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One step synthesis of mesoporous NiO–Al_2O_3 catalyst for partial oxidation of methane to syngas: The role of calcination temperature

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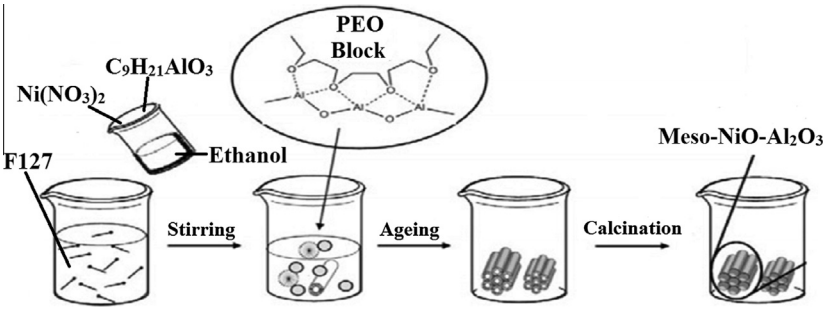
HIGHLIGHTS

- Mesoporous NiO–Al_2O_3 catalysts were prepared by sol–gel method.
- Calcination temperature exhibited great effect on physicochemical properties.
- NiO–Al_2O_3-600 showed the highest catalytic reactivity and stability.

GRAPHICAL ABSTRACT

The mesoporous NiO–Al_2O_3 catalyst was prepared by modified sol–gel method via an improved one pot evaporation-induced self-assembly (EISA) to control the volatile process.



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ABSTRACT

A series of mesoporous NiO–Al_2O_3 catalysts were prepared by sol–gel method with calcination temperature increasing from 400 °C to 800 °C. The effect of calcination temperature on the texture property and catalytic performance of NiO–Al_2O_3 catalysts for partial oxidation of methane (POM) was investigated. These catalysts were evaluated by X-ray diffraction (XRD), transmission electronic microscopy (TEM), N_2 adsorption–desorption method and temperature programmed reduction (TPR) techniques and tested in a fixed bed reactor at 550 °C. The meso-NiO–Al_2O_3 catalyst with low carbon deposition prepared at 600 °C was proved to be more active, stable. After 40 h reaction at 550 °C, the Ni–Al_2O_3-600 sample still maintained relatively high CH_4 conversion and CO yield indicating high activity and stable structure of obtained sample.

1. Introduction

In recent years, catalytic partial oxidation of methane (POM) has been an active subject for H_2 and synthesis gas (syngas) production, which is an alternative to the conventional steam methane reforming (CSMR) [1]. The CSMR process for syngas production needs expend vast amounts of energy due to its endothermic nature, while partial oxidation of methane is a mild exothermal reaction [2,3]. In addition, the suitable H_2/CO ratio (about 2) can be used to synthesize methanol, dimethyl ether and synthetic gasoline by the Fischer–Tropsch synthesis [4–6].

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Therefore, POM reaction is an economically promising process for syngas production.

Ni-based catalysts were the most extensively used in POM reaction because of highly catalytic performance and low price compared with noble metal catalysts [7,8]. However, there is still no large-scale application of POM, because Ni-based catalysts can be deactivated by coking and sintering [9]. As a result, it is a tremendous challenge for developing Ni-based catalysts with excellent performance during POM reaction and high coking and sintering resistance. Great efforts have been focused on modification of reforming catalysts [10], such as enhancing the dispersion of active components and reducing the crystal sizes. It has been reported that mesoporous Ni–Al oxide was more coking-resistant than supported catalysts because of highly dispersed metal nanoparticles at the surface of support and enhanced interaction between the nickel species and alumina support [11].

It is generally acknowledged that POM is structure-sensitive reaction. The preparation condition, such as the calcination temperature, significantly affects the texture property and the phase composition of catalysts, which further affect the catalytic performance [12]. Beatriz Valle and co-workers studied the effect of calcination temperatures on activity and stability over Ni/La_2O_3–Al_2O_3 catalyst, and found that the calcination at 550 °C minimized the formation of $NiAl_2O_4$ spinel and produced a larger amount of highly dispersed nickel oxide nanoparticles [13]. Özdemir et al. reported that high calcination temperatures enhanced interaction of metal oxide with support while long calcination time resulted in sintering of NiO particles over $Ni/MgAl_2O_4$ catalyst [14].

The high surface area and finely dispersed nickel particles at the surface of catalyst can be obtained by one-pot synthesis [15,16]. The carbon deposition could be also relieved by strong interaction between active metal and support, which depends on calcination temperature. In this work, a sequence of mesoporous NiO–Al_2O_3 samples were synthesized by a surfactant-assisted (F127) epoxide-driven sol–gel method under different calcination temperatures in order to investigate the significant role of the calcination temperature on the surface, structural properties and catalytic activity in POM reaction.

