Catalytic performances of Ni/mesoporous SiO$_2$ catalysts for dry reforming of methane to hydrogen

Fei Huang[a], Rui Wang[b,c], Chao Yang[a], Hafedh Driss[d], Wei Chu[e], Hui Zhang[a,b,*]

[a] College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, Sichuan, China
[b] Oil & Gas Field Applied Chemistry Key Laboratory of Sichuan Province, Chengdu 610500, Sichuan, China
[c] Drilling & Production Engineering Technology Research Institute, CNPC Chuanqing Drilling Engineering Co. Ltd., Guanghan 618300, Sichuan, China
[d] SABIC Chair in Catalysis, King Abudulaziz University, Jeddah 21589, Saudi Arabia
[e] Department of Chemical Engineering, Sichuan University, Chengdu 610500, Sichuan, China

ABSTRACT

Several mesoporous silicas with different morphologies were controllably prepared by sol-gel method with adjustable ratio of dual template, and they were further impregnated with aqueous solution of nickel nitrate, followed by calcination in air. The synthesized silica supports and supported nickel samples were characterized using N$_2$-adsorption/desorption, X-ray diffraction (XRD), H$_2$ temperature-programmed reduction (H$_2$-TPR), Scanning electron microscope (SEM), Transmission electron microscope (TEM) and thermo-gravimetric analysis (TGA-DTG) techniques. The Ni nanoparticles supported on shell-like silica are highly dispersed and yielded much narrower nickel particle-size than those on other mesoporous silica. The methane reforming with dioxide carbon reaction results showed that Ni nanoparticles supported on shell-like silica carrier exhibited the better catalytic performance and catalytic stability than those of nickel catalyst supported on other silica carrier. The thermo-gravimetric analysis on used nickel catalysts uncovered that catalyst deactivation depends on the type and nature of the coke deposited. The heterogeneous nature of the deposited coke was observed on nickel nanoparticles supported on spherical and peanut-like silica. Much narrower and lower TGA derivative peak was founded on Ni catalyst supported on the shell-like silica.

© 2016 Science Press, Published by Elsevier B.V. and Science Press.

1. Introduction

The dry reforming of methane with carbon dioxide has attracted more attention in recent years because of the effective utilization of greenhouse gases (CH$_4$ and CO$_2$) to produce fuel via synthesis gas (syngas, H$_2$/CO mixtures) by Fischer–Tropsch (FT) reaction [1–5]. Additionally, this is an effective way to convert renewable energy into chemicals [6–10].

CO$_2$ dry reforming of methane (DRM) could be processed on metal catalyst. The noble metals catalysts, such as Ru, Rh, Pt, Pd and Ir based catalysts, exhibited fascinating catalytic activity, selectivity, stability and low coke deposition [11–13]. However, low reserves and high cost of noble metals restricted their commercial applications. The transition metal Ni-based catalysts promote its favoritism as commonly used catalysts for the dry reforming of methane because of their economic advantages and comparatively

high activity. Unfortunately, under reforming conditions, Ni catalyst is easy to sinter to form Ni clusters, more susceptible to coke formation, and thus led to rapid deactivation [14,15].

Highly efficient catalyst design is crucial issue over DRM reaction. Many attempts have been made to develop stable Ni-containing reforming catalysts. Recent research works mainly focus on modifying supports properties using different types of supports, and the preparation method, or the addition of activity modifiers to improve Ni catalysts coke resistance in the DRM reaction [1,3,16,17]. Various ceramic oxides such as MgO, Al$_2$O$_3$, ZrO$_2$, CeO$_2$, La$_2$O$_3$, have been intensively used as nickel based catalyst for the DRM reaction [18–27]. Oxides with low concentration Lewis acidity and/or basic sites (e.g. MgO, ZrO$_2$, La$_2$O$_3$) show lower coke deposition rate [24,28]. Some supports such as CeO$_2$, ZrO$_2$ with high oxygen storage capability as a promoter for Ni catalysts dramatically increased Ni dispersion which was favorable to resist Ni particles sintering [29,30].

Besides above mentioned supports, mesoporous SiO$_2$ molecular sieves with high specific surface area, neutral acidity/basicity property and excellent thermal stability are widely used as support in the dry reforming of methane (DRM) reaction. To our best

Table 1. Adsorption properties of mesoporous silica and nickel catalysts.

Samples	Adsorption properties of mesoporous silicas and nickel catalysts			Particle size (NiO)[a] (nm)
	S_{BET} (m²/g)	TPV (cm³/g)	Pore diameter (nm)	
S1	807.4	0.855	11.23	–
S2	844.9	1.078	3.37	–
S3	700.1	1.206	3.81	–
Ni/S1	555.1	0.682	3.42	6.9
Ni/S2	492.9	1.014	3.85	5.7
Ni/S3	407.1	0.810	3.84	8.8

[a] Particle diameter was calculated from the NiO (200) planes using the Debye–Scherrer equation ($d = 0.89\lambda/\beta\cos\theta$).

knowledge, the physicochemical properties of catalysts varies with the different structure supports adapted, in which the specific surface area and pore size distribution usually play vital roles. Although some researchers have examined the properties of Ni-based silica catalysts prepared via different methods. However, there is no detailed comparative study investigating the morphologic and structure influence of silica support on Ni-based catalysts and catalytic performance in dry reforming of methane.

