



Catalytic cracking of toluene over hematite derived from thermally treated natural limonite



Xuehua Zou^a, Tianhu Chen^{a,*}, Haibo Liu^{a,*}, Ping Zhang^b, Dong Chen^a, Chengzhu Zhu^a

^aLaboratory of Nanomineralogy and Environmental Material, School of Resources & Environmental Engineering, Hefei University of Technology, Hefei 230009, China

^bGuangzhou Institution of Geochemistry, Chinese Academy of Science, Guangzhou, China

HIGHLIGHTS

- We tested the hematite derived from thermally treated natural limonite for catalytic cracking of toluene.
- Hematite played a role of oxygen carrier in reacting with carbon deposit.
- The catalysts can be magnetically reclaimed after catalytic reaction.
- The spent catalyst can be regenerated simply by thermal treatment under air atmosphere.

ARTICLE INFO

Article history:

Received 1 December 2015

Received in revised form 28 January 2016

Accepted 29 February 2016

Available online 11 March 2016

Keywords:

Natural limonite

Hematite

Toluene

Catalytic cracking

Lattice oxygen

ABSTRACT

The catalytic performance of hematite derived from thermally treated natural limonite on catalytic cracking of biomass tar using toluene as a model compound was investigated. The catalysts before and after catalytic reaction were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Magnetic Susceptibility meter (MS). The effect of reaction temperature and gas hourly space velocity (GHSV) on the catalytic performance of the newly formed hematite was studied in a laboratory scale fixed bed reactor. Furthermore, the composition of gas product was measured by gas chromatograph (GC) and the lifetime as well as the regeneration times was also evaluated. The results showed that the newly formed hematite had a high catalytic activity for the decomposition of toluene compared with that of quartz at the designed experimental temperature between 500 and 800 °C. The toluene conversion of 90% was obtained as the GHSV was not more than 5662 h⁻¹ at the reaction temperature of 700 °C. Meanwhile, the toluene was mainly decomposed into H₂, CO₂, CO and hematite was transformed into magnetite after catalytic cracking. What is more important, the spent catalysts can be reclaimed easily by a magnet, which benefited the recycle and regeneration of the catalyst. In addition, the strong resistance of this hematite to carbon deposit in lifetime test due to the existence of active lattice oxygen in hematite was documented. Therefore, this kind of low cost and high activity hematite derived from natural limonite is considered to be an advantageous catalyst for catalytic cracking of toluene.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

With the consumption of fossil fuels, the utilization of biomass as a potential renewable resource is drawing increasing attention in the past decades. Conversion of biomass into synthesis gases is an important process in the application of biomass energy. Among them, biomass gasification is thought to be one of the most promising biomass conversion technologies for renewable fuels and

* Corresponding authors.

E-mail addresses: chentianhu@hfut.edu.cn (T. Chen), liuhaibosky116@hfut.edu.cn (H. Liu).

chemicals. However, one of the most serious problems in biomass gasification is the formation of biomass tar during the process of biomass pyrolysis [1]. Tar is a complex mixture of more than 1000 species of aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbon, which can condense easily in downstream equipment [2,3]. The condensed compounds can cause serious problems by blocking the gas pipeline and depositing on the surface of gas engines, which increases the maintenance requirements and hinders the normal running of the whole system [4–6]. Thus, effective methods should be employed to decrease the concentration of tar compounds.

Several approaches for tar elimination have been widely reported such as physical treatment [7–9], thermal cracking [10,11], plasma-assisted cracking [12,13], and catalytic cracking [14–17]. Among these, catalytic cracking has been considered as the most promising and effective technique for tar conversion due to its advantages of converting tar into useful gases and greatly decrease the concentration of tar in gases.

A large number of catalysts have been extensively studied in catalytic cracking of biomass tar, such as metallic-based catalysts (Ni-based, Fe-based, noble metals-based et.al) [18–23], alkali metals [24,25], dolomites [26–28], olivine [29,30] and zeolites [31,32]. However, either the formation of carbon deposit or the high cost of catalysts restricted the utilization of catalytic cracking of biomass tar. For catalytic reactivity of catalysts and the economic reasons, much attention has been paid on the application of naturally occurring and highly active materials [14,33,34]. Kudo et al. [35] studied the pyrolysis and reforming of nascent volatiles derived from woody biomass by hematite at 690–800 °C in a fixed bed. The yield of heavy tar was decreased from 18.8 wt% to less than 0.01 wt% during the reforming by the oxidation of hematite. The Indonesian natural limonite ore was developed by Li et al. for the light fuel gas production [36]. The research showed that this kind of iron oxide dramatically promoted coal volatile decomposition at 500–800 °C. The study of iron-based catalysts were carried out by Uddin et al. [37] for steam reforming of biomass tar derived from cedar wood gasification in a two stage reactor. The tar was decomposed into hydrogen rich gases over the iron oxide catalysts by water gas shift reaction and the activity of the iron oxide catalysts seemed stable for tar decomposition. It indicated that the surface area and oxidation state of the iron oxide catalyst favored the catalytic activity for decomposition of biomass tar. In addition, Huang et al. [38] studied the biomass gasification using chemical looping with natural hematite, indicating that the iron oxides was an excellent oxygen carrier. Therefore, as mentioned above, the iron oxide is thought to be a promising catalyst used for decomposition of biomass tar due to its high tar destruction activity and good performance on light hydrocarbon reforming. However, report on the utilization of natural limonite to prepare iron oxides for catalytic cracking of biomass tar was rarely found [37,38]. Natural limonite is a naturally occurring mineral. Despite of an abundant distribution, the existence of quartz and clay minerals causes iron ore low-grade. Consequently, this iron ore has hardly been employed in steel production mainly due to the necessity of endothermic dehydration to form hematite [35]. On the other hand, the newly formed hematite derived from thermally treated natural limonite had a higher surface area and more stable structure than that of goethite [39–41], which possessed a potential as a catalyst for catalytic cracking of toluene.

