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Mechanisms of catalytic cleavage of benzyl phenyl ether in aqueous and apolar phases

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ABSTRACT

Catalytic pathways for the cleavage of ether bonds in benzyl phenyl ether (BPE) in liquid phase using Ni- and zeolite-based catalysts are explored. In the absence of catalysts, the C—O bond is selectively cleaved in water by hydrolysis, forming phenol and benzyl alcohol as intermediates, followed by alkylation. The hydronium ions catalyzing the reactions are provided by the dissociation of water at 523 K. Upon addition of HZSM-5, rates of hydrolysis and alkylation are markedly increased in relation to proton concentrations. In the presence of Ni/SiO_2, the selective hydrogenolysis dominates for cleaving the $C_{aliphatic}$—O bond. Catalyzed by the dual-functional Ni/HZSM-5, hydrogenolysis occurs as the major route rather than hydrolysis (minor route). In apolar undecane, the non-catalytic thermal pyrolysis route dominates. Hydrogenolysis of BPE appears to be the major reaction pathway in undecane in the presence of Ni/SiO_2 or Ni/HZSM-5, almost completely suppressing radical reactions. Density functional theory (DFT) calculations strongly support the proposed C—O bond cleavage mechanisms on BPE in aqueous and apolar phases. These calculations show that BPE is initially protonated and subsequently hydrolyzed in the aqueous phase. DFT calculations suggest that the radical reactions in non-polar solvents lead to primary benzyl and phenoxy radicals in undecane, which leads to heavier condensation products as long as metals are absent for providing dissociated hydrogen.

1. Introduction

Lignin is a three-dimensional amorphous polymer with methoxylated phenyl-propane units, which are randomly connected by C—O or C—C linkages [1]. It would be ideal to catalytically and efficiently convert lignin to liquid transportation fuels or fine chemicals without destroying its inherent benzene structure. However, currently lignin is primarily used as a low-grade fuel to provide heat [2,3].Three major approaches, i.e., gasification of lignin to synthesis gas [4,5], liquefaction (pyrolysis) of lignin to bio-oil [6,7], and hydrolysis of lignin to monomeric or oligomeric units [8–10], are used to depolymerize lignin. As the hydrolysis route leads to relatively selective products under much milder reaction conditions, it is rational to select lignin model compounds such as aryl ether dimers to investigate the principal fundamental chemistry of the hydrothermal depolymerization of lignin.

The most abundant C—O bonds in lignin are α-O-4, β-O-4, 4-O-5, β-1, and 5–5 linkages [11], in which the α-O-4 bond is the most active and thermally unstable one due to the lowest bond dissociation energy of the aliphatic C—O bond (218 kJ mol^{-1}) among these bonds [12–15]. To explore the mechanism of cleaving the α-O-4 bond, BPE has been selected as the model compound in this work.

The non-catalyzed pyrolysis of BPE has been extensively investigated in the past [16]. It is initiated by homolytic scission of the weak $C_{aliphatic}$—O bond above 548 K. Generally, pyrolysis was, however, carried out under more severe conditions above 593 K in the vapor phase or in supercritical solvents such as methanol [17], toluene [18], and tetralin [18]. The pyrolysis process produces high concentrations of benzyl and phenoxy radicals, which led to toluene and phenol formation as primary products, together with dimer and high molecular weight products derived from the recombination of the initial radicals. The recombination yield was usually higher than 15% with a carbon balance lower than 80%. Water, in contrast, leads to higher hydrothermal conversion rates of BPE than neat pyrolysis. Klein et al. [19] reported that the pyrolysis rate of BPE in the presence of water was approximately four times higher than that in neat pyrolysis at 605 K. We have explored BPE conversion in supercritical water (between 543 K and 623 K) as well via analyzing the influence of salts (alkali carbonates) toward BPE conversion in aqueous phase [20].

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Recently, we have reported that diverse lignin-derived aryl ethers can be cleaved with Ni/HZSM-5 or Ni/SiO_2 at 393–523 K via combined hydrogenolysis, hydrolysis, and hydrodeoxygenation integrated steps in the aqueous phase [21–24]; however, the mechanisms for cleaving of C—O bonds in these ethers have not been unequivocally established in the presence of mono- and dual-functional metal and acid catalysts. In this work, we will, therefore, investigate the roles of gas atmosphere, acid and metal sites, as well as their cooperative action in the conversion of BPE in the aqueous phase at 523 K via exploring the detailed kinetics together with the analysis of reaction pathways and mechanisms for BPE conversion at specifically varied conditions. In addition, density functional theory (DFT) modeling is comparatively employed to explore the ether cleavage mechanisms in the aqueous and apolar phases as well.

2. Experimental section

2.1. Chemicals

The chemicals were purchased from commercial suppliers and used as received: benzyl phenyl ether (TCI, >98% GC assay), nickel(II) nitrate hexahydrate (Sigma–Aldrich, ⩾98.5% GC assay), SiO_2 (Aerosil 200, Evonik-Degussa), HZSM-5 (Clariant AG, Si/Al = 45), Ni/SiO_2 (Acros, Ni loading 70%), H_2SO_4 (ROTH, ⩾95.5%), undecane (Sigma–Aldrich, >99% GC assay), H_2 (Westfalen AG, >99.999 vol.%), N_2 (Westfalen AG, >99.999 vol.%), synthetic air (Westfalen AG, >99.999 vol.%), and water (EASYpure II, resistivity:18.2 MΩ cm).

