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Partial oxidation of methane over silica supported Ni nanoparticles with size control by alkanol solvent

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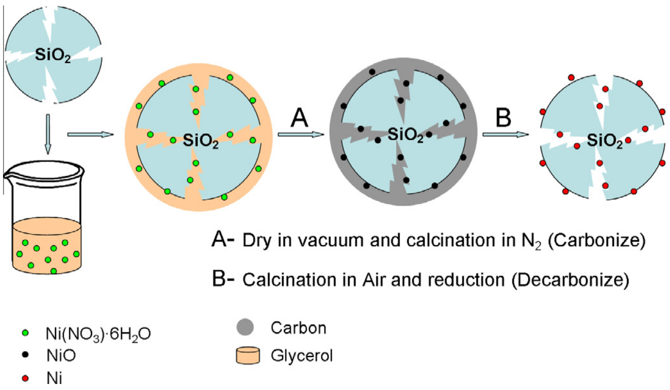
HIGHLIGHTS

- The Ni particles supported on silica were prepared using different alkanol solvents.
- The size of Ni particles was tuned by confinement of carbon templates.
- The Ni/SiO_2 catalyst prepared by glycerol solvent was proved to be more active.
- The scheme of POM was determined by surface states of nickel particles.

GRAPHICAL ABSTRACT

The sizes of Ni particles were controlled by carbon templates derived from carbonization of alkanol solvent.



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ABSTRACT

The Ni nanoparticles of narrow size distribution supported on silica were prepared using different alkanol solvents (ethanol, ethylene glycol and glycerol) by wet impregnation method. The mean size of Ni nanoparticles can be tuned using alkanol as delivery conveyors and removable carbon templates. Compared with conventional catalysts prepared using aqueous solution, the as-obtained catalysts owned smaller and uniform size of metal particle due to confinement effect of carbon templates, especially ethylene glycol and glycerol as solvent (6–8 nm). It was found catalytic activity was dependent on the size of the metal particles. The overall scheme of POM was determined by surface valence states of nickel particles which were affected by nanoparticles size. Inspiringly, the Ni/SiO_2 catalyst prepared by glycerol solvent was proved to be more active, giving CH_4 conversion of 94%, CO selectivity of 88% due to the higher reducibility, higher metal dispersion and more unsaturated surface atoms contributed by smaller metal nanoparticles.

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1. Introduction

The challenge of converting natural gas into transportable fuels and chemicals has been spurred by recent exploration and production of methane from shale basins [1]. Catalytic partial oxidation of methane (CPOM) becomes more and more promising due to mild exothermic heat of reaction and its suitable H_2/CO ratio for methanol and alkane synthesis by the Fischer–Tropsch process [2,3].

There is a popular belief that the activation of CH_4 is structure sensitive (nature of the surface) [4]. The cleavage of the C–H bond in the CH_4 molecule occurs predominantly on the edge and corner metal atoms, the fractional density of which increases with decreasing metal particles size and rising metal dispersion [5–7]. The observed rate dependence on particle size is attributed to a higher reactivity of coordinatively unsaturated surface atoms in small particles compared to low-index surface atoms prevalent in large particles [8]. However, recently intrinsic Ni/SiO_2 performances were found to be independent of nickel particle size in dry reforming at 773 K [9]. Kondratenko et al. also investigated size effect on selectivity and activity of POM using supported Rh/γ-Al_2O_3 catalysts [10]. They claimed CO formation turnover rates and CO selectivity strongly decreased with an increase in the size and the overall scheme of CPOM was size-independent. To our knowledge, the further understanding on origin of the size dependence in CPOM reaction is still needed.

Carbon deposition is a severe issue for the metal catalysts. The catalyst deactivation from coke formation was a strong function of particle size [11]. A decrease in deactivation rate was observed with decreasing particle size due to lower amount of carbon deposition on the smaller particles, which was ascribed to a higher fraction of edge and corner metal atoms [12].

The carbon deposition could result in the catalyst deactivation by coating active sites. Nevertheless, the isolation effect of carbon can be used to prevent growth up of metal nanoparticles (NPs) on support, thus controlling particle size and improving the metal dispersion. Zhang et al. immobilized Ni nanoparticles to mesoporous silica with size and location control via a polyol-assisted route for coking- and sintering-resistant dry reforming of methane [13]. The pioneering work showed excellent result in inhibition of coking and sintering. They also used a novel sublimation-deposition strategy to immobilize Ni NPs in Ce-modified mesoporous silica [14]. The confinement effect deriving from the mesoporous channels of silica support, as well as the high dispersion and reducibility contributed to highly catalytic performance and stability.

