



Research article

Hydrogen production from catalytic steam reforming of benzene as tar model compound of biomass gasification



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ABSTRACT

Tar reduction is an important issue for the development of biomass gasification process. In this work, a NiO/ceramic foam catalyst was developed and studied for catalytic steam reforming of tar model compound (benzene) using a fixed-bed reactor. Different reaction temperatures, equivalent ratios (ER), and steam/carbon (S/C) molar ratios were investigated with a space velocity of 5.6 h^{-1} . The introduction of the NiO/ceramic foam catalyst showed excellent production of hydrogen and carbon conversion. With the increase of reaction temperature from 700 to 900 °C, the yield of hydrogen increased from 140.67 to 182.06 ($\text{g H}_2 \text{ kg}^{-1}$ benzene). The increase of ER resulted in the decrease of the H_2 yield. A stability test (including regeneration of reacted catalyst) showed that the catalyst was deactivated by the deposition of carbons (confirmed from scanning electron microscopy), which could be removed using air oxidation at 750 °C. The catalytic activity of the catalyst in relation to the hydrogen production could be regained after the regeneration process. A kinetic model study of the process showed that the apparent activation energy and the pre-exponential factor were 73.38 kJ/mol and $1.18 \times 10^5 (\text{m}^3 \text{ kg}^{-1} \text{ catalyst h}^{-1})$, respectively.

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1. Introduction

Tar, as a mixture of condensable organic components in gasification process, consists of aromatic hydrocarbons such as benzene, toluene, xylene, naphthalene and phenol [1,2]. The condensation of tar at low temperature causes several technical problems such as coking catalysts, fouling, and choking downstream pipelines and equipment. These problems result in a reduction of total process efficiency and an increase of the costs of equipment management and maintenance [3–6]. Therefore, it is essential to find an efficient method to converting these tarry materials into valuable products.

Catalytic steam reforming is an attractive technique for tar destruction since it produces hydrogen and carbon monoxide, which are high-value gas products [2,6,7]. Until now, several metal catalysts, including Fe [8,9], Ni [10–13], Co [11,14,15], Pt [5], Pd [16] or combinations of metals [7,17] have been studied by a large amount of publications, dedicating to develop efficient catalysts for tar steam reforming. In particular, Ni-based catalyst has been extensively investigated for tar conversion due to its wide availability, low cost and effective catalytic reactivity in cracking aromatic hydrocarbons [6,18–20].

Tomishige and Li developed several transition metal catalysts such as Rh, Ni, and Co and compound metal catalyst for systemic biomass tar and model compounds reforming. It is found that the Ni/Mg/Al, Ni-Cu/Mg/Al and Co/Mg/Al catalysts exhibited much higher activity and resistance to coke deposition [21,22]. Alumina (Al_2O_3) has been used as a support of Ni-based catalyst by many studies [11,23]. However, Ni/ Al_2O_3 catalyst is known to be rapidly deactivated by carbon deposition on the surface of the catalyst, which can block the active sites, and result in the deactivation of catalyst [2,24,25].

Natural minerals have been used as supports such as dolomites and olivine for Ni-based catalysts [26]. However, due to their low specific surface area and easy abrasion at high temperature, tar reduction using catalysts with dolomite or olivine support is not efficient enough for the downstream applications of the produced gas. Ceramic foam has spherical-like cells connected to each other through openings or windows, and high porosities (85–90%), making it an attractive catalyst support [27]. It is noted that there are few reports of catalytic reforming of biomass gasification tar using Ni-based catalyst with ceramic foam as catalyst support. Since the ceramic foam has large porosity, high temperature stability, very low operation pressure drop and large surface area, it is worthwhile to investigate the catalytic performance of NiO/ceramic foam catalyst for steam reforming of biomass gasification tar compounds.

The catalytic steam reforming of real biomass tar over NiO/ceramic foam catalyst was investigated in our previous studies [28]. Due to the complicated components of real biomass tar, it is difficult to perform

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mechanism studies. To better understand the reaction behaviors, a model compound, such as phenol [29,30], benzene [31,32], toluene [6,25] or naphthalene [24,33] has been used for fundamental studies of catalytic tar steam reforming. Benzene was chosen as a tar model compound because it is a main constituent of high-temperature gasification tar, as well as it represents a stable aromatic structure in polyaromatics [28]. In addition, Josuinkas et al. [34] investigated the steam reforming of three tar model compounds, including benzene, toluene and naphthalene with nickel catalysts and it was reported that benzene is more reactive over a wide temperature range compared to toluene or naphthalene.

In this study, the steam reforming of tar using benzene as a model compound was carried out over a NiO/ceramic foam catalyst in a fixed bed reaction system. Various process conditions including reaction temperature, equivalent ratio (ER) and steam/carbon (S/C) molar ratio were studied. Furthermore, particular attention was paid to the catalyst stability and reusability by carrying out a stability test (4 h) including a catalyst regeneration step, in relation to hydrogen production and carbon formation on the surface of the reacted catalysts.

2. Materials and methods

2.1. Catalyst preparation and characterization

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Tianjin Kermel Company, China. Ceramic foam (Beisi New Materials Company, China) is a cylinder with diameters of 38 mm and lengths of 50 mm. The chemical compositions of ceramic foam are 79.24% Al_2O_3 , 19.29% P_2O_5 , 0.77% SiO_2 , which have been reported in our previous study [28]. Prior to the catalyst development, the ceramic foam was washed using hydrochloric acid solution (0.1 mol L^{-1}) in order to eliminate the effect of the impurities on the experiments, and then dried at 110°C for 3 h.

