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## Short Communication

# Confining Ni nanoparticles in honeycomb-like silica for coking and sintering resistant partial oxidation of methane

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## ABSTRACT

3D honeycomb-like silica surrounded by ZrO<sub>2</sub> layer (3HL-ZrO<sub>2</sub>-SiO<sub>2</sub>) was prepared via sol-gel coating method. The average cell diameter of prepared material is about 10 nm. The highly dispersed Ni nanoparticles were immobilized to cell of honeycomb by impregnation method. The synthesized catalysts were characterized by SEM, TEM, XRD, H<sub>2</sub>-TPR/TPD, TGA and N<sub>2</sub> adsorption-desorption techniques. Contributed by confinement of honeycomb-like silica, the Ni/3HL-ZrO<sub>2</sub>-SiO<sub>2</sub> catalyst showed superior anti-sintering and coking ability compared with conventional catalysts. Further, improving the oxygen storage capacity from ZrO<sub>2</sub> and highly dispersed active-sites afford excellent catalytic activity. CH<sub>4</sub> conversion up to 90%–92% was obtained. The blocking effect of honeycomb cell endowed outstanding sintering resistance referring to Ni based catalysts.

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## Introduction

Hydrogen is considered to be an environmentally friendly fuel and efficient energy carrier due to high energy density and renewability [1,2]. Methane is the most abundant source of hydrogen in nature. Recently, successful development of coalbed methane, shale gas, even icy methane hydrates provokes the interests of numerous researchers on application of methane [3,4]. As the most important intermediate product, synthesis gas plays an important role in the chemical industry

[5–7]. Syngas from partial oxidation of methane (POM) stands out due to the merits of small size of reactor, suitable H<sub>2</sub>/CO ratio for methanol and Fischer-Tropsch synthesis [8–11].

Ni based catalyst is considered as one of the most active catalysts in the POM reaction [12–14]. Ni metal is also cheaper and easier to be obtained than noble metals. Although the Ni based catalysts possess highly catalytic activity, there is still a gap to realize industrialization, because Ni based catalysts deactivate easily due to sintering and carbon deposition.

In order to solve these problems, variety of synthetic strategies were proposed [14,15]. For instance, the mesoporous

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Ni-Al<sub>2</sub>O<sub>3</sub> catalyst was synthesized to improve specific surface area and dispersion of Ni metal [14–16]. Confining Ni nanoparticles within pore of support seems an effective strategy to improve catalyst stability among preparation methods. Zhang immobilized Ni nanoparticles in the pore of SBA-15 to improve coking resistance in dry reforming of methane [17]. Our group employed polyols assisted route to confine Ni nanoparticles into the pore of conventional silica and results showed the confinement suppressed the sintering and coking of Ni nanoparticles [18]. Recently, Guicen synthesized 3D ordered mesoporous silica (pore size: 30–50 nm) using supramolecular template, which played a positive role in diffusion effects and limited phase equilibrium in geometries [19,20]. When gold nanoparticles were loaded on ordered mesoporous SiO<sub>2</sub> support, the lifetime of gold based catalyst was observably improved. The remarkable advantages of morphology and pore size inspire us to use the material as support in POM reaction.

Here a type of honeycomb-like silica was prepared, on which surface ZrO<sub>2</sub> layer was deposited. The mesoporous ZrO<sub>2</sub> material was obtained. Then the Ni nanoparticles were immobilized into the cell of ZrO<sub>2</sub> material. The strong interaction between Ni and ZrO<sub>2</sub> and high surface area of honeycomb structure endowed homogeneous distribution of the small Ni nanoparticles. The confinement effect and oxygen storage capacity of ZrO<sub>2</sub> effectively reduced sintering and carbon deposition, improving thermal stability and catalytic activity of active metal [21–23].

In this work, air was chosen to replace the oxygen as oxidizer, which was closer to the industrial requirements. Nitrogen from air can be used as diluent gas to alleviate the hot spot in the catalyst bed. The 3D honeycomb-like Ni/3HL-X (X = SiO<sub>2</sub>, ZrO<sub>2</sub>-SiO<sub>2</sub>) catalysts were synthesized and applied in POM reaction.

