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# Hydrogenolysis of lignin model compounds into aromatics with bimetallic Ru-Ni supported onto nitrogen-doped activated carbon catalyst

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ABSTRACT

Lignin is the most abundant and renewable resources for production of natural aromatics. In this paper, new bimetallic catalytic system of Ru and Ni supported onto nitrogen-doped activated carbon (Ru-Ni-AC/N) was developed and its performances on hydrogenolysis of lignin model compounds under mild reaction conditions (1.0 MPa, 230 °C, in aqueous) were investigated. The results indicate that Ru-Ni-AC/N was a highly active, selective and stable catalyst for the conversion of lignin model compounds into aromatics, e.g. phenol, benzene and their derivatives. As verified by BET, XRD, HRTEM, XPS, $H_2$-TPR and ICP-MS, the strong synergistic effects between i) Ru and Ni and ii) metals and N-groups were contributed to its excellent aromatics selectivity. What's more, the introduction of electron rich N atoms on AC was beneficial to the stabilization of metal particles, which greatly enhanced the durability of the catalyst.

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## 1. Introduction

Lignin is a natural polymer of methoxylated phenylpropane units and holds considerable potential as a renewable resource for the sustainable production of fuels and bulk chemicals [1,2]. Via fast pyrolysis process, it can be converted into a liquid mixture, which containing about 5–35% of phenolic chemicals [3]. Those phenols can be a potential feedstock to produce aromatics, e.g. phenol, benzene and their derivatives, instead of petrochemical resource via hydrogenolysis. Besides solvents, these aromatic compounds are basic feedstock in multiple chemical processes, which are more economical variable than normal biofuels [4]. Especially, phenol and its derivatives are widely used as chemical building blocks for synthetic bioplastics. As shown in Scheme 1, there is generally a competition between hydrogenolysis and hydrogenation of guaiacol [5–9] during the catalytic process. Therefore, the selective cleavage of C—O bonds without aromatic ring hydrogenation is of great importance.

Previous works revealed that noble metals such as Pd, Pt, Ru and Rh, offer high activities for hydrogenolysis reactions, but they are also highly active for hydrogenation of aromatic rings to produce cycloparaffin [10–12]. Non-noble transition metals, such as Ni and Fe, display low activity for hydrogenation reactions but high selectivity for aromatic rings [13–15]. Hong et al. [16] synthesized a series of Pd-$Fe_2O_3$ catalysts and applied them for hydrogenolysis of m-cresol. They found that the addition of Pd remarkably promoted the catalytic activity and showed high selectivity towards toluene without saturation of aromatic ring and C—C cleavage. What's more, the combination of Fe with Pd supported onto activated carbon (Pd-Fe-AC) could enhance the benzene yield dramatically compared with Fe-AC and Pd-AC during the process of vapor-phase guaiacol hydrogenolysis reaction [17].

Although activated carbon is the most potential "sustainable" host materials for metal particles, the metals deposited on carbons can be easily leached during catalytic processes owing to the weak interaction between the metals and the carbon surface [18]. Nitrogen doping was proved to be an efficient strategy to modify the surface and physicochemical properties of activated carbon support [19]. Xu et al. [20] have synthesized palladium nanoparticles supported on mesoporous nitrogen-doped activated catalyst (Pd-AC/N) and have tested its catalytic ability for biofuel upgrade. The high catalytic performance of catalyst was attributed to the special structure of nitrogen-doped activated carbon and metal heterojunction which leads to a very stable and uniform dispersion of Pd nanoparticles. It was also evidenced by our previous work [21] that

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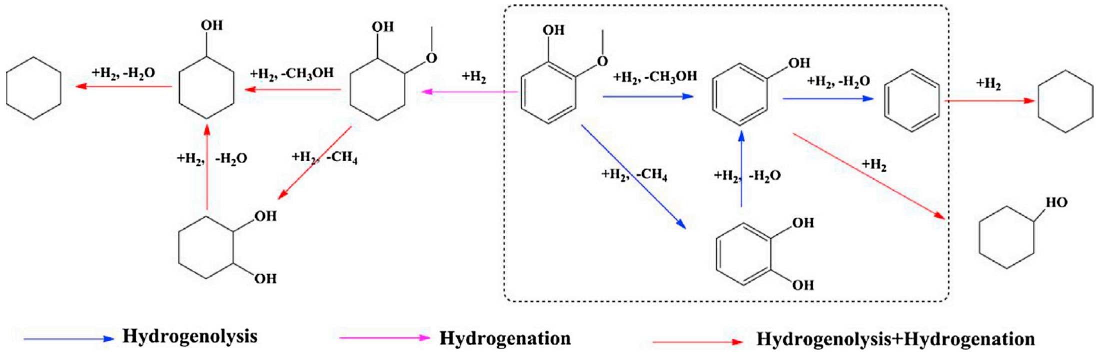

**Scheme 1.** Cleavage of C—O bonds and hydrogenation of aromatic ring.

the stability of Ir-AC/N catalyst improved a lot compared with Ir-AC, on account of the interaction between N-groups and Ir particles.

