



Mechanisms of selective cleavage of C–O bonds in di-aryl ethers in aqueous phase



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ABSTRACT

A route for cleaving the C–O aryl ether bonds of *p*-substituted H–, CH₃–, and OH– diphenyl ethers has been explored over Ni/SiO₂ catalyst at very mild conditions (393 K, 0.6 MPa). The C–O bond of diphenyl ether is cleaved by parallel hydrogenolysis and hydrolysis (hydrogenolysis combined with HO⁺ addition) on Ni. The rates as a function of H₂ pressure from 0 to 10 MPa indicate that the rate-determining step is the C–O bond cleavage on Ni surface. H⁺ atoms compete with the organic reactant for adsorption leading to a maximum in the rate with increasing H₂ pressure. In contrast to diphenyl ether, hydrogenolysis is the exclusive route for cleaving a C–O bond of di-*p*-tolyl ether to form *p*-cresol and toluene. 4,4'-Dihydroxydiphenyl ether undergoes sequential surface hydrogenolysis, first to phenol and OC₆H₄OH⁺ (adsorbed), which is then cleaved to phenol (C₆H₄OH⁺ with added H⁺) and H₂O (O⁺ with two added H⁺) in a second step. Density function theory supports the operation of this pathway. Notably, addition of H⁺ to OC₆H₄OH⁺ is less favorable than a further hydrogenolytic C–O bond cleavage. The TOFs of three diaryl ethers with Ni/SiO₂ in water follow the order 4,4'-dihydroxydiphenyl ether (69 mol mol⁻¹_{Ni Surf} h⁻¹) > diphenyl ether (26 mol mol⁻¹_{Ni Surf} h⁻¹) > di-*p*-tolyl ether (1.3 mol mol⁻¹_{Ni Surf} h⁻¹), in line with the increasing apparent activation energies, ranging from 4,4'-dihydroxydiphenyl ether (93 kJ mol⁻¹) < diphenyl ether (98 kJ mol⁻¹) < di-*p*-tolyl ether (105 kJ mol⁻¹).

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1. Introduction

Lignin is an abundant natural bio-polymer with methoxylated C₉ phenyl-propane units that are connected by C–O and C–C bonds [1]. Since the C–C_{aryl} bond dissociation energy (BDE) in the linkage of lignin is as high as 384 kJ mol⁻¹, it is reasonable to devise a strategy to selectively cleave the much weaker C_{aryl}–O or C_{aliphatic}–O linkages (BDE: 218–314 kJ mol⁻¹) in lignin to form phenolic fragments [2–4]. The most abundant C–O bonds in lignin are α–O–4, β–O–4, 4–O–5, β–1, and 5–5 linkages [3]; however, the 4–O–5 bond (BDE: 314 kJ mol⁻¹) [4] is the strongest. Usually, diphenyl ether is selected as the simplest model compound of 4–O–5 linkage for investigating the C–O bond cleavage chemistry.

Diphenyl ether cleavage requires harsh reaction conditions, such as near- or supercritical water at high temperature 673–773 K [5,6]. Siskin et al. reported that diphenyl ether was unreactive in the aqueous phase at temperatures lower than 733 K without catalyst, but with addition of 15% phosphoric acid catalyst, diphenyl ether was hydrolyzed to 92% phenol at 588 K after three

days [7]. In a comparison, the basic environment with 15% aqueous sodium formate, a 6.6% conversion, also to phenol was achieved at 588 K for three days. With 15% Na₂CO₃ solution, the reaction rate was accelerated and resulted in 33% conversion to phenol at 733 K after 1 h [8]. We have also reported that 100% phenol selectivity was achieved by diphenyl ether conversion over solid base catalyst K₂CO₃/ZrO₂ at 673 K [9]. Penninger et al. investigated the diphenyl ether (DPE) conversion in supercritical water at temperatures of 688–753 K with different supercritical water densities [10]. At water density below 0.3 g mL⁻¹, the radical poly-condensation dominated, forming, e.g., diphenyl, phenyl–DPE, and phenoxy–diphenyl. Increasing the water density above 0.4 g mL⁻¹ forced the reaction to follow SN₁ H⁺-catalyzed ionic hydrolysis route, yielding phenol as sole product. A NaCl concentration above 3.1 wt.% in supercritical water (SCW) greatly enhanced the hydrolysis rate of DPE [11]. This suggests that charge transfer in the water cluster surrounding the ions generated H⁺ and OH⁻ ions in the outer hydration shells formed the active species for diphenyl ether hydrolysis. Rinaldi et al. investigated the solvent effect on the hydrogenolysis of diphenyl ether over Raney nickel under 5 MPa H₂ at 363 K and concluded that a higher Lewis basicity of solvent such as methanol, 1,4-dioxane, and THF suppressed hydrogenation of aromatic products and showed no effect to C–O bond hydrogenolysis [12].

