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Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes

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ABSTRACT

The kinetics of the catalytic hydrodeoxygenation of phenol and substituted phenols has systematically been investigated on the dual-functional catalyst system Pd/C and H_3PO_4 in order to better understand the elementary steps of the overall reaction. The reaction proceeds via stepwise hydrogenation of the aromatic ring, transformation of the cyclic enol to the corresponding ketone, hydrogenation of the cycloalkanone to the cycloalkanol and its subsequent dehydration as well as the hydrogenation of the formed cycloalkene. The presence of dual catalytic functions is indispensible for the overall hydrodeoxygenation. The dehydration reaction is significantly slower than the hydrogenation reaction and the keto/enol transformation, requiring a significantly larger concentration of Brønsted acid sites compared to the available metal sites for hydrogenation.

1. Introduction

Bio-oil, produced by pyrolysis or liquefaction of lignocellulosic biomass, is a promising potential raw material for liquid energy carriers and in particular liquid transportation fuels. It cannot be used directly, because it contains a high concentration of oxygen, and the presence of unsaturated and phenolic moieties makes it instable [1–3]. In contrast to the conventional crude oil, which is a mixture of hydrocarbons containing 98 wt.% carbon and hydrogen, 1.8 wt.% sulfur and only 0.1 wt.% oxygen [1], bio-oil is an acidic (pH = 2.5) aqueous solution containing up to 50 wt.% oxygen [4,5]. Such high oxygen values cause a rapid catalyst deactivation in hydrodeoxygenation using sulfide CoMo and NiMo catalysts [6]. The highly active oxo-functionalized molecules also readily oligomerize, requiring advanced catalytic technology to directly hydrodeoxygenate the crude bio-oil under mild conditions.

Bio-oil contains ca. 30 wt.% of lignin-derived phenolic components (phenols, guaiacols, and syringols) which are of high energy density [2,3]. Hydrodeoxygenation (HDO) of such phenolic compounds to cycloalkanes has been reported using heterogeneous metal sulfide catalysts at moderate temperatures (573–873 K) with high-pressure hydrogen (13–16 MPa) in fixed bed reactors [1,7]. However, the incorporation of sulfur into products over these catalysts stimulated us to develop catalysts, which are not based on sulfides [1]. Combined with supported metal catalysts, water as the main component of bio-oil can act as suitable solvent for the selective hydrogenation or oxidation of the bio-derived chemicals [8–14]. Water also allows straightforward product separation, if the targeted products are hydrocarbons without polar functional groups.

Recently, we reported a new route for quantitative conversion of an aqueous mixture of bio-derived phenolic monomers to cycloalkanes and methanol using metal catalysts (Pd or Ni) in the presence of acids (H_3PO_4 or Nafion/SiO_2) [15,16]. Here, we describe the detailed kinetic behavior of phenol, anisole, catechol, and guaiacol on the dual-functional catalysts of Pd/C and H_3PO_4 to form the targeted cycloalkanes, including the pathway of the individual reaction steps and the most important reaction steps of the conversion of phenol. We have also explored the relationship between catalytic activity and reaction conditions, such as the reaction temperature, pH of the aqueous solution, the nature of the metal as well as the catalyst support.

2. Experimental section

2.1. Chemicals

All chemicals were obtained from commercial suppliers and used as provided: phenol (Merck, 99.5% GC assay), anisole (Aldrich, 99.0% GC assay), guaiacol (Fluka, >98.0% GC assay), catechol (Aldrich, crystalline, >99.0% GC assay), 4-*n*-propylphenol (SAFC, >97.0% GC assay), 4-methylguaiacol (Aldrich, 99.0% GC assay), 4-ethylguaiacol (Aldrich, >98.0% GC assay), 4-*n*-propylguaiacol (SAFC, >99.0% GC assay), eugenol (Aldrich, 99.0% GC assay), 4-hydroxy-3-methoxyphenylacetone (Aldrich, 96.0% GC assay),

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4-allyl-2,6-dimethoxy-phenol (Alfa Aesar, 98.0% GC assay), cyclohexanol (Sigma–Aldrich, 99.0% GC assay), 2-methoxycyclohexanol (Alfa Aesar, 99.0% GC assay), palladium (II) nitrate hydrate (Strem Chemicals, 99.9%-Pd), hydrogen (Air Liquide, >99.999%).

2.2. Commercial catalysts used

Pd/C (Aldrich, loading amount: 5 wt.%), Ru/C (Aldrich, loading amount: 5 wt.%), Pt/C (Aldrich, loading amount: 5 wt.%), Rh/C (Aldrich, loading amount: 5 wt.%), Pd/C (Aldrich, loading amount: 1 wt.%).

2.3. Preparation of supported catalysts Pd/Al_2O_3, Pd/SiO_2, and Pd/ASA

We synthesized 2 wt.% of Pd-based catalysts supported on alumina (Degussa), silica (Degussa), and amorphous-silica–alumina (ASA, containing 20% of alumina) with incipient wetness impregnation using palladium (II) nitrate hydrate as Pd precursor, then air-calcined at 573 K for 4 h and hydrogen-reduced at 588 K for 4 h [17].

