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Comparative study on phenol and naphthalene steam reforming over Ni-Fe alloy catalysts supported on olivine synthesized by different methods

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ABSTRACT

Ni/Fe bimetallic catalysts were synthesized on an olivine support using the wetness impregnation (WI) and thermal fusion (TF) methods, and catalytic cracking and steam reforming on different tar model compounds (phenol and naphthalene) were investigated in a fixed bed reactor. The effects of the reaction temperature and space-time on the catalytic cracking activity of phenol and naphthalene were tested, and the influences of steam on the carbon molar ratio (S/C) and different synthesized methods on the steam reforming of phenol and naphthalene were also studied. In addition, the carbon deposited on the catalyst was analysed using temperature program oxidation (TPO), Raman spectroscopy and transmission electron microscopy (TEM) methods. The elemental composition of the catalyst was analysed by X-ray fluorescence (XRF), and the physiochemical properties of the catalysts were characterized via X-ray diffraction (XRD), the BET surface area, scanning electron microscopy (SEM), TEM, Raman spectroscopy, temperature program reduction (TPR), and X-ray photoelectron spectroscopy (XPS). The results showed that the structure of TF-Ni/Fe/olivine changed considerably compared with that of calcined olivine (mainly the Mg_2SiO_4 phase) and that a portion of Fe was fused into the olivine structure and reorganized into a new (Mg, Fe) Fe_2O_4 phase. After reduction, the Ni-Fe alloy was detected on both catalysts, and the particle size of the Ni-Fe alloy on TF-Ni/Fe/olivine was smaller than that of WI-Ni/Fe/olivine. The TF-Ni/Fe/olivine cracked phenol into small-molecule gas (CO and H_2) and a small quantity of olefin. By contrast, phenol was polymerized to naphthalene in the absence of a catalyst. The phenol and naphthalene steam reforming conversion on WI-Ni/Fe/olivine were both higher than that of TF-Ni/Fe/olivine. A 100-h stability test of phenol steam reforming on TF-Ni/Fe/olivine and WI-Ni/Fe/olivine was conducted, and TF-Ni/Fe/olivine showed higher stability in the early stages of the experiment due to stronger interactions between the active sites and olivine support. The deposited carbon from naphthalene steam reforming was more difficult to eliminate because it contained more C_β and C_γ, which had higher degrees of graphitization.

1. Introduction

As a carbon-neutral renewable energy, biomass energy plays an important role in reducing greenhouse gas emissions, and thus the efficient use of biomass energy is critical [1]. Biomass can be converted into syngas by gasification, which is an efficient method for converting lower energy density biomass into syngas with high energy density and ease of storage. The resulting syngas facilitates further uses in clean combustion, synthetic liquid fuels, and so on [2]. However, the problem of tar generated during the biomass gasification process is one of the foremost obstacles to commercialization of this technology [3–5]. Biomass tar is a mixture of hydrocarbon aromatic compounds and oxygen-containing aromatic compounds that can be derived from lignin, cellulose and hemicellulose. In the conventional gasification temperature range of 700–950 °C, the primary tars (mainly the mixture of oxygenated compounds) are completely destroyed, secondary tars are characterized as phenolic and olefin compounds (represented by phenol), and tertiary tars including methyl derivatives of aromatics (represented by toluene) and polycyclic aromatic hydrocarbon (PAH) (represented by naphthalene) still exist [6–8]. Tars not only block the

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downstream pipeline, causing environmental pollution but also result in substantial energy loss (approximately 15% of the biomass energy) [9].

Catalytic reforming of tar is a more effective approach for tar removal compared with thermal cracking and physical capture because it reduces energy consumption and also avoids secondary pollution. Moreover, this approach can improve the carbon conversion efficiency. The catalysts for tar removal require high activity and long-term stability, including carbon deposition resistance ability [10]. In many cases, Ni-based catalysts are favoured by researchers because of their high catalytic activity and lower cost, but the drawbacks of sintering and carbon deposition problems with the Ni-based catalyst can lead to catalyst deactivation [11–13]. The synthesis of multi-metal (Ni-Fe, Ni-Pt, Ni-Cu, etc.) catalysts on different supports (Al_2O_3, MgO, olivine, etc.) that leverage the synergistic effect between different metals can suitably solve the above-mentioned problems [14–16]. Among the multi-metal catalysts, Ni-Fe catalysts appears to be promising because Fe can interact with Ni to form a Ni-Fe alloy, and Fe species have a high redox property. Similar to noble metal species, the Ni-Fe bimetallic catalysts have been confirmed as effective for catalytic reforming of biomass tar and tar model compounds [17,18]. Tar conversion ranged from 64 to 86% and the catalyst life was three times greater than that of the monolithic Ni catalyst (Ni-αAl_2O_3) [19]. The main component of the olivine support is $(Mg_x, Fe_{1-x})_2SiO_4$. Olivine has been extensively studied because it has a certain catalytic activity, attrition resistance and low cost, which are highly favourable for use as an in-bed catalyst in the fluidized bed [20–22]. The catalytic effect of olivine is attributed to the presence of segregated iron with different oxidation states (i.e., Fe^{3+}, Fe^{2+} and Fe^0) at the particle surface. Selected studies showed that low-valence iron has a higher catalytic activity. For instance, Fe^0 plays an important role in bond breaking of C—C and C—H in hydrocarbons [23,24]. Combined with the advantages of the Ni—Fe bimetallic and olivine support, preparation of Ni—Fe alloy olivine catalysts is of particular interest for large-scale application, for both efficiency and economic reasons. In many cases, researchers use the corresponding metal salt solution via wetness impregnation (WI) or co-precipitation (CP) methods to load the metal onto the olivine support [25,26]. Loading of the metal onto the olivine support using thermal fusion (TF) is a relatively new approach that can significantly increase the binding capacity between the metal and the support structure [27,28]. In addition, the catalyst is more resistant to attrition after the thermal fusion process and still has a considerable catalyst activity compared with the traditional preparation method [29,30].

