Core–Shell Al₂O₃-Supported Ni for High-Performance Catalytic Reforming of Toluene as a Model Compound of Tar

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Abstract Core–shell Al₂O₃-supported nickel catalyst was prepared and the products were tested in fixed-bed reactor for biomass tar steam reforming. In our work, toluene is treated as tar destruction model compound. The products were characterized by the means of H₂-TPR, XRD, BET, TEM and SEM. Comparing with the nanoparticles alumina-supported counterparts, the catalyst showed not only superior activity, more yields of outgases but also better stability. The stable shells provide the unique environment around active sites and the strong interaction between Ni and the core–shell supports seems to be responsible for the catalyst activity and stability in toluene steam reforming. The methods presented in this work can be generalized in materials design and control synthesis of other nano materials.

Keywords Core–shell · Ni/Al₂O₃ catalysts · Steam reforming · Catalytic activity

1 Introduction

With the depletion of fossil fuel sources and the global warming issues, the utilization of biomass gasification has attracted tremendous interest as a potential source of renewable energy. However, during high- and medium-temperature gasification process, a high content of tar is produced. Tar does harm to living environment, human health and causing attrition in fluidized bed reactors as well as decreasing the efficiency of the process [1,2]. In addition, tar contains a large amount of energy and can be converted into CO and H₂ by steam reforming [3–5]. Hence, the tar removing and conversion is a key issue for a successful application of biomass gasification [6–9]. It can be improved by catalytic reforming process using catalysts with high activity in tar cracking.

Nickel-based materials have been widely used in organic synthesis, organic semiconductors, supercapacitor electrode materials, catalytic for hydrogen generation, dye mordant in textile industry because of the plentiful availability, high activity and low cost of nickel [10–13]. Nickel-based catalytic also has been investigated in tar removing and con-
version [14]. However, a rapid deactivation is found due to coke formation caused by sintering effects at high temperature [15,16]. The novel catalytic that is more active at high temperature and of course less sensitive to carbon deposition is required [17]. Recently, we have successfully prepared core–shell alumina supported Ni catalysts and investigated the activity for catalytic reforming of toluene at high temperature and atmosphere pressure. We assume that due to the uniqueness of such core–shell architectures, these materials will exhibit enhanced activity performance.

2 Experimental

2.1 Preparation of the Catalysts

Al₂O₃ core–shell microsphere support was prepared by our previously reported method [18]. Ni/Al₂O₃ catalysts were prepared by an impregnation method. The Al₂O₃ power was added under stirring into an aqueous solution of nickel nitrate and kept at room temperature for overnight. The mixture was evaporated out at 80 °C. After this, the solid was dried at 110 °C overnight, and finally calcined at 700 °C for 3 h. The resultant samples were designated 15 wt%Ni/Al₂O₃ (CS). The reference Ni/Al₂O₃ catalysts were also prepared by the same procedure using the commercial γ-Al₂O₃ as the catalyst supports. The samples were denoted as 15 wt% Ni/Al₂O₃ (C1 or C2), where the supports of C1 and C2 were commercially obtained γ-alumina with average size of 10 and 20 nm from Evonik Degussa (China) Co., Ltd. and Shanghai Sharenano Co., Ltd., respectively.

2.2 Steam Reforming of Toluene

Activity tests were carried out at 700 °C under atmospheric pressure in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. The catalyst particle (0.5000 g, 40–60 mesh) was placed into the middle section of the quartz tube reactor. Before the catalytic measurement, the catalyst was reduced in 10 % H₂/N₂ from room temperature to 700 °C at a heating rate of 10 °C/min and the temperature was maintained at 700 °C for 2 h under a flow of pure hydrogen at atmospheric pressure with a flow rate of 60 ml/min. After the reduction process, the temperature was fixed at a certain temperature. The liquid quantity of toluene and water were controlled by double plunger micro-pump. After mixed with H₂ and heated at 300 °C, the mixture was introduced into the reactor. The effluent gas cooled in an ice trap was analyzed with an online gas chromatograph (GC1609) which was equipped with a thermal conductive detector (TCD). The conversion and the selectivity were calculated as given in the literature [19].

2.3 Catalyst Characterization

2.3.1 X-Ray Diffraction

Powder X-ray diffraction (XRD) was performed on a Rigaku D/Max-2550 apparatus using Cu Kα radiation at 40 kV and 200 mA in the 2θ scanning range of 20°–90°. The average diameter D of the Ni particles on the reduced catalysts was estimated using the Scherrer formula $D = \frac{K \lambda}{β \cos θ}$, where λ is the X-ray wavelength (1.5408 Å), β is the full-width at half-maximum, θ is the diffraction angle of the Ni(111) diffraction peak, and K is a constant (0.9).

2.3.2 Transmission Electron Microscopy

Transmission electron microscopy which performed on a JEOL JEM-200CX apparatus operating at 120 kV was used to investigate the crystal sizes and properties in both the fresh and used Ni–Al₂O₃ catalysts.

2.3.3 Scanning Electron Microscopy

The microscope of the catalysts was studied on field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan) equipped with an EDX analytic system energy dispersive spectrometer.

2.3.4 Temperature Programmed Reduction

Temperature-programmed reduction (H₂-TPR) was carried out on a homemade instrument. In a typical experiment, 10 mg of samples (40–60 mesh) was loaded in a quartz reactor, which was placed in a furnace and heated from room temperature to 1,100 °C with a heating rate of 10 °C/min, and 10 % H₂/Ar (V/V) with a total flow rate of 30 ml/min was used as a reducing agent.

2.3.5 N₂ Physisorption Measurements

The Brunauer–Emmett–Teller (BET) specific surface areas were obtained by N₂ physisorption using a Micromeritics ASAP 2020 instrument at −196 °C. Before measurements, the samples were degassed under vacuum at 150 °C for 5 h.

3 Results and Discussion

3.1 Characterization of the Fresh Catalysts

3.1.1 XRD and BET Study

The physisorption results of the Ni–Al₂O₃ catalysts synthesized at various carriers are summarized in Table 1. Com-