## Experimental section

### Catalyst preparation

#### *The preparation of 3HL-SiO<sub>2</sub> materials*

3D honeycomb-like silica (3HL-SiO<sub>2</sub>) was synthesized according to the report [19]. To put it briefly, 0.5 g of Pluronic F127, 1.25 g of KCl, 0.6 g of TMB (1,3,5-trimethylbenzene) were dissolved in 30 mL of HCl solution (1 M) and stirred for 1 h at 15 °C. Then 2.08 g of TEOS (tetraethoxysilane) was added into the mixed solution. The molar ratio of composition F127/KCl/TEOS/TMB/HCl/H<sub>2</sub>O was 0.00147/0.62/0.37/0.185/1.85/100. After stirring for 24 h at 15 °C, the mixture was transferred into an autoclave (100 mL) for crystallizing 24 h at 140 °C. After cooling and filtration, the precipitates were dried at 65 °C for 5 h. To remove templates, 0.3 g of SiO<sub>2</sub> sample was mixed with 2 mL of H<sub>2</sub>O<sub>2</sub> (30%) and 5 mL of HNO<sub>3</sub> solution (15 M) in Bunsen beaker. Stirring for 2–5 h at 80 °C, then the mixed solution was washed with deionized water several times and dried in a drying oven.

#### *The preparation of 3HL-ZrO<sub>2</sub>-SiO<sub>2</sub> materials*

The materials modified by ZrO<sub>2</sub> were prepared following a method proposed in the literature [20]. 0.041 g of zirconium

n-propoxide, 2.3 mL of glacial acetic acid, 1 mL of HCl solution (12 M), 0.492 g of 3HL-SiO<sub>2</sub> were mixed together in 30 mL of ethanol. After stirring for 4 h, the mixture was aged for 24 h at 65 °C. The obtained powders were calcined for 6 h at 350 °C. The obtained sample was marked as 3HL-ZrO<sub>2</sub>-SiO<sub>2</sub>, therein Zr accounting for 2% total weight of the support.

#### *The preparation of Ni/3HL-SiO<sub>2</sub> and Ni/3HL-ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts*

The 0.9 g of 3HL-SiO<sub>2</sub> powders were dispersed in 20 mL of ethanol and stirred for 1 h, which was named as A mixture. 0.4953 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 2 mL of deionized water under ultrasonic, which was named as B solution. Then B solution was added into A solution and the mixture was stirred until all the ethanol evaporated out. Drying at 65 °C, the obtained powders were calcined for 6 h at 650 °C. The prepared sample was marked as NiO/3HL-SiO<sub>2</sub> catalyst. The NiO/3HL-ZrO<sub>2</sub>-SiO<sub>2</sub> catalyst was prepared by similar method.

For comparison, the supported NiO/SiO<sub>2</sub> and NiO/ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts were prepared by conventional impregnation method using commercial silica (200–300 mesh, Sinopharm Chemical Reagent Co., Ltd). Briefly, 0.4953 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 3.46 mL of deionized water under ultrasonic for 30 min. Then the solution was added into 0.9 g of silica under stirring. After drying for 12 h at 100 °C and calcining for 6 h at 650 °C, the NiO/SiO<sub>2</sub> catalyst was obtained. The Ni/ZrO<sub>2</sub>-SiO<sub>2</sub> catalyst was prepared by similar impregnation method. 0.4953 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.0941 g of Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O were dissolved in 3.46 mL of deionized water and the solution was added dropwise into 0.87 g of silica. Following preparation processes were same with NiO/SiO<sub>2</sub> catalyst. The weight loading of Ni is 10% based on the mass of catalyst.

After reduction, the NiO/3HL-SiO<sub>2</sub>, NiO/3HL-ZrO<sub>2</sub>-SiO<sub>2</sub>, NiO/SiO<sub>2</sub> and NiO/ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts were marked as Ni/3HL-SiO<sub>2</sub> and Ni/3HL-ZrO<sub>2</sub>-SiO<sub>2</sub>, Ni/SiO<sub>2</sub> and Ni/ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts respectively.

### Catalyst characterization

The X-ray diffraction (XRD) data of catalysts was obtained by a SHIMADZU-6000 automated powder diffractometer, using Cu K<sub>α</sub> radiation. The 3D structural morphology characteristic of catalysts could be observed via scanning electron microscopy (FESEM, JSM 7001-F, JEOL, Japan) and transmission electron microscope (Tecnai G2-F30 TEM). The specific surface area was measured by the N<sub>2</sub> adsorption-desorption isotherms with single-point BET method using Micromeritics apparatus, equipped with model TriStar 3020. Temperature programmed reduction (TPR) information was determined on a conventional setup equipped with a thermal conductive detector. 50 mg samples was heated to 400 °C at a rate of 10 °C/min under N<sub>2</sub> flow for 30 min to eliminate adsorbed water. After cooled down to room temperature, the sample was switched to a 25% H<sub>2</sub>/N<sub>2</sub> (V/V, 60 mL/min) mixture, the temperature of samples was programmed to 900 °C at rate of 10 °C/min. The thermal analyzer (SETARAM) was used to evaluate the amounts of carbon deposition on used catalysts at a ramp of 10 °C/min in air from room temperature to 900 °C. H<sub>2</sub>-TPD was conducted in order to evaluate metallic Ni dispersion. 100 mg of sample was loaded into the reactor and flushed with N<sub>2</sub> gas

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