2.2. Preparation of Ni/HZSM-5

Ni/HZSM-5 catalyst was synthesized by the wetness impregnation method as follows, $Ni(NO_3)_2 \cdot 6H_2O$ (5.6 g) was first dissolved in H_2O (5.0 g) as a transparent green solution, and subsequently, such aqueous solution was slowly dropped into zeolite HZSM-5 powder (10 g) with stirring. After metal incorporation for 2 h, the catalyst was sequentially dried at 373 K for 12 h, air-calcined (flow rate: 100 mL min^{-1}) at 673 K for 4 h, and hydrogen-reduced (flow rate: 100 mL min^{-1}) at 733 K for 4 h.

2.3. Catalyst characterization

Atomic absorption spectroscopy (AAS): A UNICAM 939 AA-spectrometer was used to measure the Ni concentrations of Ni/SiO_2 and Ni/HZSM-5.

BET surface area: The surface areas and pore diameters were determined by the nitrogen sorption measurement. A PMI automated BET sorptometer was used to measure the nitrogen adsorption at 77 K and before measurement, the samples were first outgassed at 523 K for 20 h.

H_2 chemisorption: The catalysts were first activated at 733 K for 3 h in H_2 and 1 h in vacuum and then cooled to 313 K. An isotherm of H_2 adsorption (chemisorption and physisorption) was measured within a pressure range from 1 kPa to 40 kPa. Then, the physisorbed H_2 was removed by outgassing the sample at the same temperature for 1 h, and another adsorption isotherm (physisorption) was taken. The concentration of chemisorbed H_2 on the metal was determined by extrapolating the differential isotherm to zero P_{H2}, and this value was used to calculate the dispersion of Ni with the assumption of H:Ni atomic ratio = 1.

Transmission electron microscopy (TEM): A JEM-2010 JEOL transmission electron microscope operating at 120 kV was used to record the TEM images. Before measurement, the catalyst was ground and then suspended in ethanol and subsequently dispersed by ultrasonic treatment. After that, the dispersion was dropped on a copper grid-supported carbon film.

IR spectra of adsorbed pyridine: IR spectroscopy with pyridine as probe molecule was used to determine the acid site concentrations and distributions. The IR spectra were measured with a PerkinElmer 2000 spectrometer operated at a resolution of 4 cm^{-1}. The sample was activated at 723 K for 2 h in vacuum, and a background spectrum was recorded after the temperature decreased to 423 K. The activated sample was exposed to pyridine vapor (1.0×10^{-5} MPa) at 423 K for 0.5 h. After removing physisorbed pyridine by outgassing at 423 K for 0.5 h, the spectra were recorded. For quantification, molar integral extinction coefficients of 0.73 cm μmol^{-1} and 0.96 cm μmol^{-1} were used for Brønsted (BAS) and Lewis acid sites (LAS), respectively.

2.4. Catalytic test

The detailed reaction conditions are described in the corresponding figures as footnotes. In a typical experiment, the catalytic reactions were carried out in a slurry autoclave reactor loaded with Ni/HZSM-5 in the water solvent at 523 K in the presence of 4 MPa H_2 (STP). A mixture of benzyl phenyl ether (0.010 mol), 10 wt.% Ni/HZSM-5 (0.050 g, 8.62×10^{-5} mol Ni), and H_2O (80 mL) was firstly added into a Parr reactor (Series 4848, 300 mL). After the reactor was flushed with H_2 by three times, the autoclave was charged with 4 MPa H_2 (ambient temperature) and the reaction was conducted at 523 K with a stirring speed of 700 rpm at different reaction times. The temperature of the autoclave was increased in approximately 20 min. from ambient to reaction temperature (523 K). Because it is a two-phase reaction, the kinetics data are collected at different duration times. After reaction, the reactor was cooled by ice to ambient temperature, and the organic products were extracted by ethyl acetate and analyzed by GC and MS. The products were analyzed by a gas chromatography (GC) and GC–mass spectroscopy (GC–MS) on 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). Internal standard, i.e., 2-isopropylphenol, was used to determine the liquid product concentration and carbon balance. The carbon balance for all reported experiments in liquid phase was better than 95 ± 3% in this work. The calculations of conversion and selectivity were based on carbon mole basis. Conversion = (the amount of raw materials change during reaction/total amount of raw materials) × 100%. Selectivity = (C atoms in each product/total C atoms in the products) × 100%. Rate = (moles of reactants cleaved)/(reaction time in hour). TOF = (moles of reactants cleaved)/(moles of surface active sites × reaction time in hour).

2.5. Density functional theory (DFT) calculation

All the quantum chemical calculations of BPE in hot water and undecane were performed using Gaussian 09 program [25]. The DFT/B3LYP functional with 6-311++G(d,p) basis set was applied. The accuracy of the B3LYP functional was checked by comparing with the second-order Möller–Plesset perturbation theory (MP2) [26]. The transition state of each reaction pathway is located using the linear (LST) and quadratic synchronous transit (QST) methods [27,28]. A series of single point energy calculations of interpolated structures between the initial and the final states along the reaction pathway are performed. The maximum energy structure along this reaction path is used as an estimate transition state in the QST calculation. Each identified transition state was confirmed by the sole imaginary vibrational frequency. The solvation effects on the hydrolysis in water and the pyrolysis in undecane were described