Journal of Molecular Catalysis A: Chemical 363–364 (2012) 304–310

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Catalytic cracking of tar derived from rice hull gasification over palygorskite-supported Fe and Ni

Haibo Liu[a,c], Tianhu Chen[a,**], Dongyin Chang[a], Dong Chen[a], Hongping He[b,c], Ray L. Frost[c,*]

[a] School of Resource and Environmental Engineering, Hefei University of Technology, China
[b] Guangzhou Institute of Geochemistry, Chinese Academy of Science, Guangzhou, China
[c] Science and Engineering Faculty, Queensland University of Technology, Brisbane, Australia

ARTICLE INFO

Article history:
Received 28 February 2012
Received in revised form 4 July 2012
Accepted 5 July 2012
Available online 16 July 2012

Keywords:
Palygorskite clay
Nickel oxide
Catalytic cracking
Biomass tar
Hydrogen yield

ABSTRACT

The catalytic performance of Fe–Ni/PG (PG: palygorskite) catalysts pre-calcined and reduced at 500 °C for catalytic decomposition of tar derived through rice hull gasification was investigated. The materials were characterized by using X-ray diffraction, hydrogen temperature reduction, and transmission electron microscopy. The results showed that ferrites with spinel structure ($(Fe, Ni)_3O_4$) were formed during preparation of bimetallic systems during calcination and reduction of the precursors (Fe–Ni/PG catalysts) and NiO metal oxide particles were formed over Fe6–Ni9/PG catalyst. The obtained experimental data showed that Fe–Ni/PG catalysts had greater catalytic activity than natural PG. Tar removal using Fe6–Ni9/PG catalyst was as high as Fe10–Ni6/PG catalyst (99.5%). Fe6–Ni9/PG showed greater catalytic activity with greater H_2 yield and showed stronger resistance to carbon deposition, attributed to the presence of NiO nanoparticles. Thus, the addition of nickel and iron oxides played an important role in catalytic cracking of rice hull biomass tar.

1. Introduction

Biomass gasification offers the potential for producing a fuel gas that can be used for power generation or synthesis gas applications. Pyrolysis of biomass has several environmental advantages over fossil fuels: namely lower emission of CO_2 and other greenhouse gases [1]. However, one of the major issues in biomass gasification is dealing efficiently with tar reduction during the pyrolysis process. This presents significant impediment to the application of biomass gasification. The condensation products present in tar may cause problems in downstream handling, making catalytic hot gas cleaning a necessary step in most gasification applications. Catalytic decomposition appears to be a very attractive way to convert tar components into H_2, CO and other useful chemicals.

Most research has focused on steam reforming of various hydrocarbon feedstock over supported-Ni and expensive metal catalysts [2–8]. Furusawa et al. [9] reported that Co/MgO catalyst had higher activity than any types of Ni/MgO catalysts. This was attributed to the difference in catalytic performance between Co/MgO and Ni/MgO. Asadullaha et al. [10] reported that almost all carbon in the biomass was converted into gas products using $Rh/CeO_2/SiO_2$ catalysts and the deactivation of the catalyst caused by carbon or char deposition on the catalyst surface was not severe. On the other hand, $Rh/CeO_2/SiO_2$ catalysts have some disadvantages due to the high cost of Rh and the limited availability of this expensive metal. In general, Ni catalysts showed high catalytic activity for the removal of tar and are very effective in tar removal. However, coking on the catalyst surface and sintering of Ni particles caused the loss of the catalytic activity [11]. In addition, to avoid a fast deactivation of Ni catalyst by coke, researchers used CeO_2 as a catalyst additive. It is well known that CeO_2 supported catalysts can promote the reaction of active carbon with O_2 enhancing the catalytic activity and resistance to coking [12–14].

