



## Full Length Article

# Green synthesis of Ni supported hematite catalysts for syngas production from catalytic cracking of toluene as a model compound of biomass tar



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## ABSTRACT

In this work, natural limonite (NL) was selected as the precursor of hematite (H) to prepare the Ni-based catalysts (Ni<sub>x</sub>/H) for catalytic cracking of toluene. The influences of nickel loading and reaction temperature on catalytic cracking of toluene as well as the lifetime of catalyst were evaluated and the gas products were determined. The catalysts before and after catalytic cracking were characterized by XRD (X-ray diffraction), H<sub>2</sub>-TPR (H<sub>2</sub> temperature-programmed reduction), TEM (Transmission electron microscopy), XPS (X-ray photoelectron spectroscopy). The results showed that the catalytic activity of Ni<sub>x</sub>/H was obviously improved after the Ni addition due to the formation of Ni-Fe alloy. Toluene conversion increased at first with increasing of Ni loading from 0 to 6% and then decreased from 6 to 10%. High toluene conversion of 96% and stability were achieved as the Ni loading was 6% at the reaction temperature of 800 °C. Meanwhile, toluene was mainly decomposed into CO, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and hematite was transformed into magnetite due to the consumption of active lattice oxygen during the catalytic cracking reaction. However, the decrease in catalytic activity of Ni<sub>x</sub>/H with the increase of reaction time should be attributed to the metal carbide type coke formation.

## 1. Introduction

Conversion of biomass into synthesis gases by gasification has been considered as the most promising biomass conversion technology for renewable energy and chemicals [1]. However, during the process of biomass pyrolysis, the formation of biomass tar not only reduces the utilization of biomass energy and increases the maintenance expense of the system, but also seriously affects the long-term stable operation of gasification system [2]. Therefore, converting the biomass tar into small molecule gases is of crucial importance during the biomass gasification process. Up to now, several methods for tar elimination have been reported. Among them, catalytic cracking is considered to be one of the most effective methods [3]. That is mainly because of the biomass tar can be further transformed into small molecules such as H<sub>2</sub>, CO and CH<sub>4</sub> when catalysts are applied, and thus the concentration of tar in the synthesis gas is greatly decreased [4].

In the catalytic cracking of biomass tar, Ni-based catalyst has attracted much attention due to its high activation ability of C–H and C–C bonds in the hydrocarbon molecules [5–7]. However, despite the high activity of Ni-based catalysts, the catalytic performance is remarkably affected by the serious sintering of Ni particles and coking on the catalyst surface [8]. An advocated and effective method is to modify

the Ni-based catalysts by alloying with some other transition metals (Fe, Mn, Ce, Co, etc.) for the synergistic effects [9]. Fe has attracted much attention by many researchers because of the low-cost and its good performance in improving the catalytic performance of Ni-based catalysts. The addition of Fe can not only improve the conversion of biomass tar but also effectively inhibit the formation of carbon deposit owing to the formation of Ni-Fe alloy and the high oxygen affinity of Fe [10]. In consideration of the reactivity and the cost, some widely distributed and abundantly reserved natural minerals, such as dolomite [11], palygorskite [12], iron oxide [13,14] and olivine [15] have been recommended as alternative catalysts or/and supports for catalytic cracking of biomass tar. Świerczyński et al. [15] found that the addition of Ni over olivine enhanced the catalytic activity due to the interaction between Ni and Fe in olivine. Liu et al. [16] reported that the addition of Fe to Ni supported palygorskite catalysts highly improved the dispersion of Ni particles and promoted the formation of Ni-Fe alloy, facilitating the improvement of catalytic reactivity of catalysts for benzene removal. In addition, hematite has been used as an oxygen carrier for tar removal, owing to its rich lattice oxygen in the structure [17,18]. Hematite as a catalyst itself exhibited outstanding ability of oxygen transportation during the biomass conversion which suppress the coke formation and improve the catalytic performance. However, until now

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there are rare studies focuses on the utilization of hematite as a support and the interaction between hematite and nickel for the conversion of biomass tar. As we know, Fe-Ni species, especially Fe-Ni alloy, has been proved to be an effective active site for catalytic cracking of tar. Hence, the investigation of hematite supported nickel for tar removal is an interesting issue.

