



Low-temperature catalytic steam reforming of toluene over activated carbon supported nickel catalysts



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ABSTRACT

In order to decrease the reaction temperature of catalytic cracking of tar derived from biomass gasification and prolong the lifetime of catalyst, nickel supported on activated carbon (Ni/AC) catalysts were prepared by impregnation method and used in steam reforming of toluene, a model tar compound, in a fixed bed reactor. The physiochemical properties of the catalysts were analyzed by N₂ adsorption, X-ray diffraction (XRD), and transmission electron microscopy (TEM), etc. The effects of nickel content, calcination temperature and reaction temperature on carbon conversion were investigated, and the catalytic performance of the Ni/AC catalyst was compared with those of Al₂O₃/olivine-supported nickel catalysts. The results showed that the Ni/AC catalyst with 10 wt% of nickel loading and 600 °C of calcination temperature had the best low-temperature catalytic activity at 600 °C for toluene reforming, and the carbon conversion achieved about 99%. The high performance of the 600-10%Ni/AC catalyst was probably accounted for the AC support, which had a large BET surface area and unique porous structure, and therefore, a fine nickel particle size distribution on it. It also could be known by XRD analysis that nickel loaded on the surface of AC was in the form of metallic state after calcination, thus decreasing the use of hydrogen for reduction before reaction, so the catalyst preparation process can be simplified and the cost will be saved.

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1. Introduction

Biomass resource is a renewable carbonaceous energy. Unlike fossil fuels, there are some advantages for biomass utilization, as biomass is distributed all over the world and it can make full use of biomass to produce clean energy as well as reduce carbon dioxides (CO₂) emission [1]. Generally, biomass can be burned directly, which not only causes low energy conversion efficiency, but also pollutes the environment and harms the people's health [2,3]. Among other's thermochemical processes for biomass conversion, biomass gasification is recognized as one of the most promising solutions for above energy and environment problems [4,5]. Biomass gasification is a process to convert biomass fuel into a low to medium-BTU producer gas as H₂, CO, CH₄, etc.; whereas, some unwanted byproducts like tar are also produced, which is

recognized as one of the most problematic parameters in any gasification systems [6]. Therefore, the removal of tar in biomass gasification process has attracted widely attention from academic researchers [7–10].

The tar derived from biomass gasification is a complex mixture of all organic compounds present in the producer gas including aliphatics, aromatics and heteroatom-containing species [11]. These tars can lead to some severe problems, such as clogging and corrosion in the engines and turbines, blocking in the pores of filters, as well as low gasification efficiency [12]. Recently, significant progress has been made in the use of catalysts to remove tars. Catalytic hot gas cleaning is regarded as one of the most promising approaches for tar removal under moderate conditions and also increases the product gas calorific value for the biomass gasification [13]. Alternatively, nickel-based catalysts were effective for tar elimination and had an ability to improve producer gas quality [14]. Traditionally, nickel was always supported on natural materials such as olivine [15], dolomite [16] or metal oxides like alumina [17]. However, these supports have some limits for extensive application of the nickel-based catalysts. For example,

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calcined dolomite can be easily eroded as it is a soft and fragile material; and nickel supported on olivine leads to sintering due to its low surface area; although Al_2O_3 has larger surface area than olivine, it is prone to carbon formation compared to above two supports [14]. As a promising alternative, carbonaceous materials have been reported to be an excellent catalyst or catalyst support in tar catalytic cracking because of their low cost, high efficiency and their neutral or weak base property [18–20].

Recently, some studies have been carried out to examine the activity and stability employing activated carbon (AC) as support for tar removing due to its highly porous textural structure [21]. As reported by Lu et al. [22], AC was chosen as the support to study the effects of three copper precursors (*i.e.* copper nitrate, copper acetate, copper sulfate), Cu loading and reaction temperature for toluene decomposition. It was found that the copper particles were highly dispersed on the AC and the copper-based catalysts exhibited the best activity by copper nitrate impregnation. The toluene conversion increased and then decreased with the copper loading increasing at the low temperature of 270 °C, and the highest toluene conversion was 73%. Meryemoglu et al. [23] studied the influence of particle size of support on reforming activity and hydrogen selectivity with activated carbon supported platinum catalyst in aqueous-phase reforming and the glucose was used as model compound of biomass. It was found that although Pt particles loaded on the supports were the same size, smaller-sized activated carbon supported Pt catalyst exhibited higher activity and hydrogen selectivity at 250 °C. Therefore, AC-support catalyst is beneficial for catalytic tar conversion at relatively low temperature.