Up to now, a number of methods have been developed for controlling the size of metal particles [15,16]. Especially, encapsulation strategy of colloidal NPs in porous inorganic shells or hosts was developed [17–19]. For conventional supported catalysts, it was noticed that metal NPs embedded in support have a trend of aggregation during calcination process. Differing from conventional impregnation method using water as solvent, now we prepared supported Ni/SiO_2 catalysts with alkanol solvent and investigated the effect of particle sizes controlled by carbon template on catalytic performance. Silica was used because of its neutral acidity/basicity [20], high degree of metal reduction [21], and low oxygen donation to the metal [22]. In order to eliminate other effect factors, the catalysts with the same Ni loading amount (5 wt%) were synthesized under same preparation process and reduction condition.

2. Experimental section

2.1. Catalyst preparation

The Ni/SiO_2 catalysts were prepared by a modified impregnation method using different kinds of alkanol solvent including ethanol, ethylene glycol and glycerol. 0.78 g nickel nitrate hexahydrate was dissolved in 5 mL alkanol solvent. The resulted solution was added dropwise into 3 g SiO_2 (40–60 mesh) while stirring the mixture. Then the mixture was sonicated in an ultrasound cleaner (SK1200H, 40 kHz, 100 W) to make the solution dispersed evenly. 3 h later, the products were dried in vacuum for 4 h (60 °C for ethanol sample, 170 °C for ethylene glycol, 240 °C for glycerol). Lastly, the samples were calcined successively at 700 °C in N_2 for 3 h and in air for 2 h. In comparison, the catalyst using deionized water as solvent was prepared by parallel method. Prior to the reaction, the catalysts were separately reduced in flowing of mixture gas (20% H_2 balanced with N_2) at 700 °C for 4 h. The catalysts prepared using water, ethanol, ethylene glycol and glycerol solvent with a targeted nickel loading of 5 wt% are referred to as Ni/SiO_2-H_2O, Ni/SiO_2-Et, Ni/SiO_2-EG, Ni/SiO_2-GL, respectively.

2.2. Catalyst characterization

Nitrogen adsorption–desorption measurement at −196 °C was carried out on an ASAP2020 from Micromeritics. Prior to measurement, the sample was degassed at 300 °C under vacuum for 3 h to eliminate the adsorbed species. Total surface area was calculated from a multipoint BET analysis of the N_2 desorption isotherms.

X-ray powder diffraction (XRD) data of the fresh, reduced and used catalysts were obtained on a SHIMADZU-6000 automated powder diffractometer equipped with a nickel filtered Cu Ka radiation. Inductively coupled plasma (ICP) was performed on an IRIS intrepid II XSP instrument to obtain the Ni loading amount.

The TEM images were taken over a JEOL JEM-2010 instrument operated at 100 kV. The reduced samples were obtained after reduction under a flow of pure H_2 (70 mL/min) at 700 °C for 5 h at a ramp of 1 °C/min. In order to obtain images of used catalyst samples, the reactant flows were stopped simultaneously with the catalysts at the desired temperature, and the catalysts were then flushed and cooled in He before being sealed. The particle size distributions were obtained from random 50–100 particles.

The test of carbon deposition was carried out by the same reactor under the same reaction condition. The coke quantity was measured by the TA Q600 thermo-gravimetric analyzer. The test of contact angle was conducted on Powereach JC2000D2G from Shanghai Zhongchen Digital Technology Equipment Co., LTD. Silica sheet was obtained by tabletting at 12 MPa for 2 min.

H_2-TPD analysis was performed in order to evaluate metallic Ni surface area, dispersion and average Ni particle size. Prior to TPD analysis, 100 mg of catalysts were loaded into the reactor and flushed with He gas flow (90 mL/min) to remove any adsorbed species for 30 min. All of the catalysts were reduced under pure H_2 (50 mL/min) gas flow for 1 h at 400 °C, where the reduction rate is maximum according to the TPR results. Then the catalysts were flushed with He gas flow (90 mL/min) for 1 h and cooled to 30 °C. 10% H_2/Ar were pulsed into the reactor, then the samples were flushed with He gas flow (90 mL/min) for 1 h to remove weakly adsorbed H_2. Temperature was linearly increased from 30 °C to 900 °C under He gas flow at 20 °C/min in order to obtain TPD spectra. The Ni dispersion was calculated from the H_2 uptake results [23].

H_2 TPR was performed in a conventional setup equipped with a thermal conductive detector. 30 mg of NiO/SiO_2 were heated to 110 °C at rate of 10 °C/min under Ar flow of 50 mL/min and kept at this temperature for 1 h to remove adsorbed water. After cooled down to room temperature, the sample was switched to a 25% H_2/N_2 (V/V, 60 mL/min) mixture. The sample temperature was programmed to 900 °C at rate of 10 °C/min.

2.3. Catalyst evaluation

All experiments were performed using a tubular quartz reactor with internal diameter of 10 mm and furnace heated by electric