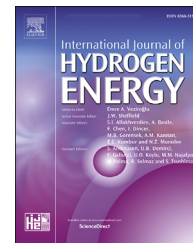




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Thermocatalytic decomposition of methane over mesoporous Ni/xMgO·Al₂O₃ nanocatalysts

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ABSTRACT

This paper describes a facile method to produce mesoporous nanostructure Ni/Al₂O₃, Ni/MgO, and Ni/xMgO·Al₂O₃ (x: MgO/Al₂O₃ molar ratio) catalysts prepared by “one-pot” evaporation-induced self-assembly (EISA) method with some modifications for investigating in the thermocatalytic decomposition of methane. Detailed characterizations of the material were performed with X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and N₂ adsorption/desorption, hydrogen temperature-programmed reduction (H₂-TPR), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and temperature-programmed oxidation (TPO). The characterizations demonstrated that the synthesized catalysts with various MgO/Al₂O₃ molar ratios possessed mesoporous structure with the high BET area in the range of 216.79 to 31.74 m² g⁻¹. The effect of different surfactants and calcination temperatures on the characterizations and catalytic activity of the catalysts were also examined in details. The experimental results showed that the catalysts exhibited high catalytic potential in this process and the 55 wt.% Ni/2 MgO·Al₂O₃ catalyst calcined at 600°C possessed an acceptable methane conversion (~60%) under the harsh reaction conditions (GHSV = 48000 (mL h⁻¹ g_{cat}⁻¹)).

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Introduction

Currently, it is necessary for the scientific community to improve new alternative energies to control the negative

impacts of fossil fuels such as depletion and the unsteady price of them and at the same time the serious environmental damage produced by their consumption (release of greenhouse-gas (GHG)). H₂ can be considered as an attractive and clean energy carrier because of no pollution and the

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ability to produce three times more energy ($39.40 \text{ kWh kg}^{-1}$) than other fuels, such as liquid hydrocarbons ($13.10 \text{ kWh kg}^{-1}$) [1–3]. However, due to the high ability of hydrogen in reaction with other components (oxygen and carbon), H_2 is not a primary fuel and so it should be produced using other resources such as natural gas, coal, biomass, etc. [4,5]. Although, at the current time different methods for the production of hydrogen have been industrially developed [5–7], but 98% of energy is produced from fossil fuels [3]. The production of H_2 is based on the partial oxidation of hydrocarbons and steam reforming of methane, which have been considered as the most cost-effective hydrogen production methods [8–10]. However, the certain amounts of CO and CO_2 emissions are considered as the backside of these methods. Hydrogen with impurities especially carbon monoxide with more than 10 ppm cannot be directly applied in the proton exchange membrane fuel cells, due to the poisoning of the anode catalyst [11–13]. The use of the purification methods for removing these impurities has a negative impact on the economics of the process [14]. Compared with the two processes mentioned above, thermocatalytic decomposition of methane recently has received much attention as an environmentally friendly technology for the production of pure hydrogen without CO_x . In addition, the production of valuable nano-carbon filaments has a positive impact on the economics of the thermocatalytic decomposition of methane process. So far, there is no developed industrial technology for this process because of the low stability of the catalysts employed in this process and the development of a highly active and stable catalyst for this process is still a major challenge [15]. The most serious concerns in the industrialization of the thermocatalytic decomposition of methane are carbon formation on the catalyst surface ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and the thermal sintering of the catalyst support and active metal during this process. It must be mentioned that there are three main steps in this catalytic reaction: external and internal diffusion of the reactants and finally the reaction between the adsorbed reactants with the catalyst surface and the formation of products. During these three steps, the catalytic productivity is strongly influenced by nature, dispersion, loading, particle size and the state reduction of the catalysts (active sites) [16].

Nobel metals-based catalysts such as Ru, Pt, and Pd have been employed in the thermocatalytic decomposition of methane due to high activity and excellent resistance against coke formation during this reaction. However, the high cost and limited availability of the noble metals restrict their use and the development of base metal catalysts for this process is of great importance. Transition metals such as Ni, Co, and Fe are highly active because of the partially filled 3d orbitals, which accelerate the methane cracking by partial acceptance of electrons. Among these transition metals, nickel is considered as a promising candidate in methane decomposition reaction [11,17]. On the other hands, the carrier plays a vital role in the performance and stability of a catalyst and for this reason, it has been intensely examined for the aforementioned CH_4 decomposition reaction. Al_2O_3 has been generally used as a catalyst support, although other support materials such as MgO, TiO_2 , SiO_2 , ZrO_2 , Mg– SiO_2 , H^+ -ZSM-5, USY, LaNiO_3 , MCM-22&41, and CuAl have also been investigated [18–25]. The required characteristics for a potential

support in this reaction are high thermal stability and ability to keep the dispersion of active sites under decomposition conditions [16,26].

The magnesium aluminate spinel (MgAl_2O_4) can be considered as a candidate for the catalyst support in this reaction due to its high thermal shock and mechanical resistance, high melting point ($2135 \text{ }^\circ\text{C}$), mesoporous nanocrystalline structure and high specific surface area [27–29]. Different synthesis methods have been employed for the preparation of magnesium aluminate, such as a wet-chemical technique [30], coprecipitation [31], surfactant assisted precipitation [32,33], sol-gel auto combustion procedure [34], self-heat-sustained (SHS) method [35], molten-salt technique [36], microwave-assisted combustion synthesis [37], etc. Most of these synthesis methods are complicated and costly and the conventional techniques also lead to the preparation of this ceramic powder with the low specific surface area. Among various synthesis routes, the surfactant-assisted methods (hard or soft templates) make possible the preparation of powders with the high surface area and porosity [38–41]. Comparing with other the surfactant-assisted synthesis routes, those using poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers [(EO) x (PO) y (EO) x] (such as (EO) $_{20}$ (PO) $_{70}$ (EO) $_{20}$ triblock copolymer (Pluronic P123)) as soft templates has attracted a lot of attention since they are economical, commercially available and give materials with relatively uniform mesoporous structure. In previous studies, Al_2O_3 thin films with the use of evaporation-induced self-assembly method were synthesized [42] and this method was also employed for the catalyst preparation with mesoporous structures [43]. Another study presented the use of triblock copolymers as soft templates for the preparation of 3-dimensional (3D) mesoporous materials [44]. Morris et al. [41] proposed the one-pot synthesis method for the synthesis of alumina-supported metal oxides, which is also applicable for the preparation of various metal oxides such as MgO, CaO, NiO, TiO_2 , and Cr_2O_3 .

In recent years our research group developed a surfactant-free self-assembly sol-gel method using propylene oxide as a gelation agent for the synthesis of mesoporous nanocrystalline MgO– Al_2O_3 powders [1,29]. We showed that the MgO· Al_2O_3 powder with MgO/ $\text{Al}_2\text{O}_3 = 2$ exhibited acceptable catalytic activity for the thermocatalytic decomposition of methane. Herein, we report for the first time the use of MgO· Al_2O_3 powders in this process which were prepared by “one-pot” evaporation-induced self-assembly (EISA) method with some modifications. Also the effect of different surfactants and calcination temperatures on the activity and stability of Ni/MgO· Al_2O_3 catalysts were investigated in details. We are sure that the fabrication strategy for the Ni-based catalysts supported on the magnesium aluminate powder may provide a valuable reference for the design of catalysts with high potential for the thermocatalytic decomposition of methane to pure hydrogen.

Experimental section

Catalysts preparation

The one-pot evaporation-induced self-assembly (EISA) method was employed for the synthesis of the mesoporous

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