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Effect of substitution by Ni in $MgAl_2O_4$ spinel for biogas dry reforming

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ABSTRACT

Mesoporous nanocrystalline $Mg_{1-x}Ni_xAl_2O_4$ (x = 0.10, 0.13, 0.17 and 0.20) with large surface area were synthesized via a simple one-step sol-gel method using nonprecious metals. The prepared $Mg_{1-x}Ni_xAl_2O_4$ catalysts exhibit good catalytic performance towards methane and carbon dioxide dry reforming reaction. The catalysts were evaluated by various techniques, including XRD, BET, TPR, TPO, EPR, Chemisorption, SEM and TEM. All the Ni incorporated $MgAl_2O_4$ samples possessed high BET area (296–305 $m^2\ g^{-1}$) and pore volume (0.47–0.56 $cm^3\ g^{-1}$) with small pore size (6.4–7.4 nm) in meso region after calcination at 700 °C. The TPR results suggested strong interaction effect in Ni–Mg and the reducibility property of the catalysts improved with the increase of nickel doping. $Mg_{0.8}Ni_{0.2}Al_2O_4$ exhibited the highest activity for biogas dry reforming with 72.6% CH_4 and 80.7% CO_2 conversion at 700 °C. Electron paramagnetic resonance (EPR) results indicated that the incorporation of Ni in $MgAl_2O_4$ spinel lattice led to the lattice distortion and formed oxygen vacancies which are a benefit for the dry reforming reaction.

Introduction

Biogas is a versatile renewable energy source, composed mainly of 55–70 vol% CH_4, 27–44 vol% CO_2, small amounts of <3 vol% H_2S, <1 vol% H_2 and traces of NH_3. Except the conventional using of biogas as fuel by direct combustion, biogas also can be used as very applicative feed gas for dry reforming reaction to produce synthesis gas (syngas: CO and H_2), which is recognized as important and low-cost chemical raw materials for producing liquid hydrocarbons in the Fisher-Tropsch reaction or in the methanol production [1–3]. There are several ways to produce synthesis gas such as steam and dry reforming [4], autothermal reforming [5,6], partial oxidation [7,8], ethanol steam reforming [9–12] and glycerol steam reforming [13,14]. Among these methods biogas reforming (dry reforming) is an attractive method since the synthesis gas is being produced from greenhouse gases (CH_4 and CO_2), which is of low cost and environmentally benign with good chemical benefit [15,16].

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Several types of catalysts have been studied as effective catalysts for biogas reforming including the precious metals and the transition metals [17,18]. For instance, Ru and Rh-based catalysts as precious metals have the excellent catalytic activity [19]. Among the transition metals, nickel and cobalt catalysts show promising activity in biogas reforming [18,20]. Previous theoretical calculation studies indicate that dry reforming of CO_2 and CH_4 reaction is thermodynamically favored above 640 °C. It brings the main obstacle in this reaction of carbon formation, which causes the catalyst deactivation during on stream reaction [15,21]. The carbon deposition on the surface of the catalysts takes place through the methane decomposition and CO disproportion reactions [22]. These two reactions are structure sensitive and the rate of carbon formation depends on the physicochemical properties such as the dispersion of active species, crystal size, active metal-carrier interaction and the acidic and basic characteristics of the catalyst [23]. Compared to the nickel and cobalt based catalysts, the precious metal catalysts possess a lower affinity to carbon formation. However, because of the lower price of Ni compared to precious metals, using nickel as an active phase in biogas reforming catalysts is a commercial choice. For minimizing the carbon formation rate and the content of deposited carbon, the addition of promoters, type of support and the preparation method are considered as effective methods [24]. The basic characteristics of the catalyst and catalyst support have been previously employed to catalyze the dry reforming which can dramatically affect the rate of carbon formation [25,26]. In dry reforming reaction based on the reaction mechanism, the adsorption and dissociation of acidic CO_2 take place on the surface of the catalyst support. The use of promoters and catalyst supports with basic properties can enhance the adsorption capacity of the CO_2 and consequently increase the resistance of the catalyst against carbon formation. Magnesium aluminate spinel ($MgAl_2O_4$) as an excellent catalyst support has exhibited high thermal stability and basic properties [21,27–29]. The textural characteristics of the carrier can also affect the Ni nanoparticles (NPs) dispersion and consequently the catalytic activity and carbon formation. Metallic Ni particles are the active sites for dry reforming reaction however they tend to sinter under the reaction conditions, which reduces the number of active sites [30,31]. The incorporation strategy can be the best way to tackle this problem by doping Ni into the $MgAl_2O_4$ spinel structure.