In this study, a novel kind of catalysts were prepared by loading Ru and Ni on nitrogen-doped activated carbon (AC/N), and their performances in hydrogenolysis of lignin based monomeric substrates (guaiacol, alkyl substituted guaiacol, syringol, etc.) were tested under mild reaction conditions (1.0 MPa, 230 °C, in aqueous). The influence of major reaction parameters, such as metal loading, $H_2$ pressure, reaction temperature and solvent, were fully investigated and the possible reaction pathways were also proposed. Moreover, the interaction among Ru, Ni and the electron rich N atoms were analyzed in detail by BET, XRD, HRTEM, $H_2$-TPR, XPS and ICP-MS to dissect the good aromatics yield and enhanced durability of the new catalyst.

## 2. Experimental

### 2.1. Materials

Commercially available chemicals including metal precursors of Ru, Ni, Pt and Fe, 1,10-phenanthroline, lignin phenolic model compounds and other organic reagents were purchased from SCRC, Alfa Aesar or TCI and used as received. Activated carbon support (Vulcan XC72R) was provided by Cabot Corporation.

### 2.2. Catalyst preparation

#### 2.2.1. The preparation of AC/N support

The AC/N support were prepared according to reference [21]. Generally, 5 g 1,10-phenanthroline monohydrate was dissolved in 25 mL ethanol, and then mixed slowly with aqueous solution of $H_2SO_4$ (5 g 98% $H_2SO_4$ diluted with 25 mL deionized water). Ethanol and water were removed by distillation after the mixture stirred for 4 h. Followed, 2.5 g of the synthesized phenanthroline sulfuric acid salt, 5 g activated carbon (Vulcan XC72R), 80 mL of deionized water and 50 mL of ethanol were added into a 250 mL round-bottom flask and stirred at room temperature for 12 h. After all solvents were evaporated, the obtained black solids were calcined at 900 °C in a tube furnace under $N_2$ atmosphere for 6 h with a heating rate of 5 °C $min^{-1}$. Finally, the nitrogen-doped activated carbon support was obtained.

#### 2.2.2. The preparation of mono- and bi- metallic catalysts

All catalysts were prepared by incipient wetness impregnation method. Chloride nickel hydrate ($NiCl_2{\cdot}6H_2O$), rhodium chloride hydrate ($RuCl_3{\cdot}6H_2O$), palladium chloride hydrate ($PdCl_2{\cdot}H_2O$), iron chloride hydrate ($FeCl_3{\cdot}6H_2O$), and activated carbon (AC), nitrogen-doped activated carbon (AC/N) were used as metal precursors and supports, respectively. Take 1%Ru-5%Ni-AC/N as an example, 0.02 g $RuCl_3{\cdot}3H_2O$ and 0.15 g $NiCl_2{\cdot}6H_2O$ were dissolved into 5 mL water, then 0.75 g nitrogen-doped carbon support was added into the solution with stirring for 5 h at room temperature. After that, water was removed by a rotary evaporator and the obtained powder was dried at 110 °C overnight. The dried samples were reduced in a $H_2$ flow at 200 °C for 5 h prior to use. The obtained catalyst was denoted as x%Ru–y%Ni-AC/N, where x% and y% refer to the mass percentage of Ru and Ni.

### 2.3. Catalyst characterization

BET (Brunauer-Emmett-Teller) and Barrett-Joyner-Halenda (BJH) were conducted using an ASAP-2020 analyzer. XRD (Powder X-ray diffraction) was recorded at a Bruker D8 diffractometer with Cu target and Kα (λ = 1.54 Å) radiation. HRTEM (High-resolution transmission electron microscopy) images were performed with FEI Tecnai G20 instrument. EDS elemental mappings were carried out on Hitachi SU8000 instrument and XEDS elemental analyses were performed with JEM-2100F electron microscope which equipped with an Oxford X-MaxN80 T energy dispersive X-ray spectroscopy. The XEDS elemental analyses were tested by controlling the position of irradiated area within 5 nm. During TEM samples prepared, the powder samples were dissolved in ethanol under ultrasonication for 5 min, and then several droplets of the sample were laid on a copper grid coated with carbon film.

The XPS (X-ray photoelectron spectroscopy) spectra were performed with a Thermo Escalab 250XI system using an Al Kα (1486.6 eV) as the X-ray source and deconvoluted with XPS PEAK41 software. The binding energies were calibrated using a criterion of C 1 s peak (284.8 eV) as a reference.

$H_2$-TPR ($H_2$-temperature programmed reduction) was carried out on a Chemisorption Analyzer (Micromeritics AutoChem II 2920) equipped with a thermal conductivity detector (TCD). For $H_2$-TPR analysis, about 100 mg of sample was used for each measurement and pre-treated in a Ar flow at 200 °C for 2 h. TPR was initiated from room temperature to 900 °C at 10 °C $min^{-1}$ with a mixture flow of 10% $H_2$/Ar (20 mL $min^{-1}$).

ICP-MS (inductively coupled plasma mass spectrometry) was performed on an Agilent 7700ce system. After each reaction, the aqueous solution was diluted with water to 100.0 mL prior to subject to the analyzer.

For $H_2$-TPD ($H_2$-temperature programmed desorption) analyses, Micromeritics AutoChem II 2920 Chemisorption Analyzer was used as instrument. The sample (100 mg) was pre-treated under Ar flow at 300 °C for 2 h, and then cooled to 230 °C for 2 h. After exposed to a 10% $H_2$/Ar flow (20 mL $min^{-1}$), the physical adsorption of $H_2$ was purged by Ar flow for 2 h until pulses base line became stable. Furnace temperature was increased from 100 to 800 °C with a heating rate of 10 °C $min^{-1}$ in a Ar flow.

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