Full Length Article

Preparation of high-dispersion Ni/C catalyst using modified lignite as carbon precursor for catalytic reforming of biomass volatiles

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HIGHLIGHTS

- Demineralization caused the pore corrosion and decreased the activity of Ni/C.
- High Ni loading and well dispersed Ni/C was prepared by acid treatment of lignite.
- H_2O_2 oxidation can improve the carboxyl group content of raw and modified lignite.
- Carboxyl group content is a key parameter for Ni/C preparation.
- Inherent minerals have a good influence on Ni/C for biomass volatile reforming.

GRAPHICAL ABSTRACT
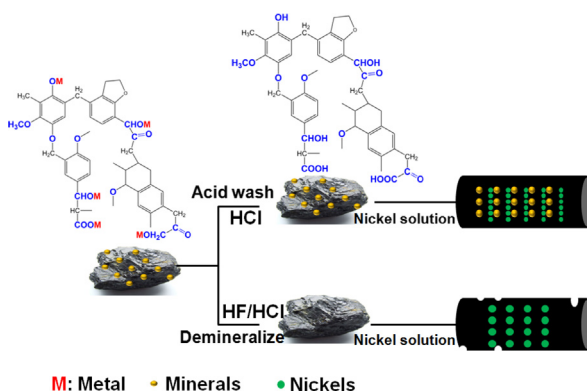
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ABSTRACT

Lignite is rich in oxygen-containing species (OCSs) and able to load Ni via ion exchange to prepare Ni/C catalyst. However, the OCSs usually exists in the form of organic salts, which can reduce the capacity of Ni ion exchange. In this paper, Shengli lignite (SL) was treated with HCl and HCl/HF to selectively remove the organic salts and insoluble minerals, respectively, and the modified lignite was oxidized by H_2O_2 to further increase the carboxyl content. The treated lignite was used to prepare Ni/C catalyst and the activity for biomass volatile reforming was evaluated. The results show that demineralization (DM) caused the corrosion of pore structure of SL and gave a Ni/C catalyst with a low specific surface area (SSA) of 222.1 m^2/g. Oxidation with H_2O_2 further destroyed the structure of DMSL and provided a Ni/C with the lowest SSA of 141.1 m^2/g. Acid wash (AW) with HCl resulted in the increase of ion exchange capacity of SL and gave a Ni/C catalyst with larger SSA, higher loading, lower particle size and well dispersion of Ni particle in comparison with SL and DMSL. H_2O_2 treatment of AWSL significantly increased the amount of carboxyl group to 3.8 mmol/g and gave a Ni/C with the largest SSA of 291.1 m^2/g, highest Ni loading of 17.3% and smallest Ni crystallite size of 3.4 nm, as well as most active for corncob volatile reforming.

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1. Introduction

Lignite has a high ability of spontaneous combustion since the rich in oxygen-containing species (OCSs) [1–3]. Due to abundance in OCSs, lignite was reported present high ion-exchanging ability with metal, such as Ni, and great dispersion of the Ni within the coal matrix [4,5].

We previously reported a novel catalyst with dispersed metallic Ni particles in a Ni crystallite size (NCS) of 5.6 nm and a relatively high specific surface area (SSA) by loading Ni on Shenli lignite (SL) char. The catalyst that nickel-loaded on lignite was successfully utilized for volatile reforming in biomass gasification [6]. However, lignite contains a relatively high ash content, which might affect the ion-exchange capacity as well as the catalyst activity. Therefore, modified lignite provides a potential way to value-added utilization of lignite. Minerals in lignite can be divided into the minerals which exist independently (kaolin, montmorillonite, pyrite, calcite and quartz, etc) and inorganic elements associated with the organic matter. The Na, K, Mg and Ca are usually exchanged in carboxylate groups [7], which can affect the Ni loading and dispersity. Lignite has a certain catalytic activity in gasification reactions since the existence of high content of minerals [8–10]. The catalytic activity of minerals is dependent on their chemical form exists in the coal matrix, as well as the concentration and dispersion. It was proved that the alkali and alkaline earth metals in coal have a certain affect in the reactivity of lignite char [11,12]. Ca and Mg usually exist in carbonates form and show predominantly organic affinity [7,13]. To investigate the catalytic activity of minerals in lignite, DM and AW are need before catalyst preparation.

The OCSs, especially carboxylic groups, are able to exchange ions with external molecules and the exchanged ions are highly dispersed around the coal matrix [4]. The oxidation of lignite may play an important role in improving of SSA and microporosity and the amount of ion exchange in catalyst preparation. Potassium permanganate, peroxyacetic acid, sodium hypochlorite, oxygen and hydrogen peroxide were used for increasing OCSs content [14–20], especially for environmentally friendly oxidant of hydrogen peroxide [21,22]. The ion exchange capacity of the lignite can be enhanced by oxidation treatment to provide the carboxyl group.

