Development of nano Ni_xMg_yO solid solutions with outstanding anti-carbon deposition capability for the steam reforming of methanol

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ABSTRACT

In this study, different types of nano Ni_xMg_yO solid solutions for the steam reforming of methanol were prepared via three different preparation methods. The solid solutions were characterised systematically by using a suite of characterisation techniques. TEM analysis demonstrated that Ni particles in these solid solutions were in nano-scale with an average size of 9.6–12 nm. The catalytic performance of these catalysts was evaluated using a fixed-bed reactor operated under atmospheric pressure at four different temperatures, i.e., 400, 500, 600 and 700 °C, and at two steam-to-carbon ratios (S/C), i.e., S/C = 1 and 3. Results showed that the nano Ni_xMg_yO material (Ni_xMg_yO-hydro), which was prepared using a hydrothermal method, achieved the highest methanol conversion efficiency of 97.4% and hydrogen yield of 58.5% under a S/C ratio of 3. The evaluation on carbon deposition resistance showed that nano Ni_xMg_yO-hydro had no detectable carbon deposited under a S/C ratio of 3. In addition, physical and chemical properties of these catalysts were also studied by using H_2-Temperature-Programmed Reduction/Desorption(H_2-TPR/D), CO_2-Temperature- Programmed Desorption(CO_2-TPD) and X-ray Photoelectron Spectroscopy(XPS). The outstanding carbon deposition resistance of Ni_xMg_yO-hydro was attributed to the "isolation effect" of the Ni_xMg_yO solid solution structure, which restricts Ni nano particles from aggregation. The high basicity of the surface of Ni_xMg_yO-hydro catalyst also resulted in the enhanced adsorption of CO_2 and therefore contributed to anti-carbon deposition by providing oxygen to promote the gasification reaction between carbon and CO_2.

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1. Introduction

In the past few decades, energy consumption increased rapidly worldwide, especially in emerging countries such as China and India [1]. However, the use of fossil fuels to meet the increasing energy demand has already led to severe environmental problems, such as global warming and poor air quality [2]. Since 1990s, as a clean energy carrier, hydrogen, has attracted significant attention globally due to its high energy density, high conversion efficiency and environmental-friendly nature [3]. Currently, hydrogen is produced commercially via processes such as catalytic reforming of natural gas, partial oxidation of heavy oil and coal gasification, etc. [4].
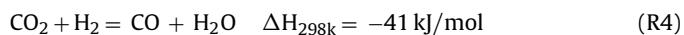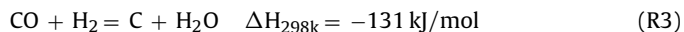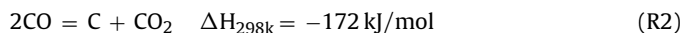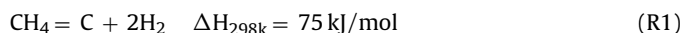
To date, significant amount of work has been carried out to develop catalysts for hydrogen production through catalytic reforming of a variety of raw materials, such as natural gas, biomass, bio-oil and alcohols [5–9]. Among the transition metal catalysts being studied, Ni-based catalysts have been studied extensively due to their high catalytic performance in the steam reforming of oxygenated hydrocarbons and low cost, which make these catalysts widely used commercially [10–12]. However, the use of Ni-based catalysts is usually associated with problems during the steam reforming process, such as deactivation of catalysts and reactor occlusion due to oxidation, sintering, and poor carbon resistance [13].

Generally, carbon deposition occurs via following reactions: hydrocarbon decomposition (R1), CO disproportionation (R2) and

CO hydrogenation (R3) [14]. However, both (R2) and (R3) are accompanied by reverse water-gas shift reaction (R4) [14,15].

$$CH_4 = C + 2H_2 \quad \Delta H_{298k} = 75 \, kJ/mol \tag{R1}$$

$$2CO = C + CO_2 \quad \Delta H_{298k} = -172 \, kJ/mol \tag{R2}$$

$$CO + H_2 = C + H_2O \quad \Delta H_{298k} = -131 \, kJ/mol \tag{R3}$$

$$CO_2 + H_2 = CO + H_2O \quad \Delta H_{298k} = -41 \, kJ/mol \tag{R4}$$

Normally, carbon deposition during reforming process can be suppressed by introducing more steam into the reaction system to promote reverse reactions of (R3) and (R4) to form more CO_2 and less CO, which subsequently inhibits (R2). However, the penalty of such is the increased energy consumption due to the endothermic property of reverse reactions of (R3) and (R4) and the excessive amount of unreacted steam in the reaction system. Another approach to mitigate carbon deposition is to use noble metals such as Pt, Pd, Rh and Ag as active component(s) in the catalysts, which could alleviate the aggregation of Ni particles and subsequently lower the rate of carbon formation [16,17]. The doping of rare earth elements in reforming catalysts was also found effective in inhibiting carbon deposition [18–20]. It is reported that CeO_2 in the catalyst could provide lattice oxygen for coke removal due to its unique redox properties and high oxygen capacities [18,19]. The basic La_2O_3 was also found effective in the activation of CO_2 to remove surface carbon species [20]. In addition, low acidity was found suppress carbon formation via the inhibition of direct decomposition of hydrocarbons [21]. Therefore, alkali or alkali earth elements, such as B, K, Mg and Ca, are often added into alumina catalysts to adjust surface acidity of the catalysts [22–24].