Currently, nickel-based catalysts, such as commercial nickel catalysts and olivine-supported nickel catalysts, achieved more than 90% tar conversion at the temperature above 800 °C [24,25]. Besides, char was studied as catalyst or support to remove tar at low temperature, which presented a low catalytic activity [19]. As is known, high temperature not only needs large amounts of energy, but also gives rise to carbon deposition on the catalysts in the process of tar removal. Therefore, using AC-support catalyst for tar catalytic conversion at relatively low temperature would be a good solution to save energy as well as to avoid catalyst deactivation caused by carbon deposition. However, the effects of preparation conditions of AC-supported nickel-based catalyst for tar catalytic steam reforming were rarely investigated. Thus, in this work, nickel supported on activated carbon (Ni/AC) catalysts were prepared by impregnation method to study the catalytic performance in the steam reforming of toluene (model tar compound). The effects of calcination temperature, nickel loading, reaction temperature and different supports on the toluene carbon conversion were investigated. In particular, the depletion and structural changes of AC support were also studied to examine the service life for tar removal.

2. Experimental

2.1. Catalyst preparation

Commercial activated carbon granules (Shanghai Titan Scientific Co. Ltd., China), alumina (Shanghai Titan Scientific Co. Ltd., China) and olivine (Hubei Mineral, China) were grounded in an agate mortar and sieved to obtain particles in the range of 0.3–0.45 mm for use. The catalysts were prepared by wet impregnation method, and nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as precursor. The detailed preparation process of the catalyst on AC was described as follow. Firstly, the AC was impregnated with aqueous nickel nitrate solution for 4 h; secondly, the excessive water was evaporated by vacuum distillation and then dried overnight in air. In order to remove internal water of the catalyst, it is needed to continue to dry at 105 °C for 4 h; at last, the dried AC-supported

catalyst was calcined in ultra-pure N_2 atmosphere at a heating rate of 10 °C/min to the target temperature (600, 700 and 800 °C) with 3 h holding time. The as-synthesized AC-supported catalysts were defined as 600-10%Ni/AC, 700-10%Ni/AC and 800-10%Ni/AC, respectively. These catalysts were then stored in a dryer until required for the reforming experiments. For the catalysts with different nickel contents (8 wt%, 12 wt% and 15 wt%), the preparation was similar to that of 600-10%Ni/AC catalyst, and they were denoted as 600-8%Ni/AC, 600-12%Ni/AC and 600-15%Ni/AC, respectively.

For comparison, nickel supported on Al_2O_3 (10%Ni/ Al_2O_3) or olivine (10%Ni/olivine) catalyst was also prepared by the similar method as 10%Ni/AC catalyst. However, Al_2O_3 -supported and olivine-supported nickel catalysts were calcined in air at 800 °C and 1000 °C, respectively, and before use, the catalysts were reduced in situ at 700 °C by H_2 for 1 h.

2.2. Catalyst characterization

The specific surface area and porosity were obtained from nitrogen adsorption/desorption isotherms at 77 K performed on a Quantachrome autosorb-1 analyzer. Before analysis, the samples were dried at room temperature and then vacuum degassed at 573 K for 5 h. The actual nickel contents detected by inductively coupled plasma mass spectrometry (ICP, Optima 8300, PerkinElmer, USA) were 8.9, 11.2 and 17.6 wt%, respectively based on 600-8%Ni/AC, 600-10%Ni/AC and 600-15%Ni/AC catalysts. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer with a copper $K\alpha$ radiation source operated at 40 kV and 30 mA. Transmission electron microscopy (TEM) was examined using a FEI Tecnai G2 F20 S-TWIN microscope. 100 metal nanoparticles were analyzed for each catalyst in order to construct the particle size histograms. Temperature programmed reduction (TPR) was performed on a Micromeritics Autochem 2920 instrument with 10 mg of catalyst under a 10% H_2/Ar flow (50 ml/min) from 298 to 1173 K at a heating rate of 10 K/min.

2.3. Apparatus and test procedure

The toluene catalytic steam reforming was conducted in a fixed bed reactor system whose schematic diagram was shown in Fig. 1. The system consists of four subsystems: feeding system, toluene steam reforming reaction system, gas cleaning system and product gas analysis system. Deionized water and toluene were pumped by a peristaltic pump (BT100-2J) and a highly precise syringe pump (SDS-MP09), respectively, and mixed together into a vaporizer which was heated to 200 °C. Nitrogen was used as the carrier gas with a flow rate of 50 ml/min. In any toluene catalytic reforming experiments, the liquid hourly space velocity (LHSV) and steam to carbon ratio (S/C) were fixed at 0.87 h^{-1} and 2.0, respectively. The toluene reforming reaction system is comprised of a stainless steel reactor tube (20 mm inner diameter and 600 mm length), an electric furnace and programmed temperature controller. In each test, 0.5 g of catalyst was placed in the middle of the tube and supported by quartz wool. During the experiment, the reactor was heated electrically and two K-type thermocouples monitored the temperature of the furnace and the actual temperature of the catalyst bed, respectively. The gas cleaning system includes a series of condensers and a silica gel dryer. The outlet gases (H_2 , CO , CH_4 , CO_2) were analyzed online by a gas chromatograph (GC-2060) with TCD using molecular sieve 5A and TDX-101 packed columns. Meanwhile, the gas flow rate was measured by a soap-bubble meter via a six-way valve.

Carbon-based conversion to gas (C-conversion) was used to evaluate the degree of the conversion of toluene and the activity of the catalysts. It was calculated as the fraction of the carbon

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