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Thermocatalytic decomposition of methane over mesoporous nanocrystalline promoted Ni/MgO·Al₂O₃ catalysts

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ABSTRACT

Thermocatalytic decomposition of CH₄ is an interesting method for the production of hydrogen. In this article, the catalytic and structural properties of the La, Ce, Co, Fe, and Cu-promoted Ni/MgO·Al₂O₃ catalysts were investigated in the thermal decomposition of CH₄. Mesoporous MgO·Al₂O₃ powder with the high BET area (>250 m²/g) was synthesized by a novel and simple sol–gel method. The different instrumental methods (XRD, BET, SEM, H₂-TPR and TPO) were used for evaluating the physicochemical characteristics of the samples. The addition of Cu to Ni/MgO·Al₂O₃ dramatically improved the catalytic performance and the Cu-promoted catalysts exhibited the highest CH₄ conversion and H₂ yields among the promoted and unpromoted catalysts. The Cu-promoted catalyst possessed the highest stability in CH₄ conversion during 10 h of reaction. The results also indicated that the Ni–Cu/MgO·Al₂O₃ catalyst with 15 wt.% Cu showed the highest catalytic activity and stability at higher temperatures (>80% CH₄ conversion).

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Introduction

One of the main challenges facing the world is providing energy with the low release of greenhouse-gas (GHG). The major sources of greenhouse-gas emissions are because of the natural gas, oil and coal combustion for different purposes. Therefore, it is required to develop novel energy sources with low release of GHGs to decrease the content of greenhouse gases [1].

H₂ can be considered as the green energy carrier because it is the simplest, the lightest, the most abundant component and created from renewable resources [2]. Hydrogen can be

considered as a substitution for fossil based fuels without releasing any greenhouse gases [3,4]. In recent years, the research activities have been concentrated on the development of safe production methods with low production price and also the storage and usage technologies [1].

Different methods for the generation of H₂ have been industrially developed [5–7]. Among the industrial production methods, the methane reforming with water vapor and the methane catalytic partial oxidation have been considered as the most cost-effective hydrogen production methods [8]. These mentioned production methods have some disadvantages such as high CO₂ emissions and hydrogen with low purity. The produced H₂ with these methods is not suitable for

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fuel cells applications, and the cost of purification is still a challenge [9].

The thermocatalytic decomposition of CH_4 has been identified as a favorable procedure for the production of high purity hydrogen. This production method is an appropriate technology due to the possibility of the production of pure H_2 , lower energy consumption and production of carbon nanotubes (CNTs)/carbon nanofibers (CNFs) [10,11]. From the thermodynamic view point, this reaction is endothermic ($\Delta H_{293}^0 = 74.8 \text{ kJ/mol}$) and operation at high temperature is essential [12,13]. As mentioned before, the produced hydrogen with this method has higher purity compared to hydrogen produced with other conventional methods. However, the catalyst deactivation is still a challenge in this process. The catalyst deactivation in this process is related to the coverage of the active centers by accumulated carbon [10]. It is found that the reaction parameters such as reaction temperature can affect the reaction rate [14]. In earlier reports, the catalysts based on the Ni, Fe, and Co are reported to be active in thermocatalytic decomposition of methane [15–18]. There are several catalytic factors and reaction parameters that affect the activity of the catalyst in this reaction such as metal loading, type of support, promoter and active metal, synthesis method, reaction temperature and pressure, feed flow rate, etc. [19]. For example, in the research conducted by Li et al. [20], they studied many catalytic features of the thermocatalytic decomposition of methane. It was shown that the catalytic activity was completely depended on the mentioned catalytic factors.

Among these metals, nickel is highly active even at low reaction temperatures. It is reported that the addition of other metals can improve the activity of the nickel catalyst and also increase the catalytic stability even at higher temperatures [10].

