



Directional synthesis of ethylbenzene through catalytic transformation of lignin



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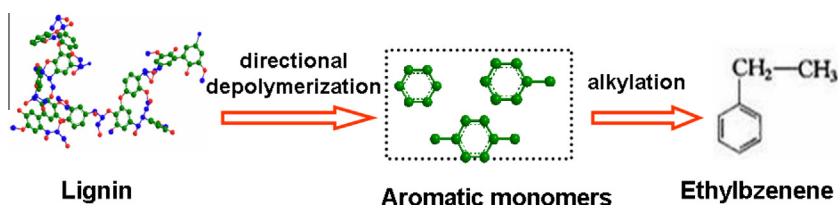
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HIGHLIGHTS

- A new approach for directional production of ethylbenzene from lignin was achieved.
- The process involves lignin depolymerization and alkylation of aromatic monomers.
- Lignin can be directionally converted to benzene over Re-Y/HZSM-5 catalysts.
- EB selectivity of up to 72.3 % was obtained by selective alkylation of monomers.

GRAPHICAL ABSTRACT



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ABSTRACT

Transformation of lignin to ethylbenzene can provide an important bulk raw material for the petrochemical industry. This work explored the production of ethylbenzene from lignin through the directional catalytic depolymerization of lignin into the aromatic monomers followed by the selective alkylation of the aromatic monomers. For the first step, the aromatics selectivity of benzene derived from the catalytic depolymerization of lignin reached about 90.2 C-mol% over the composite catalyst of Re-Y/HZSM-5 (25). For the alkylation of the aromatic monomers in the second step, the highest selectivity of ethylbenzene was about 72.3 C-mol% over the HZSM-5 (25) catalyst. The reaction pathway for the transformation of lignin to ethylbenzene was also addressed. Present transformation potentially provides a useful approach for the production of the basic petrochemical material and development of high-end chemicals utilizing lignin as the abundant natural aromatic resource.

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1. Introduction

Lignin is a main constituent of lignocellulosic biomass, and the amount of lignin residue in the paper industry is more than 50 million tons/year (Zakzeski et al., 2010a,b). Lignin is also a bulk by-product in the production of second generation ethanol fuel using the crop waste (Sannigrahi et al., 2010). It was revealed that lignin is a three dimensional amorphous polymer, polymerized through three primary phenylpropane monomers (para-coumaryl alcohol,

coniferyl alcohol and sinapyl alcohol) (Calvo-Flores and Dobado, 2010; Zakzeski et al., 2010a,b). These monolignol units in the lignin polymer are mainly connected by the ether bonds and C–C bonds. Generally, the lignin macromolecule contains a variety of special groups (such as methoxy, hydroxyl), which also affect the physical and chemical properties of lignin (Zakzeski et al., 2010a,b).

In the recent years, there is considerable interest in the production of chemicals and bio-fuels from lignin through hydrogenation reduction, oxidation, pyrolysis, catalytic pyrolysis, aqueous phase reforming or enzymatic conversion (Calvo-Flores and Dobado, 2010; Effendi et al., 2008; Sena-Martins et al., 2008; Zakzeski et al., 2010a,b). For hydrogenation reduction of lignin, typical reactions involve lignin depolymerization followed by the removal of

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the extensive functionality of the lignin subunits to form simpler monomeric compounds such as phenols and BTX (benzene, toluene and xylenes). These aromatic compounds can then be hydrogenated to alkanes or used in the synthesis of other fine chemicals. The products derived from the hydrogenation of lignin, depending on catalysts and reaction conditions, generally contain a wide range of compounds such as phenols, aromatic hydrocarbons, alkanes and low oligomers (Kleinert et al., 2009; Xu et al., 2012; Yan et al., 2008; Zakzeski et al., 2010a,b). The remaining challenges for hydrogenation of lignin include improving selectivity of target product and suppressing catalyst deactivation.

On the other hand, a variety of catalysts including noble metals, transition metals and metal oxide catalysts have been investigated for the catalytic oxidation of lignin (or its model compounds), generally producing a mixture consisting of aromatic aldehydes, acids, alcohols, and quinones compounds (Deng et al., 2010; Stark et al., 2010; Voitl and Rohr, 2008; Zakzeski et al., 2010a,b). So far, the selectivity and yield of a specific product (for example, vanillin aldehyde) by catalytic oxidation of lignin are very low (Deng et al., 2010; Voitl and Rohr, 2008), and need to be further improved. Moreover, catalytic pyrolysis of lignin over zeolites has been also investigated, mainly producing a variety of aromatic hydrocarbons (such as benzene, toluene, xylenes, alkylbenzenes, naphthalenes and indenes) (Jackson et al., 2009; Mullen and Boateng, 2010; Zhao et al., 2010). Besides, pyrolysis of lignin tends to form various phenolic compounds (Nowakowski et al., 2010; Shen et al., 2010).