Herein, sol-gel method was utilized to synthesize mesoporous SiO₂ by varying the amount of 1-Dodecanol as template. With the content of 1-Dodecanol increasing during the synthetic process of silica, morphology and structure of silica dramatically varied. The textural structure and morphology of silica materials synthesized was assumed by N₂ adsorption-desorption isotherms (BET), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) methods. The silica supports were impregnated with nickel precursor and the nickel content was 10 wt%. The properties of the deposited NiO were examined by X-ray diffraction (XRD), nitrogen adsorption/desorption, transmission electron microscope (TEM) and H₂ temperature-programmed reduction (H₂-TPR). The catalytic activity, selectivity and stability of nickel catalysts for carbon dioxide reforming of methane were investigated in detail.

2. Experimental

2.1. Synthesis of mesoporous silica and nickel catalysts

Mesoporous silica was synthesized by the modified sol-gel method reported in reference [31]. Firstly, 100 mg CTAB (Cetyltrimethylammonium Bromide, C₁₆H₃₃(CH₃)₃NBr, Sinopharm) as template agent was dissolved in 50 mL deionized water and the pH of the solution was kept at 11 by adding ammonia water. And then, a fixed amount of 1-Dodecanol was added to the above solution and stirred well, meanwhile, the temperature of the mixture was heated to 60 °C and kept the mixture at that temperature for 0.5 h. After that, 0.75 mL teraethyl orthosilicste (TEOS, 98%, Sinopharm) was added dropwise to the above mixture. After continuously stirred for 2 h, the temperature of the mixture was gradually decreased to room temperature and the above suspension was further centrifuged. After filing, the precipitate was washed using water and ethanol for several times, and then dried overnight in an oven at 80 °C. Finally, the obtained powder was calcined in a muffle furnace in airflow by heating to 550 °C at a rate of 2 °C/min, and kept at 550 °C for 5 h. The prepared mesoporous silicas were labeled as S1, S2 and S3, respectively, where the "S" indicates "silica" and the number (1, 2 and 3) designates the quality of template agent 1-Dodecanol used in the preparation process (1 = 0 mg, 2 = 10 mg, 3 = 30 mg), respectively. The specific surface areas and porosity of the silica prepared were measured by low-temperature nitrogen adsorption with the use of the BET method (Table 1).

Nickel catalysts were prepared by incipient wetness impregnation with aqueous solutions of nickel nitrate, which was the same method as that of our earlier reports [32,33]. Synthesized mesoporous silicas (S1, S2 and S3) were used as a catalytic support in all catalyst preparations. Before impregnation, mesoporous silica support was dried in an oven at 80 °C for 2 h. The concentrations of the impregnating solutions (nickel nitrate concentration) were calculated to obtain 10 wt% nickel in the final catalysts. After impregnation, the catalysts were dried overnight in an oven in the air at 80 °C. Then they were calcined in airflow at 550 °C for 5 h. The catalysts were labeled as Ni/S1, Ni/S2 and Ni/S3, respectively.

2.2. Characterization of catalysts

The specific surface areas, total pore volumes, and average pore diameters of silica carrier and nickel catalysts were measured by nitrogen adsorption-desorption isotherms using Quadrasorb S1 instrument (Quantachrome, USA) at −196 °C. Before measurements, the samples were degassed in vacuum at 300 °C for 3 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}), the average pore size distributions were derived from adsorption branches of isotherms using Barett–Joyner–Halenda (BJH) method, and the total pore volumes (V_{total}) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.99.

The X-ray diffraction (XRD) patterns were recorded on an X'Pert PRO MPD apparatus (PANalytical, Netherlans) with an X'Celerator detector and Cu $K\alpha$ radiation (λ=1.5406 Å, 40 kV, 40 mA) at a scanning rate of 0.02 °/s. The average crystallite size of silica carrier or NiO was calculated according to the Scherrer equation with a certain diffraction peak.

Transmission electron microscopy (TEM) images of the samples were obtained on a FEI Tecnai G2 microscope. Prior to measurements, the samples were dispersed in ethanol with the help of ultrasonic treatment. The nickel particle histograms were obtained using more than 100 detected nickel particles from the TEM images.

The morphology of the samples was inspected using S-3400 FEI (Hitachi, Japan) scanning electron microscope (SEM) operated at an accelerating voltage of 20 kV with BSE mode.

Temperature-programmed reduction (TPR) of the oxidic nickel catalyst was performed on a home-made fixed bed reactor analyzer equipped with a thermal conductivity detector (TCD). Prior to reduction, 100 mg catalyst sample was pretreated in a N₂ flow at 100 °C for 1 h and then cooled down to room temperature. After that, the sample was heated from 100 °C to 800 °C at a rate of 10 °C/min in a 5 % H₂/N₂ flow.

Simultaneous differential scanning calorimetry and thermogravimetric analysis of used nickel catalyst were carried out in a flow of air (20 mL/min) at a heating rate of 1 °C /min with a DSC-TGA STA449F3 thermal analyzer (NETZSCH, Germany). The DSC-TGA data was obtained at the temperature ranging from 40 to 800 °C. The sample loading was typically 10–15 mg.