The motivation for this work is to find a new catalyst system, such as a binary catalyst, which not only replaces nickel catalyst but also the expensive metal catalyst Rh. For the catalyst, it is expected that the interaction of two kinds of metal oxides play an important role in the catalytic decomposition of biomass tar derived from biomass gasification. Thus, this present work focuses on the investigation of using iron and nickel oxide catalysts supported on palygorskite clays for tar removal instead of single nickel catalyst or expensive metal catalysts. Little research has been undertaken using iron catalysts, including the binary oxide catalyst of iron and nickel oxides for tar removal [15,16]. The steam reforming of methane has been studied over 1 wt% Fe/ZrO_2 catalyst but low methane conversion was measured at 800 °C [15]. Uddin et al. [16] reported that the activity of the iron oxide catalysts for tar

---

[*] Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804.
[**] Corresponding author. Tel.: +86 0551 2903990.
E-mail addresses: chentianhu168@vip.sina.com, chentianhu1964@126.com (T. Chen), r.frost@qut.edu.au (R.L. Frost).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2012.07.005

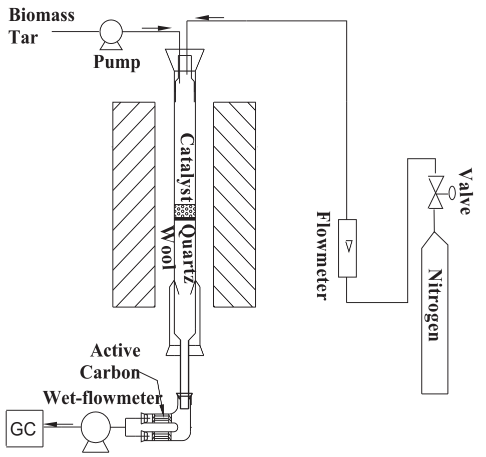

Fig. 1. The system for activity measurement.

decomposition seemed stable with cyclic use but the activity of the catalysts for the water gas shift reaction decreased with repeated use. Palygorskite (PG) clay, a hydrated magnesium aluminosilicate, shows high crystallinity, inner pore size (0.38 × 0.63 nm) and high specific surface area (228.5 m^2/g) [17]. In general, it consists of 65.5 wt% SiO_2, 5.4 wt% Al_2O_3, 14 wt% MgO, 3.2 wt% Fe_2O_3 and trace amounts of other minerals. Thus, palygorskite clays have been proven to be a useful support.

Previous research has focused on the effect of temperature on catalytic bed and catalyst loadings for tar decomposition. The effect of catalysts preparation methods and the study of additive types and additive loading on catalytic cracking biomass tar over palygorskite-supported Fe and Ni have been investigated [18,19]. On the basis of this previous research, the application of palygorskite-supported Fe and Ni oxides are investigated in the present work. The purpose of this study is to prepare Fe–Ni/PG catalysts and determine the catalytic performances of Fe–Ni/PG catalysts for tar removal derived from rice hull gasification.

2. Experimental

2.1. Preparation of the catalysts

Palygorskite-supported iron and nickel oxides catalysts were prepared by incipient wetness impregnation of palygorskite with aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, followed by overnight drying at 105 °C. For the catalyst testing, all catalysts were pelletized, crushed and sieved to 0.85–0.425 mm, followed by calcination in air for 2 h at 500 °C. The reaction product was then reduced in hydrogen, derived from a hydrogen generator at a flow rate of 80 ml min^{-1}, and held at 500 °C for 1 h. The amount of nickel and nickel oxide loading on the catalyst support was controlled between 0 and 12 wt% by changing the concentration of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ solutions. In this study, Fex–Niy/PG (y = 0, 3, 6, 9, 12 wt%, when the x = 6 wt%; x = 0, 1, 6, 8, 10, 12 wt%, while y = 6 wt%) were prepared for catalyst testing.

2.2. Catalytic testing

Biomass tar, catalyzed to produce H_2-rich, was derived from rice hull gasification. The tar consists of C 79.2 wt%, H 5.3 wt%, N 1.6 wt%, O 7.4 wt%, ash 5.3 wt% and a small amount of the elements Cl and S.

