



Short communication

Formation of magnesium silicate on surface of silica for steam reforming of liquefied petroleum gas



Xiujing Zou, Zonglei Tian, Xueguang Wang*, Mingwu Tan, Weizhong Ding, Xionggang Lu

State Key Laboratory of Advanced Special Steel, Shanghai University, Yanchang Road No. 149, Shanghai 200072, China

ARTICLE INFO

Article history:

Received 11 March 2015

Received in revised form 8 May 2015

Accepted 9 May 2015

Available online 12 May 2015

Keywords:

Magnesium silicate

Coated

Silica

Liquefied petroleum gas

Steam reforming

ABSTRACT

Magnesium silicate coated on silica (Mg_xSiO) was developed through the reaction of hydroxyl groups on the silica surface with $MgCl_2$, followed by hydrolyzing with ammonia. The results of XRD, FTIR and N_2 sorption demonstrated that magnesium silicate ($MgSiO_3$) was uniformly formed on silica surface, producing BET surface areas higher than SiO_2 . CO_2 -TPD and NH_3 -TPD results revealed that $MgSiO_3$ formation increased both acidic and basic sites on the silica surface. Ni catalysts supported on Mg_xSiO were used for steam reforming of liquefied petroleum gas and exhibited better catalytic activity, stability and coke resistance compared with the counterpart on MgO/SiO_2 prepared by conventional impregnation method.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells operating with hydrogen have attracted considerable attention for stationary and mobile applications because of their quick start-up, zero emissions and high intrinsic energy efficiency [1]. Steam reforming of natural gas is currently the most economical process for the supply of hydrogen [2,3]. The facilities for hydrogen production have to be constructed near natural gas pipelines because the storage and transportation of liquefied natural gas require large energy inputs due to the low liquefaction temperature of methane [4]. Liquefied petroleum gas (LPG), a widely used residential fuel, composed mainly of propane and butane without sulfur, is a preferred potential feedstock for distributed hydrogen production for fuel cell applications due to its higher energy density than natural gas, easy storage and transportation, and well-established distribution infrastructures for the fuels [5–7].

In the aspect of hydrocarbon reforming, Ni based catalysts have been recognized as promising catalysts because of their high catalytic activity and low cost [8]. However, the reforming catalysts of higher hydrocarbons can suffer from catalyst deactivation, which results from carbon deposition during the thermal cracking of hydrocarbons at high temperatures [9,10]. An effective approach for solving this problem is to develop a novel catalyst with not only high activity but also high resistance to coke deposition. Therefore, a great deal of effort has been made to improve the activity, stability, and resistance to coke formation of nickel-based catalysts through adding promoters, modifying catalyst supports, improving catalyst preparation routes, etc. [11–13].

Recently, magnesium silicate and its derivatives due to their tunable properties have been attracted a considerable amount of researches for advanced applications as catalyst or catalyst support [14–20]. Magnesium silicate materials were usually synthesized above 1000 °C, leading to low surface area and small porosity, which limit their catalytic applications. Silica possesses good thermal stability and high specific surface area. However, silica supported Ni catalysts exhibit poor catalytic performance for reforming of hydrocarbons. It can be expected that magnesium silicate coated on silica with a relatively high surface area and special acidity/basic properties should be an excellent support of Ni catalysts for the reforming of hydrocarbons.

In this work, magnesium silicate coated on silica (Mg_xSiO) with a high specific surface area was successfully prepared through the reaction of hydroxyl groups on the silica surface with $MgCl_2$, and followed by hydrolysis with ammonia. Magnesium silicate was formed at a low calcination temperature of 600 °C. To the best of our knowledge, this is the lowest prepared temperature ever reported for the formation of $MgSiO_3$ on the SiO_2 surface. Mg_xSiO supported Ni catalysts were compared with the counterpart on silica support for the steam reforming of LPG as a model compound.

2. Experimental

2.1. Material preparation

Mg_xSiO with different nominal Mg/Si molar ratios (x) was prepared according to the following procedure. 12 g silica was added into 80 mL of an aqueous solution of $MgCl_2$ (0.625–3 mol/L) under stirring. The mixture was maintained in a sealed bottle at 50 °C for 24 h and formed

* Corresponding author.

