



CO₂ reforming of toluene as model compound of biomass tar on Ni/Palygorskite

Tianhu Chen^{a,*}, Haibo Liu^{a,b}, Peichao Shi^a, Dong Chen^a, Lei Song^a, Hongping He^c, Ray L. Frost^{b,*}

^aSchool of Resources and Environmental Engineering, Hefei University of Technology, Hefei, China

^bSchool of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Australia

^cGuangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

H I G H L I G H T S

- ▶ We have made on palygorskite-supported nickel catalysts.
- ▶ We tested catalytic CO₂ reforming of biomass tar.
- ▶ The influence of reaction temperature and concentration of CO₂ on H₂ yield has been studied.
- ▶ As reaction temperature and concentration of CO₂ increased, the amount of carbon deposit decreased.

A R T I C L E I N F O

Article history:

Received 10 September 2012

Received in revised form 4 December 2012

Accepted 10 December 2012

Available online 23 December 2012

Keywords:

Toluene

Biomass tar

CO₂ reforming

Palygorskite

Catalytic cracking

A B S T R A C T

Catalytic CO₂ reforming of biomass tar on palygorskite-supported nickel catalysts using toluene as a model compound of biomass tar was investigated. The experiments were performed in a bench scale installation a fixed bed reactor. All experiments were carried out at 650, 750, 800 °C and atmospheric pressure. The effect of Ni loading, reaction temperature and concentration of CO₂ on H₂ yield and carbon deposit was investigated. Ni/Palygorskite (Ni/PG) catalysts with Ni/PG ratios of 0%, 2%, 5% and 8% were tested, the last two show the best performance. H₂ yield and carbon deposit diminished with the increase of reaction temperature, Ni loading, and CO₂ concentration.

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1. Introduction

With the depletion of fossil fuel sources as well as global warming issues, the utilization of biomass is receiving increased attention as a potential source of renewable energy. Among the biomass utilization technologies, gasification has attracted increased interest by producing a gas rich in H₂ and CO [1,2]. Biomass gasification is a promising technology for fuels for power generation and chemical production. One of the main disadvantages for commercialising biomass gasification is the product gas quality. Among the impurities present in product gas, tar represents a serious impediment that has received significant attention in literature [3–5]. In addition, tar can deposit on surfaces of filters, heat exchangers and engines, reducing component performance

and increasing maintenance requirements. It must also be remembered that tar can polymerize to form more complex structures and aerosols. Tar removal methods can be divided into two types: primary and secondary [3]. Primary methods include the measures taken in the gasification step to prevent tar from being in the fluidized bed furnaces or to convert it into small-molecule gases. Secondary methods include chemical or physical treatments downstream of the fluidized bed furnaces. Among these measures, the catalytic reforming process is very attractive technique for tar removal. The catalysts used in the catalytic reforming process include metallic catalysts, mainly Ni-based catalysts [5,6–10], alkali metallic catalysts, dolomites, olivine [11] or a combination of metals on mineral substrate [12].

Tar is a complex mixture of organic compounds which formed in the thermochemical processing of biomass. Therefore, many researchers used model compound in the tar remove studies, example of phenol [13,14], naphthalene [15,16] and toluene [5,9,10,17]. In the present research work, toluene was chosen as a model compound of biomass tar because it is found in significant

* Corresponding authors. Tel.: +86 551 2903990 (T. Chen), tel.: +61 7 3138 2407; fax: +61 7 3138 1804 (R.L. Frost).

E-mail addresses: chentianhu168@vip.sina.com, chentianhu1964@126.com (T. Chen), r.frost@qut.edu.au (R.L. Frost).

quantities, especially at low reaction temperature, being clearly surpassed by benzene [18]. Various kinds of catalysts and operation conditions were described in studies about tar catalytic cracking using toluene as model compound. Simell et al. [19] studied tar-decomposing activities of dolomites and limestone catalysts using toluene as a model compound. Their tests were carried out in a fixed-bed reactor at 900 °C under 2 MPa using an N₂–H₂O–CO₂ gas mixture. Wang and Gorte [20] analyzed 1 wt% Pd/alumina and 1 wt% Pt/ceria catalysts in a fixed bed reactor. The S/C ratio was from 1:1 to 3:1 and reaction temperature was from 853 to 1043 °C. Juutilainen et al. [21] studied several catalysts (nickel based-catalyst, zirconia, dolomite, alumina, alumina-doped zirconia) at different temperatures from 550 to 900 °C. In their tests, they used a synthetic gasification gas mixture in the presence of oxygen from 1% to 20%. Simell et al. [22] tested several catalysts included alumina, dolomite, SiC and nickel-based catalysts. These researchers studied toluene decomposition in different gas atmospheres. The tests were carried out in a fixed-bed tube reactor at 900 °C under 2 and 5 MPa pressure. Swierczynski et al. [9] studied olivine and Ni/olivine catalysts in the fixed bed using toluene as a model compound with reaction temperatures from 560 to 850 °C. The ratios of steam/toluene varied from 7.5 to 24. Kuhn et al. [11] evaluated four olivine catalysts by reforming model compounds (naphthalene, toluene and methane). Treatments for olivine catalysts prior to reaction and the formation of free Fe phase played an important role in catalyst activity. Zhang et al. [12] employed Ni/olivine catalysts doped with CeO₂ in toluene steam-reforming experiment. The ratio of S/C was 5 at temperatures from 700 to 830 °C. Nordgreen et al. [23] analyzed metallic iron catalysts on tar decomposition at temperatures from 700 to 900 °C. Tar decomposition on nature olivine and Ni/olivine in dry-reforming (methane conversion) and steam-reforming (methane conversion) was studied at temperatures from 600 to 800 °C [24].