Catalytic tests were controlled by using the fixed-bed experimental system shown in Fig. 1. Tar conversion and hydrogen yield are used to evaluate the catalytic reactivity of different catalysts. The setup and evaluation are the same as that previously reported [18]. The setup consisted of three kinds of systems (a sample injection system including biomass tar and carrier gas, a reaction and collection system and an analysis system). The reactor used was a straight quartz tube operating at 700 °C (i.d. 30 mm width and 400 mm body length) and the catalyst bed was supported by means of quartz wool. All the catalysts were tested under the same experimental conditions: WHSV = 2.7 h^{-1} and atmospheric pressure. 10 g of catalyst was used in each experiment. Nitrogen was used to carry the biomass tar cracking gases into and out of the reactor; a flow rate of nitrogen was 80 ml min^{-1}. The rice hull gasification tar was introduced into the reactor with a peristaltic pump (BQ50-1J) at a flow rate of 0.45 g min^{-1}. Tar was introduced as a liquid in a silica tube. The tar did not stick to reaction walls because a special set up was used during the experiment. The tar collected from rice hull gasification power plant is thick. Thus, the introduction lines were not heated. Before and after the reaction, the introduction lines were weighed to calculate the mass of tar in the reactor. The duration of the experiment was 20 min. Granular activated carbon (GAC) was used for collecting unreacted tar and by-products as shown in Fig. 1. Almost all the unreacted and by-products can be absorbed by GAC. In this way, unreacted tar and byproducts were recovered in GAC and the amounts of unreacted tar and byproducts were calculated by subtracting the mass of the filter before reaction from remained after reaction. Thus, the efficiency of catalysts on biomass tar can be calculated using the following formula. In the formula, $M_{\text{in-tar}}$ and $M_{\text{out-tar}}$ represent the amount of tar dragged into the reactor and tar collected in the filter, respectively.

$$\text{Tar conversion} = \frac{M_{\text{in-tar}} - M_{\text{out-tar}}}{M_{\text{in-tar}}} \times 100\%$$

After the reaction, the peristaltic pump was switched off and resultant gases were carried by nitrogen into an air cell and the gas volume was determined by a wet test meter. The noncondensible gases, which include hydrogen, nitrogen, carbon monoxide and methane were analyzed by gas chromatography (GC-7890T) equipped with a C2000 column and a thermal conductivity detector (TCD). The column temperature, evaporation chamber temperature, the temperature and bridge current of detector were 70 °C, 120 °C, 100 °C, 100 mA, respectively. Hydrogen yield was calculated by the following formula. $M_{\text{H-out}}$ and $M_{\text{H-in}}$ represent the mass of hydrogen derived from catalytic cracking of tar and the mass of hydrogen element in tar dragged into the reactor, respectively.

$$\text{Hydrogen yield} = \frac{M_{\text{H-out}}}{M_{\text{H-in}}} \times 100\%$$

2.3. Catalyst characterization

X-ray diffraction (XRD) measurement was performed on a Rigaku powder diffractometer with Cu Kα radiation. The tube voltage was 40 kV, and the current was 100 mA. The XRD diffraction patterns were taken in the range of 5–70° at a scan speed of 4° min^{-1}, which was used for identifying nickel and iron oxides as well as their oxidation states on the surface of the palygorskite. Phase identification was carried out by comparison with a database.

H_2-temperature programmed reduction (TPR) measurements were performed on calcined samples under 5% flowing H_2 diluted with Ar using an electric oven-temperature programmed apparatus to investigate the nickel and iron oxide phases after calcination. A 60 ml min^{-1} feed of 5% H_2/Ar was used for reduction and the temperature was ramped at 10 °C min^{-1} to 850 °C. The effluent gases from the reactor were conducted to flow directly into the mass spectrograph (MS, Hiden QIC-20), which measured the consumption of H_2.