



Production of aromatics through current-enhanced catalytic conversion of bio-oil tar



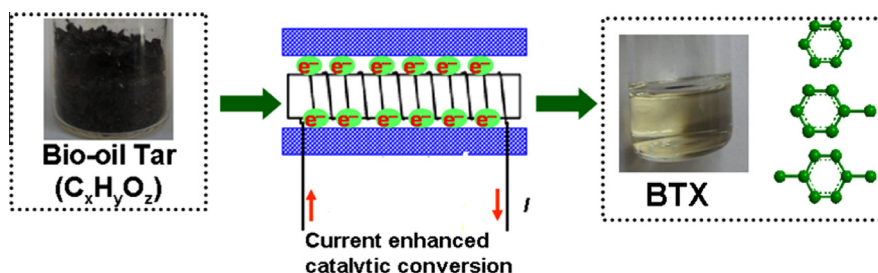
Peiyan Bi, Yanni Yuan, Minghui Fan, Peiwen Jiang, Qi Zhai, Quanxin Li*

Department of Chemical Physics, Anhui Key Laboratory of Biomass Clean Energy, University of Science & Technology of China, Hefei, Anhui 230026, PR China

HIGHLIGHTS

- A new route for directional production of BTX was achieved by CECC of bio-oil tar.
- An excellent BTX selectivity of 92.9 C-mol% with yield of 25.1 wt.% was obtained.
- The synergistic effect of current promoted deoxygenation and cracking of the tar.
- Mild condition is useful for producing chemicals and overall use of bio-oil tar.

GRAPHICAL ABSTRACT



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ABSTRACT

Biomass conversion into benzene, toluene and xylenes (BTX) can provide basic feedstocks for the petrochemical industry, which also serve as the most important aromatic platform molecules for development of high-end chemicals. Present work explored a new route for transformation of bio-oil tar into BTX through current-enhanced catalytic conversion (CECC), involving the synergistic effect between the zeolite catalyst and current to promote the deoxygenation and cracking reactions. The proposed transformation shows an excellent BTX aromatics selectivity of 92.9 C-mol% with 25.1 wt.% yield at 400 °C over usual HZSM-5 catalyst. The study of the model compounds revealed that the groups such as methoxy, hydroxyl and methyl in aromatics can be effectively removed in the CECC process. Present transformation potentially provides an important approach for production of the key petrochemicals of BTX and the overall use of bio-oil tar derived from bio-oil or biomass.

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1. Introduction

Biomass conversion into benzene, toluene and xylenes (BTX) can provide the basic feedstocks for the petrochemical industry, and these aromatics also serve as the most important aromatic platform molecules for the development of high-end chemicals (Calvo-Flores and Dobado, 2010; Sannigrahi et al., 2010; Zakzeski et al., 2010). Bio-oil, produced from fast pyrolysis of various plant components of lignocellulosic biomass, is an important renewable feedstock for the production of bio-fuels and chemi-

cals (Huber and Corma, 2007; Sun et al., 2010; Wright et al., 2010). Compared with solid biomass as the raw material, liquid bio-oil can be readily stored and transported and more suitable for the production of chemicals on a large scale. Vispute et al. (2010) outlined a unique route for bio-oil deoxygenation into chemicals including aromatic hydrocarbons, light olefins and mixed alcohols with an about 60% overall carbon yields, in which a cascade process included hydroprocessing of bio-oil over the Ru/C or Pt/C catalysts and followed by catalytic conversion of the refined bio-oil to the hydrocarbons over the zeolite catalyst. Zhang et al. (2011) explored the catalytic conversion of different biomass-derived feedstocks such as hydrogenated bio-oil, glucose, sorbitol and glycerol over the ZSM-5 catalyst, and found that the yields of aromatics and olefins increased with increasing

* Corresponding author. Tel.: +86 551 3601118; fax: +86 551 3606689.
 E-mail address: liqx@ustc.edu.cn (Q. Li).

the hydrogen to carbon effective ratio (defined as $H/C_{\text{eff}} = (H-2O)/C$). Gayubo and co-workers proposed a thermal-catalytic two-steps process for the conversion of the crude bio-oil into hydrocarbons with a HZSM-5 zeolite, and revealed that bio-oil conversion and the light olefins selectivity are significantly enhanced by co-feeding methanol (Gayubo et al., 2010; Valle et al., 2012). They also revealed that the Ni-modified HZSM-5 zeolite can produce higher aromatics (Valle et al., 2010a,b).

It has been revealed that zeolite catalysts such as ZSM-5, HZSM-5, Y-zeolite, Beta zeolite, Al-MCM-41, H-USY, SBA-15, Al-MSU and Ga/ZSM-5 are promising candidates for the transformation of biomass-related feedstocks into bio-fuels and chemicals (Alonso et al., 2010; Bozell, 2010; Carlson et al., 2008; Cheng et al., 2012; Hoang et al., 2010; Jae et al., 2011; Ma et al., 2012; Mihalcik et al., 2011; Rinaldi and Schüth, 2009; Wang et al., 2010). It should be pointed out that bio-oil possesses some unique composition characteristics such as higher content of oxygen and lower H/C_{eff} ratio, as compared with the currently used petrochemical feedstocks. Also, the bio-oil contains numerous and complex oxygenated organic compounds including acids, alcohols, aldehydes, ketones, substituted phenols, lignin and other oxygenates (Czernik and Bridgwater, 2004; Kan et al., 2010). Generally, a number of parallel and consecutive reactions occurred in the catalytic transformation of bio-oil due to the complexity of the bio-oil composition. The conversion of the oxygenated organic compounds in bio-oil into hydrocarbons can go through the reactions occurring inside the zeolite such as dehydration, decarboxylation, decarbonylation, hydrogen transfer, alkylation, isomerization and aromatization (Gayubo et al., 2010; Gong et al., 2011; Valle et al., 2010a,b, 2012; Vispute et al., 2010; Zhang et al., 2011). Consequently, the products derived from the bio-oil catalytic cracking, depending on catalysts and reaction conditions, generally contain a very wide range spectrum of compounds such as aromatic hydrocarbons, phenols, olefins, alkanes and low oligomers (Gayubo et al., 2010; Gong et al., 2011; Valle et al., 2010a,b, 2012; Vispute et al., 2010; Zhang et al., 2011). The remaining challenges for the bio-oil transformation include improving selectivity and yield of target products along with suppressing catalyst deactivation by optimizing the catalysts and cracking conditions.

