INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–13

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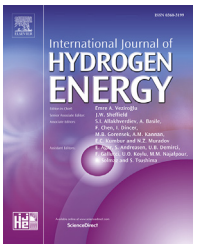

Hollow hierarchical Ni/MgO-SiO_2 catalyst with high activity, thermal stability and coking resistance for catalytic dry reforming of methane

Qing Zhang, Xiaoqian Feng, Jing Liu[*], *Liping Zhao, Xuefeng Song, Peng Zhang*[**], *Lian Gao*

State Key Lab of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, PR China

ARTICLE INFO

Article history:
Received 19 March 2018
Received in revised form
22 April 2018
Accepted 3 May 2018
Available online xxx

Keywords:
Ni nanoparticles
MgO
Silica support
Dry reforming of methane
Hierarchical

ABSTRACT

The methane dry reforming (DRM) simultaneously converts the two greenhouse gases and produces syngas (CO + H_2), which is being significant for both environmental and industrial consideration. Employing well-defined crystal oxides as precursors can produce Ni-based DRM catalysts with good sintering and coking resistance by enhancing the metal-support interactions. Adding basic promoters also is considered as an effective way to improve the coking resistance of DRM catalysts, although challenge remains in the control over the structure, morphology and interaction of the promoter in the catalyst. To well combine the two methods together for better catalytic performance, in this work a Ni/MgO-SiO_2 catalyst was synthesized through a facile one-pot hydrothermal process, during which Ni-phyllosilicate formed as the precursor of Ni particles and MgO promoter was generated in form of Mg-phyllosilicate. This Ni/MgO-SiO_2 had a hierarchical hollow sphere structure with large surface area (477.4 m^2/g). Both the Ni particles (avg. 6.0 nm) and MgO promoter uniformly distributed. This hollow hierarchical catalyst performed high activity, thermal stability and coking resistance for catalytic dry reforming of methane.

Introduction

Rapid consumption of fossil fuels has triggered a series of environmental and energy crisis. The increasing emissions of carbon dioxide induce severe global warming and climate changes as the result of greenhouse effect. Search for effective methods to realize the reduction or utilization of carbon dioxide is extremely urgent. Methane, the main component of natural gas, is another kind of greenhouse gas [1,2]. Methane is also considered as an alternative for coal and petroleum as a relative clean energy resource and a chemical source. The industrial utilization of methane has been highlighted recent years due to the worldwide discovery and exploitation of shale gas [3,4]. The dry reforming of methane (Eq. (1)) is an effective route to convert the two greenhouse gases, carbon dioxide and methane into syngas with a low H_2/CO ratio, which is suitable for the later production of long chain hydrocarbons

* *Corresponding author.*
** *Corresponding author.*
E-mail addresses: sherry-chang@sjtu.edu.cn (Q. Zhang), fxq1234567@sjtu.edu.cn (X. Feng), liujing2014@sjtu.edu.cn (J. Liu), lipingzhao@sjtu.edu.cn (L. Zhao), songxfeng@sjtu.edu.cn (X. Song), pengzhang2010@sjtu.edu.cn (P. Zhang), liangao@mail.sic.ac.cn (L. Gao).
https://doi.org/10.1016/j.ijhydene.2018.05.010
0360-3199/

through Fischer-Tropsch synthesis and oxygenates through oxo-synthesis [5–8]. This reaction simultaneously consumes these two destructive greenhouse gas and produces valuable chemical products, being of great benefit to both environmental and commercial consideration [9–11].

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO,\ \Delta H_{298} = +247\ kJ/mol \quad (1)$$

Stable and economical catalysts are in urgent need to realize the industrialization of methane dry reforming. Traditional noble metal (Rh, Ru, Pt, and Pd) catalysts present high catalytic activity, superior resistance to carbon deposition and sintering in DRM [12]. Nevertheless, considering the exorbitant price and limited reserves, noble metals are not industrial competitive with other transition metals. Nickel based catalysts are the most favorable catalysts for DRM in recent years for its high activity, abundant reserves and bargain price [13–17]. However, Ni based catalysts usually undergo severe deactivation due to sintering and coke deposition. Many researches were carried out to solve these two problems, especially the carbon deposition which plays the main role in catalysts inactivation [18–22].

Recent years, many researchers employed well-defined crystal oxides as nickel precursors (e.g. perovskites ABO_3 [23,24] , spinels ABO_4 and A_2BO_4 [25,26] , hexaaluminates $AB_yAl_{12-y}O_{19-\delta}$ [27], phyllosilicates [28,29] and solid solutions [30,31] ; B=Ni) to obtain well-dispersed small Ni particles with strong metal-support interactions [32]. Ni species are homogeneously dispersed in such defined structures. The crystal lattice effectively limits the growth and migration of Ni species, thus Ni nanoparticles with uniform distribution could be obtained after reduction. As a result, catalysts prepared from these precursors usually result in improved catalytic activity and thermal stability [32–34]. In our previous work [25], we found that Ni/γ-Al_2O_3 catalyst reduced from $NiAl_2O_4$ performed superior sintering and coking resistance than those reduced from NiO/γ-Al_2O_3.

