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Influence on nickel particle size on the hydrodeoxygenation of phenol over Ni/SiO_2

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ABSTRACT

Hydrodeoxygenation (HDO) of phenol over nickel nano-particles of different size (5–22 nm) supported on SiO_2 has been investigated in a batch reactor at 275 °C and 100 bar. Deoxygenation was only observed as a consecutive step of initial hydrogenation of phenol at the given conditions. Both the hydrogenation and deoxygenation reaction were found to be Ni-particle size dependent. Rapid hydrogenation of phenol to cyclohexanol was achieved over the catalysts with large particles, while the rate of deoxygenation of cyclohexanol was slow. For the catalysts with small Ni particles, the opposite behavior was observed Specifically, the turn over frequency (TOF) of hydrogenation was 85 times slower for 5 nm particles than for 22 nm particles. On the contrary, the TOF of cyclohexanol deoxygenation increased by a factor of 20 when decreasing the particle size from 20 nm to 5 nm. A simple kinetic model showed that the rate limiting step for phenol HDO shifted from deoxygenation to hydrogenation when the particle size was below 9–10 nm. Surface site population theory evidenced that the deoxygenation reactions were favored on step/corner sites, giving higher deoxygenation rates at small particles. For hydrogenation, the influence of particle size on the rate could be related to the size of the Ni facets with larger facets thus being better.

1. Introduction

Flash pyrolysis of biomass followed by hydrodeoxygenation (HDO) of the produced bio-oil has been identified as a prospective route for CO_2 neutral engine fuel production [1]. Through pyrolysis, practically any source of biomass can be converted into bio-oil [2]. Although much more energy dense than the original biomass, bio-oil has a low heating value compared to crude oil, a low shelf storage life, is viscous, and polar, making it unsuitable as an engine fuel. These characteristics are all associated with high contents of water and chemically bound oxygen in the bio-oil. However, as the oil has a higher volumetric energy density and is easy to handle relative to biomass it is more suitable for transport and further processing [1,3,4].

It would be advantageous if bio-oil can be upgraded to an oil similar to conventional crude oil using the HDO route, where hydrogen is used to remove the oxygen functionality in the bio-oil. This requires the presence of a catalyst, a temperature in the order of 200–400 °C, and typically a pressure of 70–200 bar [1].

Bio-oil consists of a vast number of oxygenated species and therefore many different reactions occur in HDO. It has been observed that a part of the oil (simple molecules such as short chain ketones) can easily be deoxygenated by direct removal of the oxygen functionality [5,6]. However, to deoxygenate more complex molecules, such as phenolics, an initial hydrogenation of the aromatic part of the molecule may be needed to make the oxygen group more susceptible for reaction with hydrogen [7]. Generally, phenol and phenolic derivatives are a fairly abundant part of bio-oil [8], which has been found as one of the more persistent oxy-compounds to deoxygenate [5,9]. This makes phenol an interesting model compound when investigating catalysts for HDO.

One of the major challenges in HDO is to find a suitable catalyst. Recent work has shown that nickel based catalysts have high activity for HDO reactions [10–17].

HDO of phenol over metallic catalysts and temperatures below 300 °C preferentially proceeds through a sequential reaction path as shown in Fig. 1, where hydrogenation of the aromatic ring takes place initially, producing cyclohexanone. This is rapidly hydrogenated to cyclohexanol. Deoxygenation of the cyclohexanol then

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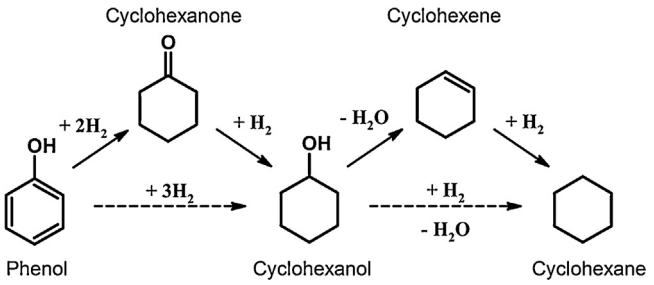

Fig. 1. Reaction scheme of HDO of phenol under mild conditions. Solid arrows indicate main pathways; while the dotted arrows indicate the steps of the kinetic model (see Section 2).

proceeds through either hydrogenolysis to cyclohexane or dehydration forming cyclohexene, which is readily hydrogenated into the final product cyclohexane [18,19]. This reaction path is fairly well established in the literature under mild conditions using noble metal/nickel catalysts. This mechanism has been reported, e.g., for HDO of phenol over Pd/C [20,21], Pt/C [22], Ni/HZSM-5 [23], Ni–MoS_2/Al_2O_3 [24], and nickel based catalysts [16,18].

In the current work HDO of phenol over Ni/SiO_2 catalysts has been investigated with special emphasis on understanding the influence of metal particle size and the relationship between the hydrogenation and deoxygenation reactions taking place for HDO of phenol.