Here we report the synthesis and characterization of mesoporous $MgAl_2O_4$ with the substitution of Mg by Ni in different content via a novel surfactant free sol-gel method and employed as an effective catalyst for CO_2 and CH_4 dry reforming. It is shown that the high catalytic performance of $Mg_{1-x}Ni_xAl_2O_4$ for biogas dry reforming is attributed to its large surface area, the strong metal-support interaction between Ni–Mg and rich oxygen vacancy caused by the substitution of Ni.

Experimental

Sample preparation

The $Mg_{1-x}Ni_xAl_2O_4$ (x = 0.10, 0.13, 0.17 and 0.20) samples were synthesized via a sol-gel method as described in our previous work [32]. For the typical process, the desired amounts of $Al(NO_3)_3{\cdot}9H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ (Molar ratio of (Mg + Ni)/Al is 1/2) were dissolved in the specific content of absolute ethanol (molar ratio of $C_2H_5OH/(Al^{3+}+Mg^{2+}+Ni^{2+}) = 40$). After this step, the C_3H_6O (molar ratio of $C_3H_6O/(Al^{3+}+Mg^{2+}+Ni^{2+}) = 11$) was added to the precursors solution under ambient temperature. By the addition of C_3H_6O and occurrence of an exothermic reaction, the gel was formed in a few minutes. The formed gel was maintained at ambient temperature for 0.5 h and dried at 85 °C for 24 h before being calcined at 700 °C for 3 h.

Characterization

The crystalline phases of the powders were examined by X-ray diffraction (XRD) analysis using a PANalytical X'Pert-Pro instrument. The specific surface area, pore volume, pore size and the distributions of pore size were determined using a BELSORP-mini II instrument. The temperature programmed reduction (TPR), temperature-programmed oxidation (TPO) and CO chemisorption techniques were performed in a Micromeritics chemisorb 2750 instrument. The nickel dispersion of the catalysts was measured by CO chemisorption at 4 °C. Prior to the pulse chemisorption experiments, all samples were reduced under H_2 flow (25 mL/min) at 800 °C and subsequently flushed under He flow.

The morphology of samples was characterized by scanning and transmission electron microscopes (SEM Nova NanoSEM 650 and TEM JEOL JEM-2010 apparatus). Electron paramagnetic resonance (EPR) experiments were conducted on a Bruker EMX X-Band EPR spectrometer with a quartz sample tube of 3.8 mm.

Catalytic evaluation

A quartz tubular fixed-bed reactor (id.: 7 mm) was employed for evaluating the catalytic reactions at ambient pressure. Before the activity test, the catalysts (particle size 0.25–0.5 mm) were pre-reduced at 700 °C for 3 h in H_2 flow (30 mL/min). After that the mixed reactant feed gas with desired molar ratio of CH_4/CO_2 was introduced through the catalyst bed and the activity tests were performed in the range of reaction temperatures from 100 to 700 °C. The outlet gas after the reaction was online monitored by a gas chromatographic instrument (Young Lin, TCD detector, Carboxen 1010 column).

Results and discussion

The XRD patterns of the calcined catalysts are shown in Fig. 1. Comparing with the standard XRD pattern of $MgAl_2O_4$ sample (JCPDS Card No. 77-1203), all the Bragg diffraction peaks in the 2θ range of 10–80° is well-indexed as $MgAl_2O_4$ crystalline as shown in Fig. 1. The diffraction peaks related to the active metal oxide (NiO) were not observed in diffraction patterns, which is due to the high dispersion of nickel oxide in the prepared samples [2]. The XRD results confirmed that the synthesis method and calcination temperature is effective to obtain the homogeneously mixed oxide sample with high dispersed nickel in the structure.