Therefore, natural limonite was chosen as a precursor for preparing hematite to catalytic cracking of toluene in this work. The influence of reaction temperatures (500–700 °C) and gas hourly space velocity (GHSV) on toluene conversion and gases composition were studied. Furthermore, the lifetime and regeneration activity of catalyst were also evaluated. The objective of this work was to prepare hematite by functionalization of natural limonite and develop this kind of relatively inexpensive and disposable naturally occurring material for catalytic cracking of toluene.

2. Experimental

2.1. Catalyst preparation

Natural limonite used in this study was sampled from Xinqiao, Tongling city, Anhui province, China. The samples were crushed

and sieved into particle size of 0.425–0.850 mm before they were calcined at 700 °C for 2 h under air atmosphere.

2.2. Catalyst activity test

Toluene was chosen as a tar model compound because it is one of the representative organic compounds of the accepted tar classification. It is also a stable aromatic compound formed with high-temperature gasification process [42]. Catalytic performance was performed at atmospheric pressure in a laboratory-scale fixed bed quartz reactor with an inner diameter of 12 mm and a length of 300 mm. The schematic overview of the setup for the catalytic cracking of toluene over hematite was shown in Fig. 1. The catalyst was held by quartz wool and placed in the middle of the reactor. The operation conditions were as follows: catalyst amount 0.5–1.5 g; toluene concentration about 1000 ppm; reaction temperature 500–800 °C. Argon (100 mL/min) was used as a carrier gas for toluene and diluent gas controlled by a mass flow meter. In addition, a heater was attached on the gas path to avoid the condensation of toluene vapor. The temperature was ramped to the desired reaction temperature with a heating rate of 10 K min⁻¹. The gaseous product passed through a cold trap maintained at a temperature of 0 °C to condense the unreacted toluene. The toluene was analyzed by a gas chromatograph (GC-7890T) equipped with a capillary column and a flame ionization detector (FID). The non-condensable gas product was analyzed using a gas chromatograph (GC-2010 PLUS) equipped with a 3X column and a thermal conductivity detector (TCD). Toluene conversion and gas yield was calculated according to the following relationship:

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

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

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained using D/max-rB diffractometer with a Cu K α radiation generated at 50 kV and 40 mA. The scan rate was 5° min⁻¹ with 0.5° divergence slit size. Phase identification was carried out by comparing with those included in the Joint Committee of Powder Diffraction Standards (JCPDS) database.

Chemical composition was measured on an X-ray fluorescence (XRF) spectrometer (Shimadzu XRF-1800) with Rh radiation.

13-point BET- nitrogen isotherms were applied in a Novawin 3000e Surface Area and Pore size Analyzer to determine the specific surface area of catalysts (SSA, m² g⁻¹). A sample quantity of 0.15 g was employed for the measurement, the sample was out-gassed at 300 °C for 24 h before N₂ adsorption–desorption.

Transmission electron microscope (TEM) measurements were performed on JEM-2100 microscope with an energy dispersive X-ray (EDX) facility. The samples were prepared by dispersing a little amount of catalyst powder in high purity ethanol before dropping the suspension to a copper grid. Images of the microstructure and the relevant selected area electron diffraction patterns were acquired using an analytical electron microscope.

X-ray photoelectron spectroscopy (XPS) analyses were performed using a Thermo Scientific K-Alpha instrument equipped with an Al K α source (10 mA, 14 kV) and operated at 1486.8 eV during the measurement.

Magnetic Susceptibility (MS) of the spent catalysts was recorded by a Bartington MS2 susceptibility meter.

Download English Version:

<https://daneshyari.com/en/article/205130>

Download Persian Version:

<https://daneshyari.com/article/205130>

[Daneshyari.com](https://daneshyari.com)