E-mail address: wxc228@shu.edu.cn (X. Wang).

the transparent gel. After this, 125 mL of diluted ammonia (2 wt.%) was added into the gel and mixed fully by shaking the sealed bottle, then kept at 80 °C for 24 h. Finally, the precipitate was filtered, washed with deionized water and dried at 110 °C overnight. For comparison, MgO/SiO₂ containing 20 wt.% MgO was prepared by wet impregnation method with Mg(NO₃)₂ aqueous solution. All the samples were calcined at 600 °C for 6 h.

Ni/SiO₂, Ni/MgO/SiO₂ and Ni/Mg_xSiO catalysts were prepared by impregnating the solid (10 g) into 50 mL Ni(NO₃)₂ aqueous solution. The mixture was evaporated at 80 °C and dried at 110 °C overnight, and finally calcined at 600 °C for 6 h under air. The loading of Ni in all the catalysts was fixed at 10 wt.%.

2.2. Material characterization

Elemental analysis of Mg and Si in the solid samples was performed by X-ray Fluorescence Spectrometer (XRF) analysis with a Shimadzu XRF-1800 spectrometer. Powder X-ray diffraction (XRD) was performed with a Rigaku D/Max-2550 diffractometer using Cu K α radiation at 40 kV and 200 mA. N₂ adsorption-desorption was conducted using a Micromeritics ASAP 2020 Sorptometer at liquid nitrogen temperature (−196 °C). The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method. Pore size distribution curves were calculated using the desorption branches of the isotherms and the Barrett–Joyner–Halenda (BJH) method. IR spectra were recorded with a BRUKER TENSOR 27 spectrometer by diluting samples in KBr. Temperature programmed desorptions (NH₃-TPD and CO₂-TPD) were performed on an autochem II 2920 chemisorption instruments. Thermo gravimetric (TG) analysis of the used catalysts was carried out on a SDT Q600 thermogravimetric analyzer in an air flow.

2.3. Catalytic test

The commercially available auto LPG, consisting of 3.1 vol.% C₂H₆, 84.0 vol.% C₃H₈, and 12.9 vol.% C₄H₁₀ (Shanghai Auto Energy Co., Ltd.), was used without further purification. The reforming reaction was performed at atmospheric pressure in a vertical continuous-flow fixed-bed reactor at 600 °C and at gas hourly space velocity (GHSV) of 30,000 mL g_{cat}^{−1} h^{−1} with a steam to carbon molar ratio (S/C) of 2.0. Before testing, the catalysts were reduced in a flow of 20 vol.% H₂/N₂ at 600 °C for 4 h. The effluent gas was dried and analyzed using an on-line GC-FID gas chromatograph for hydrocarbons, followed by another GC-TCD gas chromatograph for CH₄, CO and CO₂ and H₂. On the basis of the carbon balance in the effluent gas under the assumption of no carbon deposition, the conversion of LPG was defined as the percentage of the total molar flow rate of the carbon-containing products, i.e. CH₄, CO and CO₂ in the exit gas to the molar flow rate of carbon in the feed gas, as described in Ref. [5,6]. In all the analyses, the overall mass balance was more than 97% on the basis of carbon in the starting reactants.

3. Results and discussion

3.1. Textural and physicochemical properties of Mg_xSiO materials

Fig. 1 presented typical XRD patterns of SiO₂, MgO/SiO₂ and Mg_xSiO samples ($x = 0.1, 0.25, 0.5, 0.75$ and 1.0). Compared to SiO₂, all the Mg_xSiO samples exhibited two new diffraction peaks positioned at $2\theta = 34.9^\circ$ and 60.3° , which were in accordance with the positions of XRD peaks for MgSiO₃ (JCPDS card 47–1750). The peak intensity gradually increased with the nominal Mg/Si molar ratio in the range of 0–0.75. When the nominal Mg/Si molar ratio was further increased, the peak intensity almost kept unchanged. The diffraction peaks were very diffused and showed approximate peak widths. This result implied that MgSiO₃ formed was uniformly dispersed on silica surface. Similar to SiO₂, MgO/SiO₂ sample exhibited only a very broad band in the 2θ range from

