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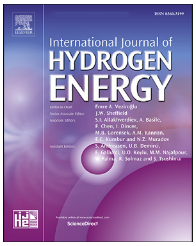

Activity of Ni/CeO_2 catalyst for gasification of phenol in supercritical water

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ABSTRACT

An effective Ni/CeO_2 catalyst prepared by the polyol reduction method for degrading phenol into CH_4, H_2 and CO_2 in supercritical water (SCW) was developed. About 80% carbon gasification efficiency can be achieved at 525 °C and 60 min with 5 wt% phenol, 0.098 kg/m^3 water density and 0.5 g Ni/CeO_2/g phenol catalyst, forming CH_4 and H_2 as the main gaseous products. Comparison study indicated that the efficiency of present Ni/CeO_2 catalyst was about 20% higher than that of a commercial catalyst, i.e., Ni/SiO_2–Al_2O_3 from Sigma-Aldrich with 65 wt%Ni, at a reaction conditions of 500 °C and 30 min. The characterization analyses of BET, TPR, XRD, XPS and TEM indicated that there was a NiCe alloy formed in Ni/CeO_2, which could be important to enhance the activities of the carbon gasification efficiencies and gas yields. A kinetic modelings were conducted and the results showed that the lnA and the activation energy (Ea) of gasification were 7.1 ± 0.5 and 58.1 ± 3.2 kJ/mol for the gaseous product, and were 2.6 ± 0.9 and Ea is 36.6 ± 5.6 kJ/mol for the char formation, respectively. The present Ni-based-metal Ni/CeO_2 catalyst is cheaper and has a potential application for the gasification to convert phenol into gases fuels in SCW process.

Introduction

Phenol is a basic unit for lignin (the natural polymer compounds in biomass) and also a common organic pollutant species found in many industrial waste effluents [1,2]. A variety of methods and techniques such as biological treatment, wet air oxidation, ozonation, peroxide oxidation, and even the supercritical water gasification (SCWG) have been applied for removing phenol from the effluents in the related wastewater pretreatment [3]. With the increasing importance of biomass and the huge amount of wastes utilization in energy industry, SCWG has been becoming a very promising process due to its potential to convert phenol to CH_4 and H_2 for energy utilization, which could provide a better solution for both industrial waste treatment and high-value energy recovery [4].

Actually, the gasification of phenol under supercritical water is still a challenge for the lower efficiency [5]. Therefore, the catalysts that can not only promote the reaction at a moderate temperature but also minimize the byproducts such as dimers are highly desired [6,7]. The presence of catalysts can greatly accelerate the reaction in SCWG by the following reactions:

$$\text{Steam reforming reaction: } C_6H_5OH + H_2O \rightarrow CO + CO_2 + H_2 \tag{1}$$

$$\text{Methanation reaction: } H_2 + CO(CO_2) \xrightarrow{catalyst} CH_4 + H_2O \tag{2}$$

$$\text{Water} - \text{gas shift reaction: } CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

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in which either homogeneous or heterogeneous catalysts are commonly used [8]. Wang et al. used KOH as the homogeneous catalysts for phenol gasification in SCW and proved that the homogeneous catalysts have issues of lower recovery and corrosion [4–9]. Therefore, the heterogeneous catalysts for phenol gasification in supercritical water have been caught more attention. Metal catalysts, such as transition metal Ni and Ru, are commonly used in the catalyst preparation. Though Ru displays good performance in catalytic gasification, it is not competitive in the application due to the cost. The use of Ni has the problems of lower efficiency and carbon deposition [10]. Therefore, it is still a great challenge in the research of SCWG of phenol to explore the high activity catalyst with good efficiency and stability.

In our previous work, it was observed that the catalytic activities can be affected by the support materials, for example, among Ru/CeO_2, Ru/La_2O_3, Ru/Y_2O_3, Ru/ZrO_2, Ru/Y_2O_3–ZrO_2, Ru/MgO and Ru/Pr_4O_7, Ru/CeO_2 is most effective on both the carbon gasification activity and the methane production at temperature of 500 °C [11]. In addition, Lu et al. added CeO_2 into Ni/γ-Al_2O_3 and showed that the deposition of carbon was inhibited since the excellent capacity of oxygen storage and oxygen mobility of CeO_2 because of the easy conversion between Ce^{4+} and Ce^{3+} oxidation states [12,13]. Kang et al. prepared Ni/CeO_2 catalyst by solution combustion synthesis and used it for effectively generating hydrogen from hydrous hydrazine and speculated that the structure of Ni–O–Ce plays a key role in the catalytic gasification [14]. However, it is still unclear about the functionality of CeO_2 on the catalytic gasification process, in which the NiCe alloy could be formed by the preparation procedures [15–17]. Although the Ni–CeO_2 based catalysts have been studied in many cases, e.g., steam reforming of ethanol, methanation reaction, and water-gas shift reaction [18–23], there is a lack of investigation for the gasification of phenols in SCW, particularly the possibility of NiCe formation.