Addition of basic promoters (e.g. K_2O [35,36], CaO [37,38], MgO [29,39,40], La_2O_3 [41], CeO_2 [42,43] and Ga_2O_3 [44]) is another effective method to improve the catalyst activity and coking resistance of DRM catalysts through increasing the basicity of supports. It is generally accepted that supports with basic properties are helpful in adsorption and activation of CO_2 species on the catalysts, suppressing the carbon formation through CO disproportionation [13,44,45]. Among these promoters, MgO was reported to exhibit superior catalytic performance and coke suppression [46]. The bargain price of MgO, as well as nickel, contributes to its competitiveness for a future industrial application in DRM. MgO promoter is also valid in promoting catalyst activity and stability through enhancing the sintering resistance and metal-support interaction [20]. Guo et al. found that the formation of $MgAl_2O_4$ phases in Ni/MgO-γ-Al_2O_3 could suppress the formation of $NiAl_2O_4$ and stabilize the Ni nanoparticles, leading to higher catalytic activity, coking resistance and sintering resistance [20]. However, MgO promoter was generally added through traditional wet impregnation method or co-precipitation method, which resulted in a weak interaction and inhomogeneous distribution on the support. The weak promoter-support interaction may cause aggregation of the promoter and coverage of metal active sites by the promoter. Therefore, the challenge still remains in the control over the structure, morphology and interaction of the MgO promoter in the catalysts.

Herein we designed and synthesized a MgO promoted Ni/MgO-SiO_2 catalyst. Ni and Mg elements were introduced onto the SiO2 support simultaneously by a one-pot hydrothermal method to guaranty both stronger metal-support and promoter-support interactions. The stronger metal-support interaction could be achieved from reduction of the well-defined Ni-phyllosilicate precursor. The homogeneous distribution of MgO during hydrothermal deposition is desired for the enhanced promotion effect to the catalysis. The growth process of the hollow hierarchical Ni/MgO-SiO_2 nanocomposites during hydrothermal condition and hydrogen reduction was investigated. Its catalytic performance and coking resistance for DMR were compared with Ni/SiO_2, IM-Ni/SiO_2, and IM-Ni/MgO-SiO_2 to investigate the effects of preparation methods, hierarchical structure, and MgO addition. The structural stability of the catalysts at high reaction temperatures was also compared and discussed.

Materials and methods

Materials

Ethyl alcohol (C_2H_5OH), isopropanol (C_3H_7OH), Tetraethyl orthosilicate (TEOS, 99%), $NH_3 \cdot H_2O$ (28%), $CO(NH_2)_2$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were obtained from Sinopharm Chemical Reagent Co. Ltd, China. All the reagents were used without additional purification.

Synthesis

Synthesis of SiO_2 spheres

SiO_2 spheres were synthesized through Stober method. TEOS (1.0 mL) was slowly dropped into the mixture of deionized water (15 mL) and isopropanol (35 mL) under magnetic stirring. Then aqueous solution of ammonia (1 mL) was dropped into the solution. After stirring for 2 h at room temperature, the precipitated silica spheres were collected by centrifugation and washed 3 times with ethanol and deionized water.

Synthesis of Ni/MgO-SiO_2 and Ni/SiO_2

SiO_2 spheres (0.12 g, equivalent to 2×10^{-3} mol), $Mg(NO_3)_2 \cdot 6H_2O$ (0.26 g, equivalently 1×10^{-3} mol) and $CO(NH_2)_2$ (2.70 g, equivalently 0.045 mol) were dispersed in the mixture of deionized water (8 mL) and ethyl alcohol (9 mL) under sonication and aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (8 mL, 0.1 M) was dropped in. After 5 h, the suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 190 °C for 36 h. The resulting precipitates were collected by centrifugation and washed 3 times with deionized water. The hydrothermal product was dried under vacuum at 60 °C for 10 h and then reduced in 5% H_2/Ar at 700 °C for 5 h. The reduced product was denoted as Ni/MgO-SiO_2.

To investigate the effect of MgO promoter, Ni/SiO_2 was synthesized as a reference sample through the same hydrothermal method using SiO_2 spheres (0.12 g), $CO(NH_2)_2$ (2.70 g)

Please cite this article in press as: Zhang Q, et al., Hollow hierarchical Ni/MgO-SiO_2 catalyst with high activity, thermal stability and coking resistance for catalytic dry reforming of methane, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.05.010