In this study, Ni/C catalysts were prepared by acid washing, demineralizing and oxidizing of lignite to study the effects of minerals and carboxyl groups on the Ni loading, NCS, Ni particle size and SSA of the catalysts. The catalytic activity of the as prepared Ni/C catalysts for cracking tarry materials from biomass pyrolysis was investigated in a two-stage fixed-bed quartz reactor.

2. Experimental

2.1. Materials

2.1.1. Preparation of acid washed, demineralized and oxidized lignite

The demineralized lignite (DMSL) was prepared by acid leaching of SL. About 20 g SL sample was stirred with 5 M HCl for 1 h at 55 °C and filtered, then the filter cake was treated with 11 M HF for 1 h at 55 °C. After filtration, the sample was treated again with another batch of 5 M HCl for 1 h at 55 °C, followed by repeated washing with deionized water (DIW) until neutral and no Cl$^-$ can be detected. As reported previously [23], for acid washed lignite (AWSL), 20 g of lignite was treated with 5 M HCl for 2 h at 55 °C, and washed with DIW until neutral and no Cl$^-$ can be detected, Filter cake was dried at 105 °C for 6 h. For oxidation treatment, 10 g of sample (SL, DMSL and AWSL) was treated with 100 mL 20 wt% of H_2O_2 solution for 2 h at 50 °C, and the oxidized sample was labeled as OXSL, OXDMSL and OXAWSL, respectively. The carboxyl and total acidity of all treated lignite

was measured by chemical titration, and the methods in detail and results are presented in Supplementary Material. The corncob with a particle size of 0.5–1.0 mm was used as the biomass sample. The proximate and ultimate analyses of the samples are presented in Table 1.

2.1.2. Preparation of Ni/C catalyst

Ni/C catalysts were prepared by method of ion exchange using SL and the treated sample (OXSL, DMSL, OXDMSL, AWSL and OXAWSL) and nickel solution under carbonization temperature (CT) of 650 °C for 1 h as reported previously [6]. The catalysts prepared with different samples were designated as Ni/SL, Ni/OXSL, Ni/DMSL, Ni/OXDMSL, Ni/AWSL and Ni/OXAWSL, respectively. All the catalysts were ground and sieved to be 1–2 mm particle size before use, and then characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG) analysis, X-ray diffraction (XRD), inductively coupled plasma atomic emission spectrometry (ICP-OES), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and N_2 adsorption. The procedures in detail were presented in Supplementary Material.

2.2. Gasification and product analyses

Gasification was carried out in the two-stage fixed-bed quartz reactor as reported previously [24]. The atmosphere of the gasification was in the presence of Ar or steam (30 kPa) for catalytic reforming (CR) and catalytic steam reforming (CSR) of volatiles from corncob pyrolysis. Space velocity (SV) and temperature of catalytic bed was set at 3600 h^{-1} and 650 °C, which were proved to be the suitable condition previously [6]. The characterization of the char and the gaseous and tarry products, as well as the calculation of carbon in gas (C_{gas}), carbon in water-soluble oil (C_{wso}) and carbon in char (C_{char}) were reported previously [25], and the details were presented in Supplementary Material.

3. Results and discussion

3.1. Characterization of catalyst

3.1.1. FTIR analysis

As shown in Fig. 1, there is a transmission band at around 3428 cm^{-1}, which can be attributed to the stretching vibration of —OH from residual water. The bands at 2920 and 2850 cm^{-1} are due to aliphatic —CH, —CH$_2$ and —CH$_3$ stretching vibrations. An apparent band appeared at 1710 cm^{-1}, which corresponding to the stretching vibration of C=O in carboxyl groups. The relatively strong band of carboxyl groups in OXSL, OXDMSL and OXAWSL are well consistent with the results of the chemical titration (Table S1). The stretching vibration of the C=C bond in the aromatic structure occurs at 1600 cm^{-1}. In comparison to DMSL and OXDMSL, the SL, OXSL, AWSL and OXAWSL exhibit more prominent bands around 1036 and 550–470 cm^{-1} regions because of the Si—O bending vibration and clay minerals, respectively [26–30]. The peaks of SL and OXSL show strikingly stronger than that of DMSL and OXDMSL at 1450–875 cm^{-1}, which attributed to the overlapped peaks of carbonates and the mineral matter, respectively [31]. Through HCl treatment, the spectra of AWSL and OXAWSL also show a peak at 875 cm^{-1}, which means the retention of external inorganic salts and the conversion of internal carboxylate.

3.1.2. TG analysis

As shown in Fig. 2a, there is about 2.0% of weight loss below 200 °C, which should be the removal of moisture and volatile organic matters. With the temperature increased from 200 to