The objective of this work was to understand the effect of CeO_2 on Ni-based catalysts and the possible formation of NiCe alloy. The Ni/CeO_2 catalysts were prepared by the polyol reduction method and employed in the SWCG of phenol. The structure and properties of Ni/CeO_2 were analyzed by TEM, BET, XPS and XRD and the catalyst performance at different reaction time and temperature was discussed. The comparison study between the present catalyst and the commercial catalyst (Ni/SiO_2–Al_2O_3) was conducted at the given conditions for the catalytic activity. Additionally, a kinetic analysis model was developed to investigate mechanism of phenol gasification in SCW.

Methods and experiments

Materials

The reagents used in this experiment are all analytical grade and come from commercial companies, in which $(CH_2OH)_2$ (Ethylene Glycol), $Ni(NO_3)_2•6H_2O$ (Nickel Nitrate), PVP (Polyvinyl Pyrrolidone), NaOH (Sodium Hydroxide) were from Tianjin Fengchuan Chemincal Co., Ltd, CeO_2, $H_2PtCl_6•6H_2O$ (Chloroplatinic Acid), phenol and the commercial catalyst Ni/SiO_2–Al_2O_3 were purchased from Aladdin and Sigma-Aldrich.

Catalyst preparation

The Ni/CeO_2 catalyst was prepared by the polyol reduction method [24]. The catalyst composition was 20 wt% Ni loaded on CeO_2. An organic matter PVP on the surface of catalyst was hard to cleaned up, which may have an impact on the results of catalytic activity. The dry Ni/CeO_2 catalyst was washed with ethanol used as medium for 24 h and dried at 100 °C for ten hours to remove PVP.

SCWG of phenol

The experimental process and equipment were reported in the previous work [25–27]. In a general experiment, 0.0196 g phenol and 0.0098 g Ni/CeO_2 catalyst (50 wt% of phenol) with 392 μL ultrapure water were weighed and added successively into a 4 mL reactor. Air was filled into the reactor to test whether it was tightened, then 200 kPa (gauge) helium gas was filled to the reactor for calculating the gas product quantitatively. The reactor was put into sand bath (model SBL-2) and preheated for two minutes at the setting temperature. After reaction, the reactor was set to room temperature. In this study, the parallel experiments were set up in each group and the replicate (2–4) measurements were carried at each data point.

Two parameters, i.e., carbon gasification efficiency (the mass of carbon in gas product divided by the mass of carbon in phenol, %) and gas yield (the amount of gas product divided by additive amount of phenol, mmol/g) were determined to evaluate the catalyst performance on the gasification of phenol in SCW.

Sample analysis

The gaseous products (mainly CH_4, H_2, and CO_2) were analyzed by a gas chromatograph (GC, model 7820A, Agilent Technologies, USA) equipped with a thermal conductivity detector and a stainless steel column (15 ft × 1/8 in. i.d.) packed with 60 × 80 mesh Carboxen 1000 (Supelco, USA).

The resulting liquid from the reaction was washed for three times with dichloromethane and filtrated by a Nylon 66 microporous filter membrane ($\varphi = 0.45$ μm), then analyzed by a GC–MS (PE SQ 8T-680) equipped with an Elite-5MS capillary column. The temperature programming in the GC–MS measurement was set as follows: the initial temperature at 35 °C for 5 min, then heated up to 180 °C with a rate of 10 °C/min and went on for 10 min; the flow rate of the carrier gas was 2 mL/min, the inlet temperature was 250 °C and the working time of the MS detector was from 1.9 to 29.5 min with the detected fragments range from 35 to 350 m/z.

Catalysts characterization

The BET surface area measurements were carried out on Tristar II 3020 system from Micromeritics Instrument and N_2 adsorption-isotherms of the catalysts were tested in liquid N_2 (−196 °C) after degassed for 3 h at 300 °C, from which the pore

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