The crude bio-oil can be separated by distillation treatment into two components, (lighter and heavier fractions). Lighter fractions can be used as a useful feedstock for the production of light olefins, hydrogen and other bio-fuels or chemicals. The heavy components, mainly consisting of substituted phenols and aromatic oligomers produced by depolymerization of lignin constituent in lignocellulosic biomass, can serve as a raw material for production of BTX or other high value aromatic chemicals. Our previous work showed that the heavy components of the bio-oil (bio-oil tar) were difficult to be transformed into light olefins or hydrogen as compared with its light components (Gong et al., 2009, 2011; Hou et al., 2009; Huang et al., 2012; Kan et al., 2010; Wang et al., 2007; Xu et al., 2011; Yuan et al., 2008). Considering the composition characteristics, the heavier fractions are more suitable for use as a feedstock for production of high value aromatic chemicals. Herein, we show a new route to directionally produce BTX by the current-enhanced catalytic conversion of bio-oil tar, using the synergistic effect between catalyst and current to promote the bio-oil deoxygenation, cracking and the selective recombination of the groups in the aromatic monomers. Present transformation can yield a high selectivity and yield of the target products-BTX under lower reaction temperature and atmospheric pressure without external hydrogen, which potentially provides an important approach for the production of the key petrochemicals of BTX and the overall use of the bio-oil tar derived from bio-oil or biomass.

2. Materials and Methods

2.1. Materials

2.1.1. Biomass feedstocks

Bio-oil was produced by the fast pyrolysis of straw stalk in a circulating fluidized bed with a capacity of 120 kg h^{-1} of oil at our Lab (Gong et al., 2009, 2011; Hou et al., 2009; Huang et al., 2012; Kan et al., 2010; Wang et al., 2007; Xu et al., 2011; Yuan et al., 2008). The crude bio-oil was distilled up to 110°C , and separated into the light component and precipitable heavier component (bio-oil tar) of (about 50 wt.%). In this work, the heavier component was employed as feedstock to study the catalytic transformation of bio-oil tar to BTX. The compositions of the volatile, GC-MS detectable fractions of the bio-oil tar (using acetone as a solvent) mainly consists of 46.1% phenols, 10.7% ketones, 5.9% acids, 2.8% alcohols, 3.4% aldehydes, 1.9% esters, 1.6% levoglucosan, 14.5% aromatic oligomers and other oxygenates, estimated by the peak area percentages of GC-MS (gas chromatography-mass spectroscopy, Thermo Trace GC/ISQ MS with a TR-5 capillary column, USA). The water content in the dried bio-oil tar can be ignored. The detailed chemical constituents of the bio-oil tar were summarized in Table A1 in Support information. Model compounds such as anisole and phenol were purchased from Sinopharm Chemical Reagent Company Limited in China (Shanghai, China).

2.1.2. Catalysts and characterizations

Different zeolites (such as HZSM-5, HY-zeolite, and MCM-41) were supplied by Nankai University catalyst Co., Ltd. (Tianjin, China) and calcined in nitrogen atmosphere at 550°C for 4 h prior to use. The elemental contents of the catalysts were measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The catalysts were investigated by NH_3 -TPD (temperature programmed desorption of ammonia) and BET (Brunauer-Emmett-Teller surface area) analyses. For the NH_3 -TPD tests, the catalysts were at 500°C under helium flow (ultrahigh purity, 100 mL/min) for 2 h, and adsorption of ammonia was carried out at 120°C for 1 h. After the catalysts were flushed with He at 120°C for 1 h, the programmed-desorption of NH_3 was run from 120 to 700°C with a heating rate of 10°C/min . The desorbed ammonia was measured by a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou China) with a thermal conductivity detector (TCD). The N_2 adsorption/desorption isotherms of the catalysts were measured at -196°C using the COULTER SA 3100 analyzer.

2.2. Experimental setups and procedures

The catalytic conversion of bio-oil tar or the model compounds (such as anisole and phenol) was carried out in a continuous flowing reaction system using a quartz fixed-bed reactor (inner diameter: 33 mm; length: 400 mm) under atmospheric pressure (Fig. 1). The reactant sample was prepared by mixing the dried and ground bio-oil tar (the particle size of $1.0 \pm 0.5 \text{ mm}$) with the sand ($1.0 \pm 0.2 \text{ mm}$) at the 1:1 weight ratio. The mixture was fed into the reactor by a micro-feeder. We compared two transformation routes, the current-enhanced catalytic conversion (CECC) and the conventional catalytic conversion (CC). For the CECC runs (Fig. 1a), an annular Ni-Cr metal wire (total linear length of 2.1 m and diameter of 1.2 mm) was entwined around a quartz column and installed in the center of the catalyst bed, and 10 g of the zeolite catalyst with a particle size of 60–80 mesh was uniformly filled in around the metal wire. A given electronic current was passed through the metal wire for the CECC runs. In a typical case,

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