



# In situ hydrodeoxygenation of phenol with liquid hydrogen donor over three supported noble-metal catalysts



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## HIGHLIGHTS

- Ru/MCM-41 performs best in the in situ hydrodeoxygenation of phenol with formic acid.
- The conversion of phenol has a maximum value when Ru/MCM-41 is reduced at 400 °C.
- Cyclohexane has a maximum yield at the 10 wt% of Ru loading amount in Ru/MCM-41.
- An increased ratio of formic acid to phenol can improve the conversion of phenol.
- CO<sub>x</sub> derived from formic acid is harmful for the increase of phenol conversion.

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## ABSTRACT

In situ hydrodeoxygenation of phenol with liquid hydrogen donor over three supported Pd, Pt, and Ru catalysts was investigated. The method of incipient wetness impregnation was used to load the three noble metals on the support of MCM-41, which is a cylindrical mesoporous material with a hierarchical structure. The in situ hydrodeoxygenation of phenol was conducted at 280 °C, under pressures from saturated vapor of solvent and compressed initial N<sub>2</sub> with gas products. Among the three catalysts, Ru/MCM-41 was found to be the best one, with highest phenol conversion of 73.9% and deoxygenation degree of 72.2%. The performance of Ru/MCM-41 increased with increasing theoretical loading amount of Ru and with reduction temperature. However, when the reduction temperature reached to 500 °C, or the Ru theoretical loading amount increased to 15 wt%, the activity of Ru/MCM-41 decreased reversely. Through the characterizations by small-angle XRD, wide-angle XRD, H<sub>2</sub>-TPR, and SEM analysis, the reason for the deteriorated performance of Ru/MCM-41 under high reduction temperature or high Ru loading amount was deduced as the collapse of MCM-41 structure and severe overlaps of Ru atoms. Hydrogen donors were also tested, and formic acid was found in best performance owing to its fast decomposition rate and high productivity of hydrogen. Though an increased feed ratio of formic acid to phenol could improve the hydrodeoxygenation potential of phenol, much simultaneously generated CO<sub>x</sub> from decomposition of formic acid might occupy active sites of the catalyst and led to a decreased growth rate of phenol conversion.

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## 1. Introduction

With increasing worldwide energy consumption, renewable fuels are urgently demanded for future energy supply [1]. Among the alternative renewable fuels, bio-oil attracts much attention due to its carbon neutrality in the carbon cycle [2] and its abundant

reserve in the forms of agriculture wastes, forest wastes, etc. [3]. However, the application of bio-oil is severely restricted due to its high content of oxygenated compounds such as acids and phenols [2]. The much oxygenated compounds causes low heating value, instability, and corrosivity of bio-oil. Therefore, it is necessary to upgrade the bio-oil to reduce oxygenated compounds by deoxygenation reactions [4–6].

The application of gaseous hydrogen in high pressure is the common way for hydrodeoxygenation of oxygenated compounds in bio-oil, but with the limits of inconvenient transportation and high cost of storage [2]. Dumesic et al. have shown that small oxy-

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genates, such as formic acid and methanol, can be selectively converted to hydrogen over supported catalysts through aqueous phase reforming process [7,8], offering an alternative hydrogen source for catalytic hydrodeoxygenation of bio-oil. Some scholars had investigated the in situ hydrodeoxygenation (in situ HDO) of some model components in bio-oil or the mixture of some model components with small oxygenates [2,6,9–11]. Xiang et al. achieved 18.1%–53.1% conversion of phenol and up to 96.1% selectivity of cyclohexanone through the hydrogenation of phenol with methanol or ethanol, over Raney Ni or Pd/Al<sub>2</sub>O<sub>3</sub> catalyst [6]. Zhang et al. studied the transfer hydrogenation of phenol over supported Pd catalysts with formic acid as the hydrogen donor [2]. The highest phenol conversion of 65.6% is obtained and almost all the converted phenol was turned into cyclohexanone. Compared with the conventional hydrodeoxygenation process using gaseous H<sub>2</sub> as the hydrogen source, the relatively low conversion of raw material and the low deoxygenation degree due to the high product selectivity to mild hydrogenation intermediate products such as cyclohexanone and cyclohexanol are the major drawbacks of the in situ hydrodeoxygenation method with liquid hydrogen donor.

Deep hydrogenation to yield oxygen-free products such as cyclohexane and benzene would be an important issue to make the in situ HDO process more promising. Therefore, in this paper, in situ HDO of phenol, as the model compound of phenolic oil, was investigated to further improve the degree of deoxygenation (DOD). The catalyst preparation conditions such as the types of noble metals, the theoretical loading amount of the metals, and the reduction temperature of the catalyst precursor, as well as some operating conditions were tested to achieve high conversion of phenol with high yield of oxygen-free products.