In this work, the low-cost and widely distributed natural limonite was selected as a precursor of hematite to prepare the Ni-based catalysts. Toluene was chosen as a model compound of biomass tar due to its abundance in the biomass tar and the stable property in the gasification process. The influences of nickel loading (0–10%) and reaction temperature (500–800 °C) on catalytic cracking of toluene as well as the lifetime of catalyst were evaluated in a fixed bed and the gas products were determined by an on-line gas chromatograph. The catalysts before and after catalytic cracking were characterized by XRD, TEM, H<sub>2</sub>-TPR, XPS to analyze the effect of coke formation on catalytic performance. The objectives of this study are to (i) investigate the interaction of nickel and hematite and the phase transformation of iron oxide during the catalytic reaction, (ii) explore the effect of coke formation on the catalytic performance of Nix/H catalysts and (iii) promote the development and application of natural limonite in biomass utilization.

## 2. Experimental

### 2.1. Catalysts preparation

Natural limonite (NL) used in this experiment was sampled from Xinqiao, Tongling city, Anhui province, China. The XRF result showed that NL is composed of Fe<sub>2</sub>O<sub>3</sub> (58.85%), SiO<sub>2</sub> (16.87%), Al<sub>2</sub>O<sub>3</sub> (4.85%), CaO (1.05%), MnO (3.16%), ZnO (1.60%), others 2.40% and the ignition loss 11.22%. NL was crushed and sieved into particle size of 250–380 μm. The Ni-based catalysts were prepared by the impregnation method: Firstly, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (purity 99.99%) and NL were dissolved in a 250 ml beaker with a certain amount of deionized water, then mixed evenly under vigorous stirring for 4 h. The mixture was further aged at ambient temperature for 24 h and then dried at 105 °C. After that, the catalysts were calcinated at 800 °C in air for 2 h. From previous study [19], goethite in limonite was completely transformed into hematite at such high temperature. Thus, the catalysts were labeled as Nix/H, where x denotes the loading content of Ni in weight percent. The mass ratio was set as m<sub>Ni</sub>/m<sub>Ni</sub> + m<sub>NG</sub> = 2, 4, 6, 8, 10%.

### 2.2. Characterization

X-ray diffraction (XRD) patterns of the catalysts were recorded between 5 and 70° at a scan speed of 2°/min using Cu Kα radiation on a D/max-rB X-ray diffractometer (50 kV and 40 mA). Specific surface areas of catalysts were analyzed by 13-point BET-nitrogen isotherms applied in a Novawin 3000e Surface Area and Pore size Analyzer. H<sub>2</sub> temperature-programmed reduction (TPR) measurements were performed on a mass spectrograph (MS, Hiden QIC-20). Transmission electron microscopy (TEM) measurements were performed on JEM-2100F microscope with an energy dispersive X-ray (EDX) facility. The catalyst surface analysis was performed using X-ray photoelectron spectroscopy (XPS) from a Thermo Scientific K-Alpha instrument equipped with an Al Kα source (10 mA, 14 kV) at 1486.8 eV. Magnetic Susceptibility (MS) of the spent catalysts were recorded by a Bartington MS2 susceptibility meter. Total coke formations on the spent catalysts were measured using Jena Mutil N/C 2100 TOC/TN analyzer.