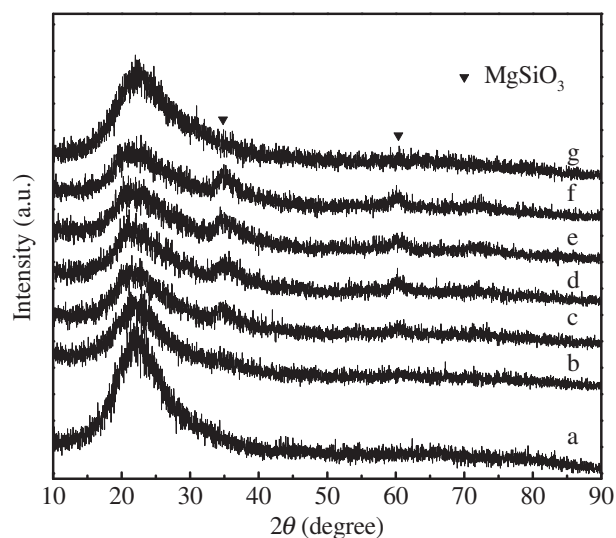


Fig. 1. XRD patterns of the prepared samples. (a) SiO₂; (b) Mg_{0.1}SiO; (c) Mg_{0.25}SiO; (d) Mg_{0.5}SiO; (e) Mg_{0.75}SiO; (f) Mg_{1.0}SiO; (g) MgO/SiO₂.

15–30° corresponding to amorphous SiO₂, implying that no MgSiO₃ was formed by the impregnation method.

The results of elemental analyses in the Mg_xSiO samples by XRF were listed in Table 1. It could be seen that the actual Mg/Si molar ratio increased rapidly to 0.36 with raising nominal Mg/Si molar ratio to 0.75. However, as the nominal Mg/Si molar ratio was further increased to 1.0, the actual Mg/Si molar ratios almost kept unchanged at 0.37. In combination with the XRD results, it could be speculated that MgSiO₃ formed on silica surface had a maximum value and homogeneously dispersed on the silica surface. In a word, excess Mg ions unreacted with hydroxyl groups were washed out in the preparation process due to weak interaction.

The BET surface areas, pore volumes and pore sizes of the samples were summarized in Table 1. It could be seen that compared with SiO₂, the prepared Mg_xSiO samples exhibited a clear increase in BET surface area, pore volume, and a decrease in pore size with raising nominal Mg/Si molar ratio to 0.75. As the nominal Mg/Si molar ratio was further increased to 1.0, BET surface area increased slightly. However, BET surface area of MgO/SiO₂ showed a clear decrease, mainly due to the existence of MgO on the surface and the blocking of part of microspores in the support. In combination with the XRD and XRF results, these results might be related to the formation of MgSiO₃, producing BET surface areas higher than SiO₂.

Fig. 2 showed the IR spectra for the Mg_xSiO samples in the wavenumber range of 1400–400 cm^{−1}. It could be seen that the development of the bands (or shoulder) at 1056, 1028 and 667 cm^{−1} increased with raising Mg/Si molar ratios. This was accompanied by a decrease in the intensity of bands at 1104, 800 and 470 cm^{−1} attributed to the Si–O–Si stretch [21–24]. The development of the bands at 1056

Table 1

Physicochemical properties for the prepared samples and deposited carbons amount over supported Ni catalysts for steam reforming of LPG.

Materials	Mg/Si mol ratio by XRF	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p (nm)	Carbon amount (mg/g _{cat}) ^a
SiO ₂	0	197	0.71	14.5	–
Mg _{0.1} SiO	0.08	254	1.00	15.7	250
Mg _{0.25} SiO	0.22	373	0.95	10.2	150
Mg _{0.5} SiO	0.33	418	0.83	7.9	93
Mg _{0.75} SiO	0.36	427	0.79	7.4	42
Mg _{1.0} SiO	0.37	432	0.72	7.0	40
MgO/SiO ₂	0.37	126	0.53	16.7	153

^a Deposited carbon amount measured by TG over supported Ni catalysts for steam reforming of LPG at 600 °C for 7 h.

Download English Version:

<https://daneshyari.com/en/article/6503386>

Download Persian Version:

<https://daneshyari.com/article/6503386>

[Daneshyari.com](https://daneshyari.com)