In reforming of tar, in addition to the characteristics of the catalyst itself, carbon deposition is one of the important factors that influence the deactivation of the catalyst. Currently, many studies only focus on the amount of carbon deposited on the catalyst, but few studies have examined the type and reaction performance of carbon deposition [3,12,16]. Elucidation of the relationship between the characteristics of carbon deposition and the reaction activity of the catalyst is critical to subsequent improvement of the relevant catalysts.

In this article, we prepared Ni—Fe bimetallic olivine support catalysts using the WI and TF methods. Phenol and naphthalene were selected as tar model compounds for investigation as typical secondary and tertiary tars. The physical-chemical properties of fresh, reduced and spent catalysts were analysed using a series of characterization methods, and the effects of reaction temperature, space-time, and steam-to-carbon (S/C) molar ratio on the gas quality and carbon conversion were studied. Moreover, the catalytic reforming stability of phenol and naphthalene over both catalysts was also evaluated. Finally, the carbon deposition on the catalysts surface was detected using TPO, Raman and TEM, and the relationship between the type of carbon deposition and the catalytic activity of the catalysts was clarified.

2. Experimental

2.1. Catalyst preparation

The olivine support material was purchased from an ore company in HB province, China. After receipt, the particles were sized between 380 and 830 μm (20–40 mesh) via screening treatments without any chemical treatment. The Ni—Fe bimetallic olivine-based catalyst was prepared using the WI and TF methods. The specific steps of the WI method are described as follows. The olivine was first calcined at 1100 °C for 4 h, and the olivine support was impregnated using a mixed aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ with mass fractions of Ni (5%) and Fe (5%) at room temperature for 24 h. After evaporation of the excess water, the samples were dried at 105 °C for 12 h, followed by calcination at 1100 °C for 4 h under an air atmosphere. The prepared catalyst was marked as WI-Ni/Fe/olivine. In the specific steps of the TF method, olivine was first calcined at 1400 °C for 4 h and mixed with quartz sand (60–80 mesh) that was previously calcined at 1600 °C to prevent fusion of the olivine. The olivine with no metal loading was marked as calcined olivine. Metallic iron (from Macklin, purity: 99.9%) and metallic nickel (from aladdin, purity: 99.5%) powder (mass fraction 5% Fe and 5% Ni) with the calcined olivine support were mechanically and evenly mixed, and the mixture was calcined at 1400 °C for 4 h by heating in an Ar atmosphere. Finally, the Ni—Fe bimetallic olivine (marked as TF-Ni/Fe/olivine) and the quartz sand were separated via screening.

2.2. Characterization techniques

The chemical compositions of the catalysts were analysed by X-ray fluorescence (AXIOSmAX-PETRO), and the crystalline structures of the catalysts were characterized using XRD (X'Pert-PRO MPD) with Cu Kα radiation ($\lambda = 1.54060$ Å) at 40 kV and 40 mA. The samples were scanned in the range of $2\theta = 10$–$80°$ with a step size of 0.02°. The reductive ability of the fresh catalysts and the carbonaceous species deposited on the catalyst surface during the cracking reaction were evaluated in temperature-programmed hydrogen reduction (H_2-TPR) and temperature-programmed oxidation with O_2 (O_2-TPO) on a ChemBET Pulsar TPR/TPO instrument (Quantachrome Instruments). The catalyst was pre-treated in a He flow at 300 °C (for H_2-TPR and O_2-TPO) for 30 min, and the reactor was quickly cooled to room temperature. After cooling, the sample was exposed to a mixture of 10% H_2/Ar (for H_2-TPR) or 5% O_2/He (for O_2-TPO) instead of He, and the temperature was increased from room temperature to 950 °C (for H_2-TPR) or 900 °C (for O_2-TPO), both at 10 °C min^{-1}. For the H_2-TPR, the temperature was held at 950 °C for 15 min. The specific surface areas and average pore diameter were measured using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) measurements based on the adsorption isotherm at liquid nitrogen temperature. Laser Raman spectra (LRS) were collected on a Horiba Labor HR800 system with 633 nm (for Ni/Fe/olivine catalysts) and 532 nm (for carbonaceous species) helium neon lasers as the excitation line. The surface characterization of the catalyst was tested using X-ray photoelectron spectroscopy (XPS) on a Kratos Ultra Spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific, Inc.) under the conditions of 20 eV and 100 eV pass energies for the survey spectra and single element spectra (Fe and Ni), respectively. The surface morphologies of the catalysts were obtained using scanning electron microscopy (SEM) with a Hitachi S4800 instrument. Transmission electron microscopy (TEM) was performed on a JEOL TEM-100CX instrument at a 200 kV acceleration voltage. The samples were dispersed as fine powders in ethanol by supersonic waves and subsequently placed on a Cu grid with a carbon film grid.

2.3. Catalytic reaction testing

The main components of the secondary tars and the tertiary tars,