### 2.3. Catalyst activity evaluation

The catalytic cracking reaction was carried out at atmospheric pressure in a laboratory-scale fixed bed with inner diameter of 12 mm and length of 300 mm, respectively. The experimental conditions were as follows: catalyst amount 0.5 g, toluene concentration 1000 ppm,

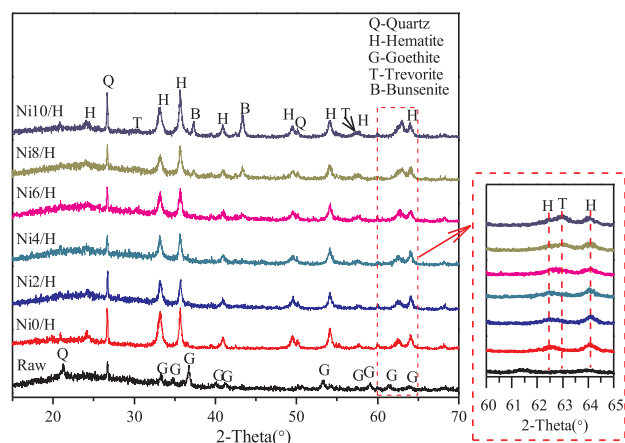


Fig. 1. XRD patterns of Nix/H catalysts calcinated at 800 °C in air atmosphere for 2 h.

reaction temperature 500–800 °C. The experimental steps were described in previous work [20]. Toluene conversion was calculated by Eq. (1):

$$\text{Toluene conversion} = \frac{C_{\text{toluene}}^{\text{in}} - C_{\text{toluene}}^{\text{out}}}{C_{\text{toluene}}^{\text{in}}} \times 100\% \quad (1)$$

where  $C_{\text{toluene}}^{\text{in}}$  is the influent concentration of toluene, and  $C_{\text{toluene}}^{\text{out}}$  is the effluent concentration of toluene.

## 3. Results and discussions

### 3.1. XRD result

The XRD patterns of NL and thermally treated Nix/H catalysts at 800 °C were shown in Fig. 1. All the patterns showed that NL was mainly composed of goethite and a small quantity of quartz. It was reported that quartz was generally regarded as a kind of inert material and always used as a reference material, thus, which would not influence the catalytic performance [17]. All the peaks of goethite disappeared when the catalysts were calcinated at 800 °C for 2 h. Instead, several new reflections at  $2\theta = 24.2^\circ, 33.2^\circ, 35.6^\circ, 40.9^\circ, 49.5^\circ, 54.1^\circ,$  and  $63.9^\circ$  were observed and identified as hematite in contrast with the pattern of JCPDS (89-2810). The transformation of goethite to hematite should be ascribed to the dehydroxylation of goethite. Previous studies [18,21] found that hematite could be used as an active component with high catalytic activity for the removal of biomass tar due to the available active lattice oxygen in the structure of hematite. The peaks at  $2\theta = 37.2^\circ, 43.3^\circ$  were found and assigned to bunsenite (NiO) after comparison with the pattern of JCPDS (71-1179). The intensity of these two peaks increased obviously with increasing of Ni loadings. In addition, trevorite (NiFe<sub>2</sub>O<sub>4</sub>) was observed at  $2\theta = 30.2^\circ, 63.0^\circ$  (JCPDS: 89-4927) when the Ni loadings was over 6% and the intensity of the peaks showed the highest in the case of Ni10/H. The formation of this spinel and its increase in intensity should be ascribed to the strong interaction between NiO and hematite during the preparation of catalysts. Liu et al. [16] reported that spinel would play an important role in suppressing the coke formation. However, it was also reported that the gradual growth in particle size of trevorite (NiFe<sub>2</sub>O<sub>4</sub>) would inhibit the catalytic activity of catalysts [22]. The specific surface area of Ni0/H, Ni2/H, Ni4/H, Ni6/H, Ni8/H and Ni10/H catalysts were detected as 13.8, 16.1, 18.0, 20.1, 18.1 and 17.9 m<sup>2</sup>/g, respectively. It was speculated that the decrease of surface area from 20.1 to 17.9 m<sup>2</sup>/g should be ascribed to the aggregation of NiO particles on the surface of the hematite. From the previous study [23], the surface area had been confirmed as a considerable parameter playing an important role in catalytic activity for catalysts.

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