The ASA support was prepared from a gel formed at pH 7.5 by mixing a solution of acetic acid and $AlCl_3{\cdot}6H_2O$ in distilled water (pH = 1.5) with a solution containing sodium silicate in NH_4OH (pH = 12). The gel was then thoroughly washed with a diluted solution of ammonium acetate to eliminate Na^+ cations, dried at 393 K overnight at ambient atmosphere, and then calcined at 943 K for 2 h in flowing air (100 ml min^{-1}).

2.4. Catalyst characterization

2.4.1. Surface areas and pore diameters

The surface areas and pore diameters were determined from nitrogen adsorption measurements carried out at 77 K on a PMI automated BET sorptometer. The samples were first outgassed at 523 K for 20 h before measurements. The surface area, micropore and mesopore distributions were calculated according to the BET and BJH theories [18].

2.4.2. H_2 chemisorption

The Pd catalysts were activated in vacuum at 588 K for 1 h and then cooled to 313 K. A hydrogen adsorption isotherm (chemisorption together with physisorption) was subsequently measured at a pressure range from 1 to 40 kPa. Then, the sample was outgassed at the same temperature for 1 h to remove the physisorbed H_2, followed by measuring another adsorption isotherm (physisorption). The concentration of chemisorbed hydrogen on the metal was determined by extrapolating the isotherm to zero hydrogen pressure and using the value to estimate the dispersions of the metal on the supports. Besides H_2 chemisorption, we also calculated the Pd dispersion from a TEM micrograph (Fig. S1). The dispersion of the 5 wt.% Pd/C calculated from the TEM measurement was 52%, which is very similar to the 55% derived from the H_2 chemisorption, showing that hydride formation and H_2 uptake into the bulk of Pd do not take place under the used conditions.

2.5. Measurements of catalytic reactions

2.5.1. Aqueous-phase HDO of bio-derived phenolic compounds

The HDO reactions were optimized by varying the pH of the aqueous solution (neutral, acidic, basic), the metal (Pd, Pt, Ru, Rh), the catalyst support (C, Al_2O_3, SiO_2, ASA), as well as by varying the reaction temperature (423, 473, 523 K). The reaction conditions used are noted in the footnotes of the tables. In a typical experiment, phenol or other lignin-derived monomers (0.0106 mol), H_3PO_4-H_2O solution (80 ml, 0.5 wt.%, pH = 2.1), and Pd/C (0.040 g, 5 wt.%) were added into an autoclave (Parr, Series 4843, 300 ml). Then, the autoclave was pressured with 5 MPa H_2 (ambient temperature). Reactions were conducted at 473 K for 0.5 h with a stirring speed of 1000 rpm. After cooling to ambient temperature, the organic products were extracted by ethyl acetate. The organic phase and aqueous phase were both analyzed by a gas chromatograph (GC, Shimadzu 2010, flame ionization detector) with a HP-5 capillary column (30 m × 250 μm). A gas chromatograph–mass spectrometer combination (GC–MS, Shimadzu QP 2010S) was used to identify the organic compounds. Internal standards (i.e., 2-isopropylphenol for the organic phase and acetone for the aqueous phase) were used to determine the liquid product concentration and carbon balance. The calculations of conversion and selectivity were based on carbon mole basis. Conversion = (the amount of aromatic ring change during reaction/total amount of aromatic ring) × 100%. Selectivity = (C atoms in each product/total C atoms in the products) × 100%. The carbon balance in the liquid phase for all reported experiments was better than 95 ± 3% in this work.

The composition of the gas phase was determined by GC (HP 6890) equipped with a plot Q capillary column (30 m × 250 μm) with thermal conductivity detector (TCD). We found 99% hydrogen and trace amounts of CO_2 and methanol in the gas phase, so in this work only the changes in the liquid phase were considered.

2.5.2. Kinetic study of phenol hydrodeoxygenation network

The kinetic study of the aqueous-phase hydrodeoxygenation of phenol to cyclohexane was divided into four steps: (i) phenol hydrogenation to cyclohexanone, (ii) cyclohexanone hydrogenation to cyclohexanol, (iii) cyclohexanol dehydration to cyclohexene, and (iv) cyclohexene hydrogenation to cyclohexane. These reactions were carried out at 473 K in the batch autoclave reactor. The reaction conditions were as follows: (i) phenol (12.5 g), Pd/C (1 wt.%, 0.020 g), 5 MPa H_2; (ii) cyclohexanone (60 g), Pd/C (1 wt.%, 0.020 g), 5 MPa H_2; (iii) cyclohexanol (140 g), H_3PO_4-H_2O (0.5 wt.%, 80 ml), 5 MPa N_2; (iv) cyclohexene (50 g), Pd/C (1 wt.%, 0.020 g), 5 MPa H_2.

After reaction, ethyl acetate was used to extract the organic phase and the extract was analyzed by GC and GC–MS using the internal standard 2-isopropylphenol. As the aqueous-phase HDO reaction is a two-phase process, the real-time sampling during reaction is very difficult. Thus, the conversion/selectivity data as a function of reaction time were collected from separate batch experiments with varying duration.

