



CeO₂ Promoted Ni-MgO-Al₂O₃ nanocatalysts for carbon dioxide reforming of methane



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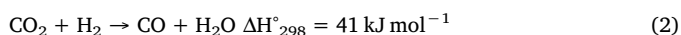
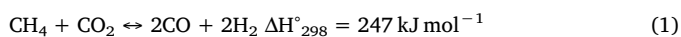
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ABSTRACT

In this study, the catalytic performance of the CeO₂ promoted Ni-MgO-Al₂O₃ catalysts with different preparation methods was studied in carbon dioxide reforming of methane (CDRM) for the production of synthesis gas. The nitrogen adsorption/desorption (BET), X-ray diffraction (XRD), temperature-programmed reduction and oxidation (TPR and TPO), scanning electron microscopy (SEM) techniques were used to characterize the samples. The obtained results showed that the Ce addition to Ni-MgO-Al₂O₃ catalyst with the high specific surface area has a significant influence on the metal crystallite size, reduction properties, and coke deposition. The CeO₂-Ni-MgO-Al₂O₃ catalyst with cerium content of 3 wt.% prepared by the impregnation method possessed the highest resistance against carbon formation in CDRM. In addition, the catalytic results confirmed that the feed ratio (CO₂/CH₄) and GHSV affected the catalytic activity. However, the CH₄ and CO₂ conversions improved when the cerium was added to Ni-MgO-Al₂O₃ catalysts.

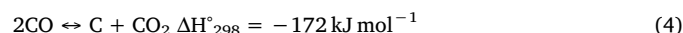
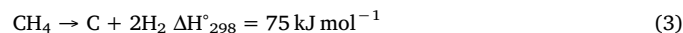
1. Introduction

In recent years, the conversion of natural gas into synthesis gas (composed of hydrogen and carbon monoxide) and hydrogen has received much attention in recent years. There are several ways for hydrogen production as a clean and renewable fuel, such as steam reforming [1–3], partial oxidation [4–6], auto-thermal reforming [7,8] and dry reforming of methane [9–16]. Carbon dioxide reforming of methane (CDRM, Eq. (1)) is desirable for the production of synthesis gas, which can be used for the production of valuable chemical components such as liquid hydrocarbons via Fischer – Tropsch, methanol, and dimethyl ether synthesis. CDRM has two important advantages as follows: (i) this reaction has great potential to remove two major greenhouse gases (methane and carbon dioxide) from the environment simultaneously, (ii) the product molar ratio (H₂/CO) is close to 1, which is suitable for industrial application, such as Fischer Tropsch. In addition, reverse water gas shift reaction (RWGS, Eq. (2)) is generally carried out with the main CDRM, which accompanied by decreasing the product ratio (H₂/CO) to lower extent than 1 [11–19].



To achieve high conversions in this reaction, high temperatures are

required, because CDRM is an endothermic reaction. Several catalysts have been investigated by researchers for this process. Supported transition and noble metals such as Ni, Co, Fe, Ru, Rh, Pt and Ir [10–14], perovskite oxides [20,21] and core-shell catalysts [22,23] have been extensively studied for CDRM. Although noble metal catalysts have high activity and resistance against coke formation than the nickel based catalysts in CDRM, but their industrial uses of these materials are prohibited due to the higher cost and lower accessibility. However, there are no industrial applications for CDRM due to coke deposition on the surface of the catalysts. Coke deposition occurs through methane decomposition (Eq. 3) and Boudouard reactions (Eq. 4) which lead to rapid deactivation [24].



Several methods, such as supports, promoters, synthesized methods, calcination temperatures, operation conditions, reducing environments, particle size and reactor configurations impressed the activity and carbon deposition of nickel based catalysts [25].

Different metals such as MgAl₂O₄, MgO, Al₂O₃ and CeO₂ have been investigated as a catalyst support in CDRM [24,25]. Several studies showed that the basic catalysts improve the carbon reaction with CO₂ and decrease the coke deposition. Among these systems, spinel groups

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are received considerable attention in CDRM. The common formula of the spinel is AB₂O₄ [26]. Nano crystalline magnesium aluminate spinel (MgAl₂O₄), is a member of a class of minerals that possesses unique features such as high chemical and thermal stability, low electrical conductivity, high melting temperatures (~2150 °C) and good catalytic properties [27]. In reforming process, MgO has been used as a promoter and a catalyst support. In addition, this component has the same crystal structure with NiO. It has been reported that NiO-MgO solid solution makes a strong ionic band between active phase and catalyst support, that causes a decrease of coke formation [28].

Using desirable metals as a promoter (such as CaO, SrO, La₂O₃, and CeO₂) is a usual technique for enhancement of the physicochemical features, and suppressing the coke deposition over the nickel based catalysts. In this regard, ceria (CeO₂) is an attractive oxide with special properties such as good reduction-oxidation potential (Ce⁴⁺/Ce³⁺), high oxygen storage capacity, high thermal resistance and it can improve the metallic (Ni) dispersion as well as gasification the deposited coke on the surface of the catalyst [29–33]. The reports showed that the basic property of the catalyst promoted with CeO₂ has a significant effect on the catalytic operation and carbon removal on the surface of the catalyst. Daza et al. [34] examined the catalytic performance of Ni/mineral clay promoted by different amounts of Ce and reported that Ce played an essential function in restriction of coke deposition and improvement of the catalytic activity in CDRM due to the enhancement of nickel dispersion and CO₂ adsorption. Also, Wang and Lu [35] reported the higher reducibility and metal dispersion of Ce promoted Ni/Al₂O₃ catalysts compared to Ni/Al₂O₃ catalyst.

