Short communication

Hydrodeoxygenation of phenol over Pd catalysts by in-situ generated hydrogen from aqueous reforming of formic acid

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ABSTRACT

Hydrodeoxygenation of phenol, as model compound of bio-oil, was investigated over Pd catalysts, using formic acid as a hydrogen donor. The order of activity for deoxygenation of phenol with Pd catalysts was found to be: $Pd/SiO_2 > Pd/MCM-41 > Pd/CA > Pd/Al_2O_3 > Pd/HY \approx Pd/ZrO_2 \approx Pd/CW > Pd/HSAPO-34 > Pd/HZSM-5$. The good performance of Pd/SiO_2 is owing to its proper pore structure and large specific surface area. The high level of Brønsted acid sites in SiO_2 also favors the deoxygenation of phenol.

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1. Introduction

Hydrodeoxygenation (HDO) is a frequently proposed method for upgrading of bio-oil to decrease its oxygen content and thereby increase its heating value and miscibility with fossil fuels as well as lowering its acidity [1–3]. However, a high pressure of hydrogen is needed for HDO process [4], which presents problems of expensive transportation and storage of gaseous hydrogen [5].

Therefore, a concept of "in-situ" HDO process was proposed, in which a hydrogen donor is added [5–7]. Hydrogen donors are usually light oxygenates which are easily reformed to produce hydrogen in an aqueous catalytic process. Therefore the HDO process proceeds without a feed of gaseous hydrogen.

At present, the research on in-situ HDO process is rather scarce and usually of a slight degree of hydrogenation [5–8]. The reported in-situ HDO of phenol just reached the intermediate hydrogenation product of cyclohexanone and cyclohexanol, instead of the final product of alkanes (Scheme 1) [6,8]. The key influence in this process is the performance of a catalyst in reforming of the hydrogen donor, deoxygenation of the oxygenated compound, and transfer of hydrogen atoms between the two reactions.

Reduced metal catalysts such as Ni-, Pd-, and Ru- were found active in reforming light oxygenates [9], and some were also applied in the HDO process [10]. In this paper, Pd catalysts loaded on various supports were tested for the in-situ HDO of phenol using formic acid as hydrogen donor. Phenol is used as a model compound of bio-oil, since phenolic compounds are most abundant in bio-oil and the cleavage of carbon-oxygen bond on an aromatic ring is the most challenging task for the upgrading of bio-oil HDO [2].

## 2. Experimental section

2.1. Catalyst preparation

ZSM-5 (XFnano, 99%), NaY (XFnano, 99%), SAPO-34 (XFnano, 99%), MCM-41 (XFnano, 99%), SiO_2 (XFnano, 99%), ZrO_2 (Alfa Aesar, 99%), Al_2O_3 (Alfa Aesar, 99%), and activated carbon (Alfa Aesar, 99%) were impregnated by incipient wetness in $PdCl_2$ (Sinopharm, $Pd \geq 59.0\%$) solution to prepare Pd catalysts (10 wt.% Pd) [2]. Before the impregnation, Y-zeolite was pretreated to convert NaY to HY by dissolving Y-zeolite in 10 wt.% NH_4NO_3 for 2 h under 90 °C ($V_{NH4NO3}/m_{NaY} = 10$ mL/g). The activated carbon was also pretreated by impregnating with deionized water or 2 mol/L HNO_3 solution at 90 °C for 2 h ($V_{solvent}/m_{carbon} = 20$ mL/g). Herein, CW and CA refer to the water-treated carbon and acid-treated carbon, respectively. After impregnation, the reduction of catalysts was performed in a fixed-bed reactor, where the catalysts were heated to 400 °C (heating ramp of 10 °C/min) in an atmosphere of 50% H_2 and 50% Ar (flow rate of 350 N mL/min) for 2 h.

2.2. Characterization of catalysts

The N_2 sorption isotherms of samples were recorded on Quantachrome Autosorb iQ at -195.8 °C. The X-ray diffraction (XRD)

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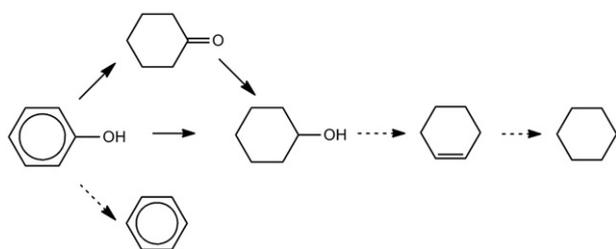
Scheme 1. Reaction pathways for hydrodeoxygenation of phenol. Solid lines: slightly degree of hydrogenation; dotted lines: deep deoxygenation and hydrogenation.

patterns were obtained on PANalytical Empyrean with Cu Kα radiation. H_2 temperature programmed desorption (H_2-TPD) were conducted in a flow of N_2 at 10 °C/min from 50 °C to 700 °C to calculate the palladium dispersion [11]. The Brønsted acid sites of samples were determined by titration method [12,13], in which NaOH solution (20 mL, 0.01 mol/L), HCl solution (0.01 mol/L), and phenolphthalein were used as reagent, titrant, and indicator, respectively.