## 2. Experimental

### 2.1. Catalyst synthesis

The catalysts with theoretical loading amounts of noble metals (Pt, Pd, and Ru) were prepared by incipient wetness impregnation method on the support of MCM-41 (XFNano Materials). H<sub>2</sub>PtCl<sub>6</sub> (Sinopharm, Pt ≥ 37.0%), PdCl<sub>2</sub> (Sinopharm, Pd ≥ 59.0%), and RuCl<sub>3</sub>·3H<sub>2</sub>O (Sinopharm, Ru ≥ 37.0%) were used as the source of active metallic components. Prior to the impregnation, the adsorption capacities of the dried MCM-41 (dried at 110 °C overnight) were estimated using deionized water as the absorbate. The required volume of metal salt solution equals to the saturated adsorption amount of water in MCM-41. For the case of PdCl<sub>2</sub>, a 0.1 mol/L aqueous hydrochloric acid solution was used as the solvent for dissolving of PdCl<sub>2</sub>, since the solubility of PdCl<sub>2</sub> in water is too low. According to the desired metal loading amount in catalyst, corresponding amount of metal salt was dissolved in the certain volume of solvent and then the incipient wetness impregnation was performed by mixing the solution with MCM-41. The impregnation was aged for 10 h under stirring and then dried at 110 °C for 8 h. Before tests, the catalysts were reduced in a fixed bed in reduction atmosphere (the mixture of 50% H<sub>2</sub> and 50% Ar in flowrate of 350 N mL/min) at 400 °C. Unless otherwise specified, the theoretical loading amounts of all noble metals are 10 wt%.

### 2.2. Catalyst characterization

The porous structure of the support was characterized by BET analysis with recorded N<sub>2</sub> adsorption-desorption isotherms at –195.8 °C through the instrument of Quantachrome Autosorb iQ. The crystalline phases of the catalysts were identified by X-ray diffraction (XRD, PANalytical Empyrean) method with a stationary X-ray source (Cu Kα) and a movable PIXcel<sup>3D</sup> detector. The incident

wavelength of the X-ray (λ) is 0.15406 nm with a scanning step size of 0.01313. The accumulation time for small- and wide- angle XRD analysis are 118.32 s and 18.87 s, respectively. Temperature programmed reduction by hydrogen (H<sub>2</sub>-TPR) were performed (Micromeritics AutoChemII 2920) to determine the reduction degree of catalysts. Before measurement, samples were pretreated in a flow of He (50 N mL/min) at 250 °C for 0.5 h, followed by cooling down to 50 °C, and then the samples were heated from 50 °C to 700 °C (heating rate of 5 °C/min) in the atmosphere of 10 vol% H<sub>2</sub> and 90 vol% Ar (50 N mL/min). The transmission electron microscopy (TEM, JEM-2100F microscope) analysis was conducted for morphology characterization with an accelerating voltage of 200 kV.

### 2.3. In situ HDO of phenol

The experiments were performed in a high pressure autoclave made of 316 stainless steel (165 mL, model of WHF0.1). The typical experimental conditions are as follows: 5 g phenol (Sinopharm, ≥98.0), 0.265 mol formic acid, 20 mL deionized water, and 0.5 g catalyst were used for experiment. The mole of H in formic acid is 1.25 times higher than that required for complete conversion of phenol to cyclohexane assuming that all the H atoms in formic acid are available for hydrogenation reaction. Before heating, the autoclave was flushed three times with nitrogen to purge air out and then maintained at 1 MPa of N<sub>2</sub> (the mass of N<sub>2</sub> held in the autoclave was measured by a mass flowmeter); the autoclave was then heated to 280 °C by heating rate around 3 °C/min and kept for 4 h at this temperature; a magnetic propeller was used for stirring at around 600 rpm in the whole heating and holding process; at the end of experiment, the autoclave was put into a cooling tank and cooled to 25 °C in the cooling rate of around –25 °C/min. The products were then taken out from the autoclave for analysis. Unless otherwise specified, experiments were conducted under the typical conditions.

### 2.4. Product analysis

The gas products were analyzed by a gas chromatography (GC, Shimadzu GC-2014). The mass of each gas component was determined by internal standard method, using N<sub>2</sub> as the standard material, which was introduced into the autoclave before reaction. Ideal gas equation of state was used for converting from volume to mole quantities. The liquid products mixed with solid residual (catalyst and coke) were first separated to aqueous, oil, and solid phase by filtration and centrifugation. The aqueous and oil phase products were then analyzed by a gas chromatography-mass spectrometry (GC/MS, Thermal Scientific ISQ). The GC/MS is equipped with a capillary column (TR-WAXMS; Size: 30 m × 0.25 mm × 0.25 μm; Stationary phase: Polyethylene glycol).

The DOD of phenol, conversions of reactants, and yields of products were calculated using the following equations. According to pre-experimental results, the gas products were predominantly derived from hydrogen donor, while the liquid products were overwhelmingly converted from phenol, with the main components of C<sub>6</sub>-cyclic compounds. Therefore, the yields of gas and liquid products were calculated on the basis of hydrogen donor (HD) and phenol in the feed, respectively.

$$DOD, \% = \left( 1 - \frac{M_{O \text{ atoms, out}}}{M_{phenol, in}} \right) \times 100 \quad (2-1)$$

$$Conversion (i), \% = \left( 1 - \frac{M_{i, out}}{M_{i, in}} \right) \times 100 \quad (2-2)$$

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