C for 5 h.

Catalyst characterization

The structure of catalyst was examined by X-ray powder diffraction (XRD) in a PW1830, Philips, 2 KW, with Cu-Kα radiation. The BET surface area of catalysts was measured by nitrogen adsorption at 77 K using BET surface area analyzer from Coulter products SA3100. Temperature programmed reduction (TPR) was carried out on a Micromeritics Autochem 2910; 0.1 g sample was placed in a U-shaped quartz tube and was heated at 450 °C for 1 h under Ar gas. Then the sample was cooled down to 50 °C. The sample was reduced in a flow of reducing gas 5% H_2/N_2 at 30 mL/min and was heated from 50 °C to 900 °C at a rate of 10 °C/min. After TPR, the metal dispersion and metal surface density of sample were measured by H_2-chemisorption. The sample was first reduced at 850 °C for 4 h under H_2/Ar. Then it was cooled down and was degassed at 120 °C for 30 min under Ar. The sample was reduced again at 450 °C for 30 min and was evacuated for another 30 min at 120 °C under Ar. H_2 pulse chemisorption was conducted in 30 mL/min of 10% H_2/Ar when the sample was cooled to 35 °C. The amount of carbon deposited on the catalyst after reaction was analyzed by thermogravimetric/differential thermal analyzer (TG/DTA) in TGA Q5000. The used catalyst (0.01 g) was heated in a platinum sample holder from room temperature to 850 °C using flowing air at a heating rate of 5 °C/min.

Catalytic testing

Catalyst testing in the reaction of CO_2 reforming of methane was performed in a tubular fixed-bed quartz reactor (i.d. = 4 mm, length = 43 cm) at 700 °C under atmospheric pressure. The amount of catalyst used in each test was 25 mg catalyst with 25 mg quartz sand as diluent. The catalyst bed with a length of 5—7 mm was fixed with quartz wool. Reactant feed composed of an equimolar mixture of CH_4 (≥99.995%, HongKong Oxygen & Acetylene Co., Ltd.) and CO_2 (≥99.9%, HongKong Oxygen & Acetylene Co., Ltd) at a total flow rate of