2.3. In-situ hydrodeoxygenation

In a typical experiment, 5 g phenol (Sinopharm, 98.0%), 10 mL formic acid (Sinopharm, 98.0%), 20 mL deionized water, and 0.5 g catalyst were loaded in a 100 mL autoclave (316 stainless steel, type WTF0.1). The volume of formic acid is 1.25 times higher than the required amount of hydrogen for phenol saturation (assuming that formic acid is entirely converted to H_2 and CO_2, and oxygen in phenol is removed in the form of H_2O). Prior to experiments, the autoclave was flushed by nitrogen three times to remove air. Then, 1 MPa nitrogen was fed into the reactor and its mass was indicated by a mass flowmeter. The feedstock was then heated to 280 °C (heating rate of ~3 °C/min), held for 4 h at this temperature, while stirring at ~600 rpm. After the experiment, the autoclave was cooled to 25 °C with a cooling rate of ~25 °C/min.

2.4. Product analysis

The compositions of gas products and liquid products were determined by a gas chromatograph (Shimadzu GC-2014) and a gas chromatograph/mass spectrometer (GC/MS, Thermal Scientific, ISQ), respectively. The conversion of phenol, the yield and selectivity of liquid product, and the degree of deoxygenation (DOD) are defined as:

$$\text{Conversion}, \% = \left(1 - \frac{M_{phenol,\text{out}}}{M_{phenol,\text{in}}}\right) \times 100 \qquad (2.4-1)$$

$$\text{Yield } (i), \% = \frac{N_i \times M_i}{N_{phenol} \times M_{phenol,\text{in}}} \times 100 \qquad (2.4-2)$$

$$\text{Selectivity } (i), \% = \frac{M_i}{M_{phenol,\text{in}} - M_{phenol,\text{out}}} \times 100 \qquad (2.4-3)$$

$$\text{DOD}, \% = \left(1 - \frac{M_{O\ atoms,\text{out}}}{M_{phenol,\text{in}}}\right) \times 100. \qquad (2.4-4)$$

Where, i — target product; M_i — mole of component i; N_i — carbon atoms of component i, $M_{phenol,\text{in}}$ — mole of phenol in the feed; $M_{phenol,\text{out}}$ — mole of phenol in the product; $M_{O\ atoms,\text{out}}$ — mole of oxygen atom in the organic liquid product.

In an experiment excluding formic acid almost no gas product was observed, which proved that the gas products are overwhelmingly derived from formic acid. Therefore, the yield of gas product is defined as the mole ratio of specific gas product to formic acid in the feed with the symbol of gas/HCOOH. The relative deviations of mass balances and carbon balances for all experiments are within 10%.

3. Results and discussion

3.1. Feature of Pd catalysts

The texture properties of all supports are analyzed and listed in Table 1. It shows that support of MCM-41 and SiO_2 exhibited the highest BET specific surface area (1025 m^2/g and 924 m^2/g), which is attributed to their small and abundant mesopores with an approximate diameter (D_{BJH}) of 3.02 nm for MCM-41 and 2.81 nm for SiO_2. The size and dispersion of Pd particles for the catalysts were shown in Fig. 1. It illustrates the lowest Pd particle size and highest Pd dispersion for Pd/SiO_2 and Pd/MCM-41.

3.2. Conversion of formic acid and gas product

The gas products from testing the Pd catalysts for in-situ HDO of phenol are shown in Table 2. Formic acid in all cases was entirely converted. The CO_2 yields are all higher than 90 mol%. It indicates that formic acid is mainly decomposed to CO_2 and H_2 instead of to H_2O and CO. This is in agreement with theoretical calculations showing that with Pd-, Pt-, and Ru-catalysts' dehydrogenation of formic acid is preferred over dehydration [14]. The yield of H_2 should be comparable to that of cogenerated CO_2, if no H_2 is consumed. However, for the CW, CA, SiO_2, and MCM-41 supported catalysts, H_2 yields are remarkably reduced. Less hydrogen in the gas product indicates that more hydrogen was consumed by HDO of phenol.

3.3. Conversion and DOD of phenol

The conversion and DOD of phenol are shown in Fig. 2. It shows that Pd/SiO_2 is the most effective catalyst with respect to both the conversion and DOD of phenol, closely followed by the Pd/MCM-41 catalyst. The CA and CW supported catalysts perform better in the conversion of phenol but worse in the DOD of phenol.

Taking the conversion of phenol as a parameter for ranking, the apparent activity of the supported catalysts follows the order:

Pd/SiO_2 > Pd/CA ≈ Pd/CW ≈ Pd/MCM-41 > Pd/HY ≈ Pd/Al_2O_3 > Pd/ZrO_2 > Pd/HSAPO-34 > Pd/HZSM-5.

When DOD is considered for activity ranking, the order would be slightly changed to:

Pd/SiO_2 > Pd/MCM-41 > Pd/CA > Pd/Al_2O_3 > Pd/HY ≈ Pd/ZrO_2 ≈ Pd/CW > Pd/HSAPO-34 > Pd/HZSM-5.

Table 1
Textural properties of the supports.

Support	S_{BET} (m^2/g)	S_{ext} (m^2/g)[a]	D_{BJH} (nm)[b]	D_{HK} (nm)[c]
NaY	388	153	0.81	0.41
HSAPO-34	769	60	–	0.43
HZSM-5	330	72	–	0.43
CW	715	112	2.56	0.63
CA	662	109	2.51	0.63
MCM-41	1015	987	3.02	–
SiO_2	924	954	2.81	–
Al_2O_3	212	195	8.55	–
ZrO_2	47	39	17.04	–

[a] External specific surface area, calculated with t-plot method.
[b] The most probable size of mesopore calculated with BJH (Barrett-Joyner-Halenda) method.
[c] The most probable size of microspore calculated with HK (Horvath-Kawazoe) method.