It was also reported that the basic MgO showed high resistance ability for carbon deposition due to its ability to activate CO_2 [25,26]. The high melting point of MgO (3073 °C) contributes to the thermal stability of the catalysts and enables the reaction take place under its hutting temperature, at which metal atoms gain sufficient energy to escape slowly from surface of the crystal [27]. However, the low specific surface area and low catalytic activation of the Ni/MgO catalyst restricted its further development and applications. The Ni_xMg_yO solid solutions have been widely studied and have been proved highly effective for the catalytic reforming of natural gas [28–31]. However, not much work has yet been carried out to understand the catalytic performance of Ni_xMg_yO solid solutions in the steam reforming of methanol, and how preparation methods affect the structure of these nano solid solutions and subsequently influence their catalytic performance and anti-carbon deposition capability.

In this study, the main purpose was to develop nano Ni_xMg_yO solid solutions with high catalytic performance and outstanding anti-carbon deposition property for the steam reforming of methanol. Different preparation methods were adopted to prepare nano Ni_xMg_yO solid solutions with different structures. These catalysts were then tested to evaluate their catalytic performance as well as the propensity in carbon deposition. Fresh and spent catalysts were also characterised to understand the differences in catalytic performance and to reveal the mechanism for the inhibition of carbon deposition.

2. Materials and experimental methods

2.1. Preparation of catalysts

All the chemicals used in this research were analytical grade purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

In this study, three different nano Ni_xMg_yO solid solutions were prepared using three different methods. The preparation of the first type of Ni_xMg_yO catalyst started from the preparation of MgO support by precipitation of $Mg(NO_3)_2 \cdot 6H_2O$ with ammonia at room temperature followed by drying in air at 105 °C for 12 h and calcination in air at 600 °C for 4 h. The catalyst containing 10 wt% nickel in Ni_xMg_yO solid solution was achieved via incipient wetness impregnation (IWI) using aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ impregnated onto the MgO support at room temperature. The catalyst was subsequently dried at 105 °C for 12 h, and then calcined in air at 600 °C for 4 h. This catalyst was denoted as Ni_xMg_yO-impre.

The second type of Ni_xMg_yO catalyst was prepared by following a similar procedure as described previously. The only difference was the added hydrothermal treatment of the catalysts at 100 °C for 24 h after precipitation. This catalyst was denoted as Ni_xMg_yO-hydro.

The third type of Ni_xMg_yO catalyst was prepared by co-precipitation of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ in an ammonia solution at a controlled concentration, followed by aging at 40 °C for 6 h. The aged mixture was then dried in air at 105 °C for 12 h, calcined in air at 600 °C for 4 h, and treated hydrothermally following the same hydrothermal process as the preparation of Ni_xMg_yO-hydro. This catalyst was denoted as Ni_xMg_yO-copre.

In addition, 10 wt% Ni/γ-Al_2O_3 was prepared for comparison purpose using incipient wetness method. The γ-Al_2O_3 support was purchased from V-SK Co., Ltd., which had a BET surface area around $200 \, m^2/g$. Before the impregnation process, the alumina support was calcined at 600 °C for 8 h to remove its surface contaminants. The impregnation was conducted under room temperature. The sample was then dried at 105 °C for 12 h and calcined in oxidizing atmosphere at 600 °C for 4 h. This catalyst was denoted as Ni_xAl_yO.

2.2. Catalytic performance test

The tests of catalytic performance were carried out in a fixed-bed reactor (I.D. = 12 mm) under atmospheric pressure. The fresh catalyst (approximately 0.5 g) was diluted with quartz sand (8 g, Ø 2–3 mm; Aladdin) and placed into the reactor on top of a layer of quartz wool. Prior to each test, the catalyst was reduced in situ with 25 vol% of H_2 in N_2 at a flow rate of 400 ml/min at 600 °C for 1 h.

A mixture of water and methanol was pumped into the testing rig at a flow rate of 1 ml/min (1 atm, room temperature) by using a liquid piston pump (Eldex Lab, Inc) with a reproducibility of ±0.3%. The pump was calibrated prior to each test and maintained frequently to ensure its repeatability and accuracy. Before being fed into the catalytic reactor, the liquid mixture was evaporated in a preheater at 300 °C. Water and methanol mixture with two molar ratios (S/C = 1 and 3) were adopted in this study, together with two different gas hourly space velocities (GHSV, 92,000 ml/($g_{cat} \cdot$h) and 114,000 ml/($g_{cat} \cdot$h)). After passing through a cold trap, the effluent was collected by using a 1 l Tedlar bag and analysed using an off-line Gas Chromatograph (GC-2014, SHIMADZU) equipped with 2 thermal conductivity detectors (TCD) and 1 hydrogen flame ionization detector (FID). In each test, N_2 gas at a flow rate of 300 ml/min was used in the reaction system as a carrier gas. The flow rate of product gas (H_2, CO_2, CO and CH_4) was calculated based on the known flow rate of N_2 and their relative concentration to N_2, which was analysed by using the GC. The calculation of methanol conversion was based on the flow rate of methanol introduced to the reaction system and the corresponding carbon balance. The concentration of other gases detected by the FID, such as ethane, was always very low and was therefore neglected. The methanol conversion, the selectivity of CO formation, the selectivity of CH_4 formation, H_2 yield and the H_2/CO ratio were determined by using following formulae [32,33]:

$$CH_3OH \, conversion \, (\%) = \frac{[CO_2]_{out} + [CH_4]_{out} + [CO]_{out}}{[CH_3OH]_{in}} \times 100\% \tag{1}$$