2. Experimental

2.1. Catalyst preparation

NiO–Al_2O_3 catalysts were one-pot synthesized by modified sol–gel method combined with evaporation-induced self-assembly (EISA) process [16]. Firstly, 1.0 g of Puronic F127 (Mav = 12,600, $EO_{106}PO_{70}EO_{106}$) was dissolved in 20.0 mL absolute ethanol. Then 1.5 mL of nitric acid (HNO_3, 67 wt%), 0.01 mol aluminum isopropoxide ($C_9H_{21}AlO_3$, 98%) and appropriate amounts of nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) were successively added into the above solution with vigorous stirring. After covered with PE (polyethylene) film to prevent the evaporation of the ethanol, the final mixture was stirred at room temperature for 5 h. Followed dried at 60 °C for 48 h in air, the collected samples were calcined respectively at 400 °C, 600 °C, 700 °C, 800 °C for 4 h. The obtained catalysts were marked as NiO–Al_2O_3-400, NiO–Al_2O_3-600, NiO–Al_2O_3-700 and NiO–Al_2O_3-800.

2.2. Catalyst characterization

The phase structure of the catalysts was assessed using an XRD diffractometer (Miniflex, Rigaku) using Ni-filtered Cu Kα radiation at room temperature from 10.0° to 80.0°. The X-ray tube was operated at 40 kV and 40 mA.

The N_2 adsorption–desorption measurements (QUADRSORB SI) was carried out at −196 °C to evaluate the effect of calcination condition on pore structure. Before test, the samples were degassed at 200 °C for 2 h. Surface areas of the catalysts were calculated in the relative pressure range of 0.05–0.3. The pore size distributions were obtained by BJH model.

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 reducibility of the samples was obtained by temperature programmed reduction (TPR) of H_2, which were conducted in a conventional device with a thermal conductive detector. Prior to H_2 reduction, the sample (200 mg) were heated to 110 °C at rate of 10 °C/min under Ar flow for 1 h to eliminate adsorbed water. After cooled down to room temperature, the flow was switched to a 25% H_2/N_2 (V/V, 60 mL/min) mixture. The reduction temperature was lifted to 1000 °C at ramp rate of 10 °C/min.

The morphology of catalysts was taken over a Tecnai G2-F30 instrument. The particle size distribution was obtained by measuring randomly the dispersed metal particles. The samples, dispersed in ethanol and ultrasonicated, were deposited on copper meshes and observed after a drying step.

2.3. Catalytic activity measurements

The catalytic activity tests were carried out in a fixed-bed quartz tubular reactor (i.d. 9 mm) at atmospheric pressure. The catalyst of 500 mg diluted with 1.0 g quartz chips (60–80 Mesh) was held on quartz wool. A thermocouple was used to test and control temperature of the catalyst bed. Prior to reaction, the catalysts were reduced in stream of H_2 at flow rate of 70 mL/min for 1 h at the temperatures, whose H_2 consumption rate was maximum obtained from TPR curve. The reactant gas mixture ($CH_4/O_2 = 2$) was fed into the reactor at flow rate of 420 mL/min (gas hourly space velocity, GHSV = 5.04×10^4 mL g^{-1} h^{-1}). The product mixtures and unconverted reactants were analyzed by a gas chromatograph (Haixin GC 920) equipped with TCD and FID detector.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. XRD analysis

The XRD patterns of reduced NiO–Al_2O_3 catalysts calcined at 400 °C, 600 °C, 700 °C and 800 °C are shown in Fig. 1. As we can

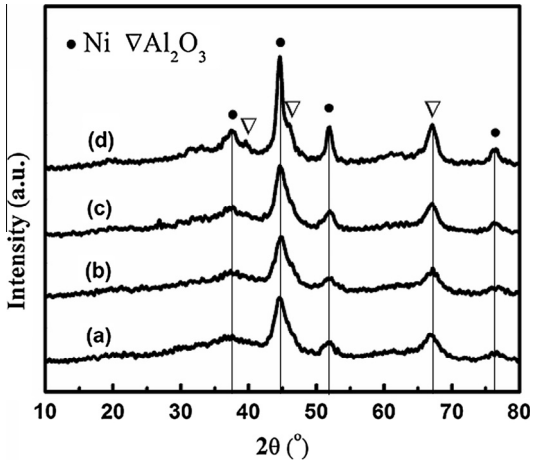

Fig. 1. The XRD patterns of reduced catalysts calcined at different temperatures: (a) Ni–Al_2O_3-400, (b) Ni–Al_2O_3-600, (c) Ni–Al_2O_3-700, (d) Ni–Al_2O_3-800.