Ethylbenzene (EB), a bulk raw material in the petrochemical industry, is mainly used in the production of styrene and polystyrene (Tukur and Al-Khattaf, 2009). Besides, EB is also employed for the synthesis of fine chemicals such as acetylbenzene, ethyl anthraquinone and methyl phenyl ketone, and for other applications like paint solvents or pharmaceuticals. Conventionally, ethylbenzene is produced by the alkylation of benzene with ethylene using mineral acids such as aluminium chloride or phosphoric acid as catalysts that cause some problems concerning handling, safety, corrosion and waste disposal (Li et al., 2009; Perego and Ingallina, 2002; Tukur and Al-Khattaf, 2009). The use of zeolite catalysts offers an environmentally friendly route to produce ethylbenzene, which can achieve superior product selectivity through pore size and acidity control (Žilková et al., 2009). The ZSM-5 catalyst is one of the most promising candidates for the selective conversion of benzene into ethylbenzene (Ebrahimi et al., 2011; Gao et al., 2009). Another zeolites with different porous frameworks and acidities have been also explored in alkylation of benzene, such as SSZ-33, ITQ-22 (Corma et al., 2009), MCM-49 (Liu et al., 2011), USY, Beta, MCM-22 (Cheng et al., 1999), Y type zeolite (Ebrahimi et al., 2011) and TNU-9 zeolites (Odedairo and Al-Khattaf, 2010; Portilla et al., 2011). Moreover, the use of ethanol instead of ethene as alkylating agent for benzene alkylation has some advantages such as longer catalyst lifetime and use of renewable biomass resource (Binitha and Sugunan, 2006; Corma et al., 2009; Gao et al., 2009; Odedairo and Al-Khattaf, 2010; Portilla et al., 2011). The remaining challenges for the produce of ethylbenzene by the benzene alkylation include improving selectivity and yield of target product, especially enhancing the benzene conversion.

In view of the structure characteristics of lignin, it has the potential to serve as a renewable starting material for the production of high-value aromatic chemicals. As far as we know, there is no report regarding directional production of ethylbenzene from lignin. Here, we explored the transformation of lignin into ethylbenzene through the directional catalytic depolymerization of lignin into aromatic monomers along with selective alkylation of aromatic monomers. This transformation may potentially provide an alternative approach for the production of the bulk basic petrochemical material and development of high-end chemicals using renewable lignin.

2. Methods

2.1. Materials

2.1.1. Biomass feedstocks

The lignin material, purchased from Lanxu Biotechnology Co., Ltd. (Hefei, China), was a brown and sulfur-free lignin powder manufactured from wheat straw. The elemental compositions in the dried lignin mainly consists of 62.55 wt.% carbon, 5.89 wt.% hydrogen, 29.91 wt.% oxygen and 1.65 wt.% nitrogen, measured by an elemental analyzer (Vario EL-III, Elementar, Germany). Analytical reagents such as anisole, benzene, ethylbenzene, phenol and ethanol were purchased from Sinopharm Chemical Reagent Company Limited in China (Shanghai, China).

2.1.2. Catalysts and characterizations

Different zeolites (HZSM-5 (25), HZSM-5 (50), HY-zeolite and 2.0 wt.% Re-Y zeolite) 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 NH₃-TPD (temperature programmed desorption of ammonia) and BET (Brunauer–Emmett–Teller surface area) analyses. For the NH₃-TPD tests, the catalyst was pretreated at 500 °C under helium flow (ultrahigh purity, 100 cm³/min) for 2 h, and adsorption of ammonia was performed at 120 °C for 1 h. After the catalyst was flushed with He at 120 °C for 1 h, the programmed-desorption of NH₃ was run from 120 to 700 °C with a heating rate of 10 °C/min. The catalyst acid strength was obtained by the adsorption–desorption of NH₃ detected on-line with a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China; a TCD detector separated on TDX-01 column; temperature-program rate: 10 °C/min up to 150 °C). The N₂ adsorption/desorption isotherms of the catalysts were measured at –196 °C using the COULTER SA 3100 analyzer (Beckman Coulter Inc., Fullerton, CA, USA).

2.2. Experimental setups and procedures

The catalytic depolymerization of lignin was performed in the continuous flow pyrolysis reactor (Huang et al., 2012). The system was mainly composed of a tube reactor (inner diameter: 33 mm; length: 600 mm), a feeder for solid reactants, two condensers and a gas analyzer. Before each run, the reactor was flushed with nitrogen at a flow rate of 300 cm³/min for 2 h, and was externally heated to a given temperature by the carborundum heater (10 °C/min). Lignin was mixed with the catalyst with a typical catalyst/lignin weight ratio of 3. In a typical test, 15 g of lignin was mixed with 45 g of catalyst, and then the solid mixture (lignin and catalyst) was fed into the reactor by the feeder with a feeding rate of about 30 g lignin/h. Each test took about 30 min. In addition, the reaction–regeneration cycles for lignin depolymerization were performed with the following mode: Runs 1–3 → Regeneration → Runs 4–6 → Regeneration → Runs 7–9. For Run 1 (R1), the solid mixture of 15 g lignin and 45 g fresh catalyst was continuously fed into the reactor with a feeding rate of 30 g lignin/h. The solid samples collected were sieved and separated into the catalyst (marked as CR1) and coke/char. For the secondary test (R2), the CR1 catalyst was used for lignin depolymerization, and the catalyst collected was marked as CR2. In a similar way, the CR2 catalyst was employed for the third round (R3), and the catalyst after the reaction was labeled as CR3. Then, the regeneration operation was performed by the combustion of the coke deposited on the CR3

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