2. Experimental

2.1. Catalyst synthesis

5 wt% Ni/SiO_2 was prepared by incipient wetness impregnation using $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich, ≥97.0%) as precursor. Silica was supplied by Saint-Gobain NorPro, type SS6*138 with a purity of ≥99.5%, a specific surface area of 250 m^2/g, and a pore volume of 1.0 ml/g. Before impregnation, the SiO_2 was grinded to a particle size of 63–125 μm. The SiO_2 was impregnated with a 0.90 mol/l solution of $Ni(NO_3)_2{\cdot}6H_2O$ in water in one step. After impregnation, the sample was dried at 110 °C for 12 h.

In order to make catalysts with different particle size but same composition, the catalysts were pre-treated/calcined and reduced in different ways prior to the catalytic activity test:

- Red. 1: The catalyst was calcined initially at 400 °C in an oven and then reduced in the batch reactor at 395 °C (catalyst temperature) and 7 bar of H_2 in a stagnant gas atmosphere for 2 h. This method is expected to yield large nickel particles due to the high pressure and the presence of water [25–27].
- Red. 2: The catalyst was calcined initially at 400 °C in an oven and then reduced in the batch reactor with a flow of 1 Nl/min H_2 at 395 °C (catalyst temperature) and 5 bar of hydrogen for 2 h. This method is expected to yield intermediate size nickel particles since water is continuously removed.
- Red. 3: The catalyst was calcined initially at 400 °C in an oven and then reduced in a continuous flow reactor with a flow of 250 Nml/min H_2 and 250 Nml/min N_2 at 400 °C and 1 bar of hydrogen for 2 h and then transferred directly to the batch reactor. This method is expected to yield smaller nickel particles than Red. 2 due to the milder conditions and more controlled removal of water.
- Red. 4: Reduction of un-calcined $Ni(NO_3)_2/SiO_2$ in a continuous flow reactor with a flow of 250 Nml/min H_2 and 250 Nml/min N_2 at 400 °C and 1 bar for 2 h and then transferred directly to the batch reactor. This method is expected to yield small nickel particles, due to the direct reduction of the nickel nitrate catalyst precursor [28].

Temperature programmed reduction (TPR) data can be found in the ESI showing that complete reduction is achieved around 380 °C.

2.2. Catalyst testing

The experiments were performed in a 300 ml batch reactor from Parr (type 4566 of Hastelloy C steel). In an experiment 1 g of catalyst and 50 g of phenol (Sigma–Aldrich, ≥99%) were poured into the reactor. The mixture was stirred with a propeller at 380–390 rpm and heated to 275 °C in a hydrogen atmosphere, giving a final pressure of 100 bar. The heating rate was around 15 °C/min. During the experiments, hydrogen was added continuously to maintain the pressure of 100 bar. The experiments had a total reaction time of 5 h. To stop the experiment, the reactor was placed in an ice bath to cool the reactor within 5 min to room temperature. The start of the experiment was taken at the time when the heater was turned on (heating took ca. 20 min) and the end of the experiment was regarded as the time when the reactor was lowered into the ice bath. By threefold repetition of an experiment, it was found that this procedure had an uncertainty in the measured yields within ±2 mol%, corresponding to less than 5% as relative standard deviation. Overall there was a good repeatability of the experiments.

A blank experiment without catalyst with 10 g of phenol and 40 ml of H_2O at 275 °C and 100 bar for 4 h resulted in a conversion of only 0.3%, showing that the reactor was not catalytically active. Calculation of Mears' and Weisz–Prater criteria [29] indicated absence of mass transfer limitations in this system with the observed reaction rates. Details on the evaluation can be found in the ESI.

In some cases shorter experiments were performed to obtain conversions well below 100% for determination of kinetic parameters. For this purpose the batch reactor was initially heated without stirring, which decreased the rate of reaction to practically zero, until the desired temperature was reached. At this point the stirring was started at 380–390 rpm (start of experiment) and the reaction could be made at close to isothermal conditions. This allowed measuring the activity in short experiments of ca. 15 min.

2.3. Product analysis

Analysis of the liquid product was done with a Shimadzu GCMS/FID-QP2010UltraEi fitted with a Supelco Equity-5 column. The products were identified using a mass spectrometer (MS) and quantified with a flame ionization detector (FID). External standards were prepared for phenol, cyclohexanol, cyclohexanone, and cyclohexane. The concentrations of the remaining peaks were calculated from the FID on the basis of the effective carbon number method [30], where the concentration of a compound is found as:

$$C_i = C_{ref} \cdot \frac{A_i}{A_{ref}} \cdot \frac{\nu_{eff,ref}}{\nu_{eff,i}} \quad (1)$$

Here C is the concentration, A the area of the peak in the FID spectrum, and ν the effective carbon number. Index i refers to the compound with the unknown concentration and index ref refers to a reference compound where the concentration is known. In all calculations based on this formula cyclohexanol was used as reference. The effective carbon number was taken from the review by Schofield [30].

The conversion, X, was calculated as:

$$X = \left(1 - \frac{C_{Phenol} \cdot V_{final}}{n_{0,Phenol}}\right) \cdot 100\% \quad (2)$$