As mention above, Ni-based catalysts have been widely used in biomass gasification or biomass gas purification. In order to enhance the nickel catalysts performance, palygorskite (PG) was employed as a catalyst support. PG is a silicate clay mineral which has a special structure and physico-chemical properties. PG has fibrous morphology with 30–40 nm in diameter and several micrometers in length. PG has large surface area, is mesoporous and thus exhibits excellent surface activity and adsorption properties [25–27]. PG is an excellent natural nanometer mineral material which can be used as catalyst carrier [28–30]. Research using PG as a catalyst or catalyst carrier in the reforming of biomass tar has not been reported in recent years.

As a greenhouse gas, carbon dioxide had aroused widespread attention because it can lead to temperature rise of the global atmosphere. Carbon dioxide can be used to make syngas production which can react with methane. Lemonidou and Vasalos [31] investigated methane reforming by carbon dioxide over 5 wt% Ni/CaO–Al₂O₃ catalyst. Catalytic activity was investigated at temperatures between 630 and 850 °C with an equimolar CH₄ and CO₂ mixture. Tsipouriari and Verykios [32] studied the kinetic behavior of the Ni/La₂O₃ catalyst in the reforming reaction of methane with carbon dioxide as a function of temperature and partial pressure of CH₄ and CO₂. Tsipouriari and Verykios [33] studied mechanistic aspects of carbon and oxygen reaction pathways to form CO over Ni/La₂O₃ and Ni/Al₂O₃ using isotopically labeled molecules. It was found that the quantity of reversibly adsorbed CH₄ and the active carbon-containing intermediate species in the carbon pathway to form CO originating from CH₄ is higher than the respective quantities derived from the CO₂ molecule. In fact, carbon dioxide was included in biomass gasification gas.

In this context, it has been considered of interest to study the performance of Ni/PG in a fixed bed reactor at temperatures between 650 and 800 °C with CO₂. In this work, the influence of Ni

loading on H₂ yields is analyzed. The influence of CO₂ concentration (C_(CO₂)/C_(C₇H₈)) on H₂ yields is analyzed with C_(CO₂)/C_(C₇H₈) ratios varied from 0.9 to 4.54. Especially, CO₂-TPD and TPO are applied to investigate the effect of the introduction of Ni/NiO on sorption of CO₂, to investigate the role of CO₂ in the catalytic reforming reaction and to evaluate the catalytic performance of Ni/PG.

2. Experimental

2.1. Experimental system

The experimental system is a bench-scale installation using a fixed reactor. A schematic of installation is shown in Fig. 1. The reactor is made of quartz reactor and the inner diameter of reactor is 25 mm. The evaporating pot is also made of stainless steel with cavity volume of 84.78 cm³. Toluene is introduced into the evaporating pot using a peristaltic pump and then nitrogen is introduced into the evaporating pot and carries toluene gas into the quartz reactor. Toluene is delivered by peristaltic pump with a flow rate of 5.92 mg/min. The gases needed in this installation (hydrogen for reducing the catalyst, argon for chromatograph and nitrogen) are metered by a mass flow controller.

The H₂ concentration in the exit gas is collected and determined by gas chromatography (GC-7890T). One column (C-2000) is used with TCD detector and argon is used as carrier gas. The time required for product gas analysis is 10 min. The experimental system worked at atmospheric pressure and reaction time was 20 min. All the experiments were carried out at temperatures between 650 and 800 °C. The total gas flow rate is 250 cm³/min using nitrogen as carrier gas. The nitrogen gas flow rate is from 200 to 250 cm³/min and CO₂ flow rate is from 0 to 50 cm³/min with ratios of C_(CO₂)/C_(C₇H₈) from 0 to 4.54. The inlet toluene-feeding rate is constant. The catalytic reaction bed is composed of silica wool as filter supporting bed and catalyst (2 g) with a size of 0.85–2 mm.

2.2. Catalysts preparation

The catalysts were prepared in our laboratory by incipient impregnation. Three catalysts were prepared and Ni loading is 0, 2, 5 and 8 wt%. A defined concentration of solution of nickel nitrate and PG were mixed and then were strongly stirred. The mixed samples were dried in vacuum conditions at 105 °C, smashed and sieved (0.85–2 mm). The particles were calcined in nitrogen atmosphere at 500 °C for 3 h and reduced by hydrogen at 500 °C for 2 h. The flow rate of hydrogen was 100 mL/min. The catalysts were labeled as NiX/PG, X represents Ni loading.

The calcined catalysts were characterized by X-ray diffraction (XRD). The morphology of reduced catalysts is characterized by transmission electron microscope (TEM). The selected area electron diffraction and energy spectrum (EDS) were also employed to characterize catalysts.

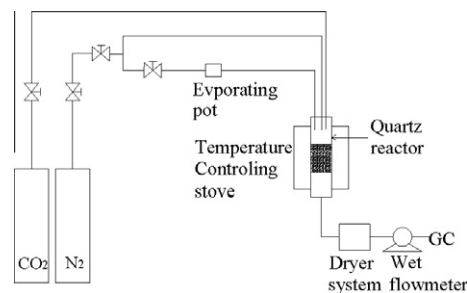


Fig. 1. Schematic of the experimental system.

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