MgAl_2O_4 because of its unique characteristics [21] (high melting point, high thermal and mechanical properties, etc.) is an attractive spinel for industrial applications. Furthermore, the magnesium aluminate with mesoporous nanocrystalline structure and high surface area is a potential support for various catalytic reactions [22]. Various methods have been employed for the preparation of MgAl_2O_4 (coprecipitation, sol–gel, solid state reaction, etc.) [23–27]. Nevertheless, some of these preparation methods are difficult and costly, which make them complex for industrial production. Also, the conventional methods such as high-temperature solid-state reaction lead to the preparation of powders with low porosity and specific surface area, which restrict the catalytic applications of the prepared spinel materials. Comparing with other traditional methods, the preparation methods involving template (hard or soft) lead to the synthesis of powders with high porosity and surface area [26–28]. However, these methods are complicated, time consuming and expensive, which prohibits the production in industrial scale. For these reasons, the surfactant-free self-assembly sol–gel technique was applied for the preparation of catalyst support in this article. This method is less complicated and has several advantages such as high purity, high chemical homogeneity, low calcination temperature, low cost, etc. [29].

In the present study, the influence of the promoters (La, Co, Fe, Ce, and Cu) on the physicochemical characteristics of the

$\text{Ni/MgO}\cdot\text{Al}_2\text{O}_3$ catalyst was investigated and the catalytic performance of the prepared samples was studied in the thermocatalytic decomposition of methane. The catalyst supports were prepared by an interesting surfactant-free self-assembly sol–gel technique.

Experimental section

Materials

$\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Samchun), $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Central Drog House), $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Rankem), $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (Samchun), $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, (Daejung), $\text{Ce}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Samchun), $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Samchun) and $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (Daejung) were used as Al, Mg, Ni, La, Co, Ce, Fe and Cu precursors, respectively. Absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, Scharlau) was used as solvent and propylene oxide ($\text{C}_3\text{H}_6\text{O}$, Merck) was also employed as gelation agent.

Preparation of Ni–M/MgO·Al₂O₃ catalysts (M = La, Co, Fe, Ce, and Cu)

The preparation of catalyst carrier was described in our earlier study [24]. In summary, firstly, the calculated amounts of $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ with a molar ratio of $\text{MgO}/\text{Al}_2\text{O}_3 = 2$ were dissolved under stirring in absolute ethanol ($\text{C}_2\text{H}_5\text{OH}/(\text{Mg} + \text{Al})$ mole ratio = 40). The viscous gel was produced within 5 min after addition of the specific content of propylene oxide ($\text{C}_3\text{H}_6\text{O}/(\text{Mg} + \text{Al})$ mole ratio = 11). Then the resulting gel was kept at ambient temperature for 30 min, dried and heat treated at 700°C for 3 h in air atmosphere. The wet incipient impregnation method was employed for the synthesis of the nickel catalysts. According to this method, the prepared $\text{MgO}\cdot\text{Al}_2\text{O}_3$ powder was impregnated with an aqueous solution of nickel and metal nitrates. After this step, the powders were dried at 80°C and subsequently calcined at 500°C for 4 h.

Characterization of catalysts

The X-ray diffraction analysis (XRD) was carried out using a PANalytical X'Pert-Pro. The crystal sizes of the samples were determined using the Debye–Scherer's equation [30].

A BELSORP-mini II analyzer was employed to determine the specific surface area and pore characteristics of the samples. A VEGA TESCAN instrument was used for evaluating the surface morphology and the shape of the accumulated carbon on the catalyst surface. A chemisorb 2750 micrometrics was used for the hydrogen temperature programmed reduction (H_2 -TPR) analysis. In this experiment, the catalysts were out-gassed under an Ar stream at 200°C for 1 h. Then, a gas stream of 10% H_2 in Ar (25 ml/min) was introduced over the catalyst and the reactor temperature raised with a heating rate of $10^\circ\text{C}/\text{min}$. In the same instrument as mentioned for TPR analysis, the temperature-programmed oxidation (TPO) of the catalysts after reaction was done for studying the amount of accumulated carbon by passing an oxidizing gas stream (5% O_2 in He, 25 ml/min) over the sample along with the raise in temperature ($10^\circ\text{C}/\text{min}$).

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