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Apart from the traditional homogeneous or heterogeneous acid and base catalyzed hydrolysis of diphenyl ether in high temperature water, the metal catalyzed selective hydrogenolysis of diphenyl ether is also feasible. Hartwig et al. reported that a Ni(COD)₂ complex combined with ligand SIPr·HCl and NaO^tBu can selectively cleave diphenyl ether in *m*-xylene at 393 K and 0.1 MPa H₂, attaining 99% yields of benzene and phenol after 16 h [13,14]. While the homogeneous catalyst has minimal steric constraints on interactions with lignin model compounds and allows extremely mild conditions, the TOF with the complex Ni catalyst is as low as 0.34 h⁻¹ [13]. The catalysts are also sensitive to high concentrations of water, which is ubiquitous in raw biomass. To establish a more sustainable, stable, water-tolerant, and applicable process, we have developed a supported Ni/SiO₂ catalyst to quantitatively convert diphenyl ether to benzene and cyclohexanol at 393 K and 0.6 MPa H₂ in the aqueous phase, achieving a TOF of 26 h⁻¹ [15]. By changing the catalyst to Ni/HZSM-5, we have achieved a one-pot conversion of diverse lignin-derived phenolic monomers and aryl ethers to cycloalkanes at 523 K in the aqueous phase via cascade reactions of hydrolysis, hydrogenolysis, dehydration, and hydrogenation [16]. However, the detailed mechanisms of the C–O bond cleavage of di-phenolic ethers over the heterogeneous Ni catalysts have not been established. Therefore, in this contribution, we investigate the mechanisms of C–O bond cleavage in *p*- (H-, CH₃-, OH-) substituted diphenyl ethers over SiO₂, ZrO₂, and Al₂O₃ supported Ni catalysts in the aqueous phase by investigating individual steps. Modeling using density function theory helps to elucidate the mechanism for 4,4'-dihydroxydiphenyl ether conversion.

2. Experimental section

2.1. Reagents

All chemicals were obtained from commercial suppliers: diphenyl ether (Sigma–Aldrich, >99% GC assay), di-*p*-tolyl ether (TCI Europe, >98% GC assay), 4,4'-dihydroxydiphenyl ether (TCI Europe, >98% GC assay), cyclohexyl phenyl ether (Sigma–Aldrich, >95% GC assay), *p*-cresol (TCI Europe, >99% GC assay), hydroquinone (TCI Europe, >99% GC assay), 1,4-cyclohexanediol (TCI Europe, *cis*- and *trans*-mixture, >99% GC assay), ethyl acetate (Roth, >99.9% GC assay), phenol (Sigma–Aldrich, >99% GC assay), benzene (Fluka, >99.5% GC assay), Ni(II) nitrate hexahydrate (Sigma–Aldrich, ≥98.5%), urea (Sigma–Aldrich, BioReagent), HNO₃ (Sigma–Aldrich, >65%), 5 wt.% Pd/C (Sigma–Aldrich), SiO₂ (Aerosil 200, Evonik–Degussa), H₂ (Westfalen AG, 99.999 vol%), N₂ (Westfalen AG, 99.999 vol%), synthetic air (Westfalen AG, 99.999 vol%), ultra pure water system (EASYPure II, resistivity: 18.2 MΩ cm).

2.2. Synthesis of dicyclohexyl ether

Diphenyl ether (20.0 g) and 5 wt% Pd/C (1.0 g) were loaded in a Parr reactor (series 4848, 300 mL). After the reactor was flushed with H₂ three times, the hydrogenation reaction was conducted at 423 K in the presence of 5.0 MPa H₂ (ambient temperature) for 18 h with a stirring speed of 700 rpm. The catalysts were separated from liquid phase by centrifugation, and the product was purified through distillation under vacuum. Purity: >99% (detected by GC), *M*_w: 182 g mol⁻¹, Formula: C₁₂H₂₂O. The ¹H, ¹³C, and COSY NMR spectra are displayed in Figs. S1–S3.