An impregnation method was used to prepare the NiO/ceramic foam catalyst. Initially, certain amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved completely into the deionized water to form a 1 mol L^{-1} of solution. The pre-treated ceramic foam was soaked into the aqueous solution for 1 h. Then, the Ni^{2+} /ceramic foam was dried in an oven at 105°C for 12 h and calcined subsequently in a muffle furnace at 900°C for 3 h at a heating rate of $7.5^\circ\text{C min}^{-1}$. The average amount of NiO loaded on the ceramic foam after calcination was around $3.50\% \pm 0.30\%$ by weight. The morphology of the blank ceramic foam, the NiO/ceramic foam catalyst and the reacted catalyst were characterized using a Hitachi S-4800 scanning electron micrographs (SEM). A FEI Tecnai

G220 S-Twin transmission electron microscope (TEM) was used to observe the size and morphology of the reacted catalysts.

2.2. Reaction system and procedures

The reaction system consists of a feeding system, a reactor, a product collector and a gas analysis system as shown in Fig. 1. Two double channel micro-infusion pumps (Smith Medical, Model WZS-50F6) were used to feed the pure benzene and water into the reactor, respectively. Mass flow meters (Sevenstar, Model D07-7B) were employed to provide accurate flows of nitrogen and air to the reaction system (air was used for providing oxygen to adjust the ER value and the regeneration of the reacted catalyst). The fixed-bed reactor is made of stainless steel ($40 \text{ mm i.d.} \times 500 \text{ mm length}$). The reactor was heated by a tubular furnace (1.5 kW , 220 V), which was connected with a temperature controller (Yudian, Model AI-518P). The NiO/ceramic foam catalyst was placed in the middle of the reactor. The temperature of the reactor was measured by a K-type thermocouple with a precision of 1°C . The products at the outlet of the reactor were recovered by a glass condenser and subsequently collected in a Tedlar gas bag for analyzing off-line by a gas chromatograph (Techcomp, Model 7890II), which is coupled with a thermal conductivity detector (TCD) to obtain the concentrations of H_2 , O_2 , N_2 , CO , CH_4 and CO_2 .

During the experiment, about $27 \text{ g} \pm 2 \text{ g}$ catalyst was used. The whole system was guaranteed as inert using N_2 as carrier gas with a flow rate of 100 mL min^{-1} . Benzene was injected into the reactor at a feed flow rate of 5.3 g h^{-1} , which is equivalent to a weight hourly space velocity (WHSV) of 5.6 h^{-1} . In this work, oxygen equivalent ratio (0.0–0.4), steam/carbon molar ratio (0.0–3.0), reaction temperature (700 – 900°C) were investigated. Each test lasted 30 min. Experiments were repeated to ensure the reliability of the results.

2.3. Data analysis method

H_2 (CO, CO_2 or CH_4) concentration, H_2 yield, Carbon conversion, H_2/CO and CO/CO_2 molar ratio were calculated using the following Eqs. (1)–(5):

$$\text{H}_2(\text{CO, CO}_2 \text{ or CH}_4) \text{ concentration (\%)} = \frac{\text{H}_2(\text{CO, CO}_2, \text{ or CH}_4) \text{ concentration in the product by GC}}{\text{The sum of the concentrations of H}_2, \text{CO, CO}_2 \text{ and CH}_4 \text{ in the product by GC}} \quad (1)$$

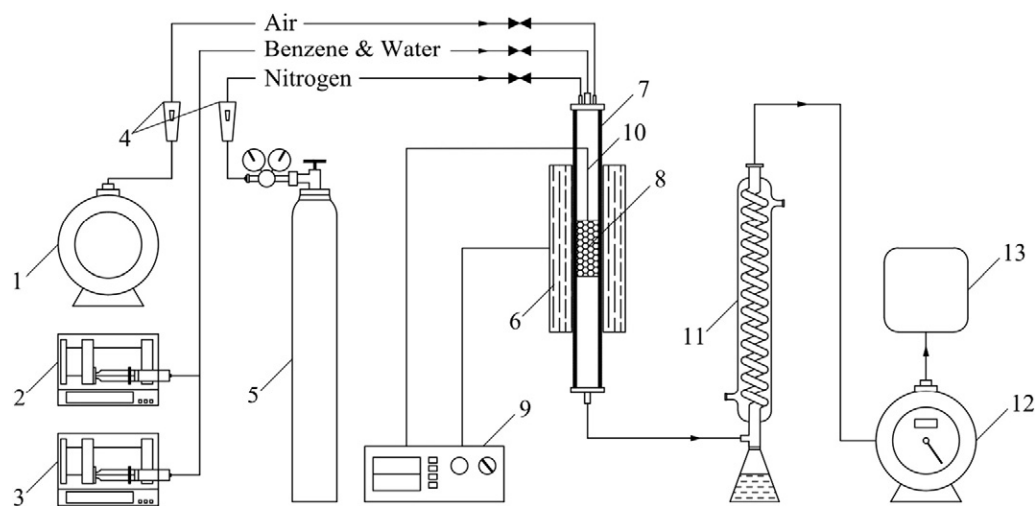


Fig. 1. The schematic diagram of a lab-scale catalytic steam reforming apparatus: (1) Air compressor; (2) Micro-infusion pump for benzene; (3) Micro-infusion pump for water; (4) Mass flow meter; (5) Nitrogen cylinder; (6) Tubular furnace; (7) Fixed-bed reactor; (8) NiO/ceramic foam catalyst; (9) Temperature controller; (10) K-type thermocouple; (11) Condenser. (12) Wet type gas meter; (13) Gas bag.

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