In this article, the performance of the Ni-MgO-Al₂O₃ nanocatalysts (MgO/Al₂O₃ = 1) with various cerium contents prepared by the co-precipitation and impregnation methods was investigated in CDRM for the syngas production.

2. Experimental

2.1. Materials

The metal salt precursors were magnesium nitrate hexahydrate (RANKEM, 99%), nickel nitrate hexahydrate (RANKEM, 98%), aluminum nitrate nonahydrate (Riedel-deHaen, 98%) and cerium nitrate hexahydrate (Merck, 99%). An aqueous NaOH solution was used as a precipitant.

2.2. Catalyst preparation

According to our previous results [36], the Ni-MgO-Al₂O₃ catalyst was prepared by the co-precipitation method. The catalysts promoted with CeO₂ were prepared by two different techniques. In the first method, the Ni-MgO-Al₂O₃ and CeO₂ promoted catalysts with different CeO₂ contents were prepared by the co-precipitation method (COP). The aging temperature of 60 °C and the pH value of 11 were chosen as preparation conditions. The prepared catalysts were calcined at 700 °C for 3 h. In the second method, the catalysts were prepared by a wetness impregnation method (IMP). For this purpose, the calcined Ni-MgO-Al₂O₃ at 500 °C was first dried at 120 °C and then impregnated with an aqueous solution of cerium nitrate to obtain desired content of cerium oxide. After impregnation, the suspension was dried at 85 °C overnight and subsequently calcined at 700 °C for 3 h with a ramp rate of 4 °C/min. In these catalysts, the nickel content was chosen 12.5 wt.% while the CeO₂ content was varied between 1–5 wt.%. The catalysts were nominated as Ce(x)-NMA, where x indicates the weight percent of cerium oxide.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) technique was used for recognition of the crystal phases of the catalysts using a PANalytical X'Pert-Pro X-

ray diffractometer using a Cu-Kα monochromatized radiation source and a nickel filter in the range of 2θ = 10–80°. The BET (Brunauer-Emmett-Teller) surface area was measured by nitrogen adsorption/desorption at liquid nitrogen temperature (–77 K) using an automated analyzer (Belsorp mini II). Before the measurement, the samples were thermally treated under an argon atmosphere at 250 °C for 3 h. Temperature-programed reduction (H₂-TPR) was performed using a Chemisorb 2750 instrument (Micromeritics). Prior to TPR test, the fresh catalyst (100 mg) was outgassed under nitrogen atmosphere at 250 °C for 2 h. The TPR diagrams were recorded from room temperature to 1000 °C with a heating ramp of 10 °C/min under the 5% H₂ in Ar gas (20 ml/min). Temperature-Programed oxidation (TPO) of the spent catalysts was carried out to identify the amount of deposited carbon in the similar instrument as described for TPR analysis by passing an oxidizing gas flow (5% O₂ in He, 20 ml/min). The morphology of the fresh and spent catalysts was examined by a scanning electron microscope (SEM, VEGA TESCAN) operated at 30 kV.

2.4. Catalytic performance

The catalytic CDRM reactions were carried out under atmospheric pressure in a quartz reactor (60 cm length, 7 mm internal diameter). A schematic diagram of the experimental fixed bed setup for CDRM was depicted in Fig. 1. For measurement of the catalytic activity, 200 mg of the catalyst (35–60 μm) was placed in the center of the reactor. Prior to the activity test, the samples were reduced in situ in the hydrogen flow (30 ml/min) at 750 °C for 3 h. A cold trap was located between the reactor outlet and the sampling port in order to remove the water in the effluent gas. The feed gas stream was consisted of CH₄ and CO₂ with various molar ratios and the activity tests were performed at different temperatures ranging from 550 to 700 °C in steps of 50 °C. The decline in catalytic activity at 700 °C was monitored up to 700 min on stream. The exhaust gas mixture was analyzed using an online gas chromatograph (Younglin, YL 6100) equipped with a TCD detector and a Carboxen 1010 column. The column temperature was set at 100 °C and Ar was used as the carrier gas. The reactants conversions (X_{CH₄} and X_{CO₂}), products yield (Y_{H₂} and Y_{CO}) and syngas ratio (H₂/CO) were calculated by the following equations (Eqs. (5)–(9)).

$$X_{\text{CH}_4} \% = \frac{C_{\text{CH}_4\text{in}} - C_{\text{CH}_4\text{out}}}{C_{\text{CH}_4\text{in}}} \times 100 \quad (5)$$

$$X_{\text{CO}_2} \% = \frac{C_{\text{CO}_2\text{in}} - C_{\text{CO}_2\text{out}}}{C_{\text{CO}_2\text{in}}} \times 100 \quad (6)$$

$$Y_{\text{H}_2} \% = \frac{C_{\text{H}_2\text{out}}}{2C_{\text{CH}_4\text{in}}} \times 100 \quad (7)$$

$$Y_{\text{CO}} \% = \frac{C_{\text{COout}}}{C_{\text{CH}_4\text{in}} + C_{\text{CO}_2\text{in}}} \times 100 \quad (8)$$

$$\text{H}_2/\text{CO} = \frac{C_{\text{H}_2\text{out}}}{C_{\text{COout}}} \quad (9)$$

Where C_{i,in} is the initial concentration of component i in the feed and C_{i,out} is the final concentration of component i in the product stream.

3. Results and discussion

3.1. Structural properties of the CeO₂ promoted NMA catalysts

Fig. 2a and b show the XRD patterns of the co-precipitated and impregnated CeO₂-NMA catalysts with various CeO₂ contents. The calcined promoted catalysts exhibited the significant diffraction peaks at 2θ = 28.4°, 32.9° and 56.2°, which interpret the cubic fluorite structure of CeO₂ with (111), (200) and (311) planes, respectively [37]. However, in COP method, the appearance of CeO₂ phase is less

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