2.3. Catalyst characterization

Atomic absorption spectroscopy (AAS) with a UNICAM 939 AA-Spectrometer determined the content of Ni in the supported

catalysts. Transmission electron micrographs (TEM) were recorded on a JEM-2010 Jeol transmission microscope operated at 120 kV. Before TEM measurement, the samples were prepared by depositing a drop of an ultrasonicated methanol suspension of the solid material onto a carbon-coated Cu grid for TEM measurement. Scanning electron microscopy (SEM) was recorded on a JEOL 500 SEM-microscope with accelerating voltage 25 kV. The power samples were used without any pretreatment. N₂ adsorption–desorption was carried out at 77.3 K using a PMI automatic Brunauer–Emmett–Teller (BET) sorptometer. For the H₂ chemisorption measurement, the Ni catalysts were reduced under 0.1 MPa H₂ at 733 K for 4 h prior to measurement. They were activated in vacuum at 588 K for 1 h before the H₂ chemisorption and then cooled to ambient temperature. The H₂ adsorption isotherms (chemisorption and physisorption) were measured at 1–40 kPa. Following the first isotherms, the samples were outgassed at ambient temperature for 1 h to remove the physisorbed H₂, followed by measuring another adsorption isotherm (physisorption). The Ni dispersions were calculated from the difference between extrapolated intercepts of the first and second isotherms with the assumption of H:Ni atomic ratio = 1.

2.4. Preparation of Ni/SiO₂ catalyst using deposition–precipitation (DP) method

An aqueous solution (250 mL) containing Ni(NO₃)₂·6H₂O (0.14 M, 10.2 g) was first divided in two fractions. To one 50 mL portion was added urea (0.42 M, 6.3 g). The other 200 mL portion together with SiO₂ (1.1 g) and HNO₃ (65%, 0.02 M, 0.32 mL) was put into a flask thermostated at 353 K. The first part with urea was slowly added into the flask, and the suspension was rapidly heated to 363 K. After reaching 363 K, the suspension was magnetically stirred for 10 h. Then, the suspension was cooled to 298 K, and the solids were filtered and washed three times with distilled water (5/1 = water/slurry). Finally, the sample was dried at 363 K for 24 h, and calcinated in flowing air (100 mL min⁻¹) at 973 K and reduced in flowing H₂ (100 mL min⁻¹) at 733 K. The Ni/SiO₂ catalyst had a Ni content of 57 wt.% as analyzed by AAS.

2.5. Catalytic tests

In a typical experiment, the catalytic reactions were carried out in a slurry autoclave reactor with Ni/SiO₂ catalyst using H₂O as solvent at 393 K in the presence of 0.6 MPa H₂. The diphenyl ether (0.010 mol), 57 wt.% Ni/SiO₂ (0.30 g, 2.91 × 10⁻³ mol Ni), and H₂O (80 mL) were added into a Parr reactor (Series 4848, 300 mL). After the reactor was flushed with H₂ three times, the autoclave was charged with 0.6 MPa H₂ and the reactions were conducted at 393 K with a stirring speed of 700 rpm. It heats up 9 min from ambient temperature to 393 K. As H₂O remained liquid under these conditions, two phases were formed as the reaction proceeded, requiring to determine the composition of both phases by stopping the reaction at different times and analyzing the mixture. At the selected times, the reactor was quenched by ice to ambient temperature, and the organic products were extracted by ethyl acetate and analyzed by gas chromatography (GC) and GC–mass spectroscopy (GC–MS) analysis on a Shimadzu 2010 gas chromatograph with flame ionization detector and a Shimadzu QP 2010S GC–MS, both of them equipped with a HP-5 capillary column (30 m × 250 μm). The calculations of conversion and selectivity were on carbon mole basis. Conversion = (the amount of raw-material decrease during reaction/original amount) × 100%. Selectivity = (C atoms in each product/total C atoms in the products) × 100%. Internal standards (i.e., 2-isopropylphenol for the organic phase and acetone for the aqueous phase) were used to determine the product concentration and carbon balance. The carbon balance was better than 95 ± 3%. TOFs for C–O cleavage

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