Turnover frequencies (TOFs) were determined as initial reaction rates when the conversion was below 10%, defined as mole of consumed reactant per mole of surface Pd atom (or per mole of H^+) per hour.

2.5.3. Kinetic study of anisole, catechol, and guaiacol hydrodeoxygenation conversion

The kinetic study of anisole, catechol, or guaiacol was carried out as follows. The reactant (0.016 mol) was mixed with 0.5 wt.% H_3PO_4–H_2O solution (80 ml) and 5 wt.% Pd/C (0.020 g), and then such mixture was hydrodeoxygenated at 423 K and 5 MPa H_2 with a stirring speed of 1000 rpm. After reaction, ethyl acetate was used to extract the organic phase, and the liquid products including aqueous phase and organic phase were analyzed through GC and GC–MS with internal standards (i.e., 2-isopropylphenol for the organic phase and acetone for the aqueous phase). As mentioned in Section 2.5.2, the conversion/selectivity data versus reaction time were collected from the corresponding separate batch experiments with varying duration.

2.5.4. Aqueous-phase HDO of phenolic mixture and catalyst recycle

Resembling the HDO of bio-oil, reaction of a phenolic monomer mixture (3.38 g) containing 2-methoxy-4-*n*-propylphenol (0.83 g, 0.005 mol), 4-*n*-propylphenol (0.68 g, 0.005 mol), 4-hydroxy-3-methoxyphenylacetone (0.90 g, 0.005 mol) and 4-allyl-2,6-dimethoxyphenol (0.97 g, 0.005 mol), Pd/C (0.080 g, 5 wt.%), and H_3PO_4–H_2O solution (80 ml, 0.5 wt.%) was carried out at 523 K and 5 MPa H_2 (ambient temperature) for 0.5 h, stirred at 1000 rpm. After reaction, the other treatments were kept the same as mentioned in Section 2.5.1.

To test the catalyst recyclability, the first run for hydrodeoxygenation of the phenolic mixture was carried out at 523 K and 5 MPa H_2 (ambient temperature) for 2 h, stirred at 1000 rpm. After reaction, the Pd/C catalyst was separated by decantation, followed by sequential washing with ethyl acetate and water, and drying at 393 K for 2 h. The catalyst was then reused in the next catalytic recycle run without any further treatment.

2.5.5. Aqueous-phase dehydration of cyclohexanol

A typical experiment for the dehydration of cyclohexanol (1.06 g, 0.0106 mol) was carried out in the Parr reactor with a H_3PO_4-H_2O solution (80 ml, 0.5 wt.%) at 373, 423, 453, and 473 K and 5 MPa H_2 (ambient temperature) for 0.5 h, stirred at 1000 rpm. After cooling, the organic layer was extracted with ethyl acetate and the internal standard 2-isopropylphenol was added to the organic phase to calculate the product concentrations. The liquid organic products were analyzed through GC and GC–MS.

3. Results

3.1. Catalyst characterization

The main physicochemical properties of the Pd catalysts are compiled in Table 1. The surface area of 1 wt.% Pd/C (934 $m^2\,g^{-1}$) or 5 wt.% Pd/C (845 $m^2\,g^{-1}$) was much higher than that of 2 wt.% Pd/SiO_2 (174 $m^2\,g^{-1}$), Pd/Al_2O_3 (92 $m^2\,g^{-1}$), and Pd/ASA (269 $m^2\,g^{-1}$). The pore diameter in Pd/C was 3.6 nm, while those in the other three materials Pd/SiO_2, Pd/Al_2O_3 and Pd/ASA were 14–18 nm as compiled in Table 1. In agreement with the higher surface area of the carbon support, the dispersion of Pd in 5 wt.% Pd/C calculated from H_2 chemisorption data (55%) was much higher than that of Pd supported on Al_2O_3 (12%), SiO_2 (24%), and ASA (40%).

3.2. Hydrodeoxygenation of phenol

Phenol was selected as the simple phenolic model compound to explore the fundamental chemistry in the aqueous-phase hydrodeoxygenation. In industry, hydrogenation of phenol (using palladium and platinum-based catalysts) is mainly used to produce cyclohexanone, which is the key material for manufacturing nylon 6 and polyamide resins [18–25]. Cyclohexanol and cyclohexanone are the main competing hydrogenated products from phenol hydrogenation, while cyclohexane is formed on supported palladium catalysts at a low yield (less than 20%) [24].

Table 1
Textural properties of the Pd-supported catalysts.

Catalyst	BET surface area ($m^2\,g^{-1}$)	Pore diameter (nm)	Dispersion (%)	Metal loading (wt.%)
Pd/C	934	3.7	51	1
Pd/C	845	3.6	55	5
Pd/Al_2O_3	92	16	12	2
Pd/SiO_2	174	18	24	2
Pd/ASA	269	14	40	2

3.2.1. Effect of catalyst support

In neutral water under conditions of 473 K, 5 MPa H_2 and 0.5 h, Pd/C yielded 98% cyclohexanol (Table 2). This is line with the expectation that high hydrogen pressure, high temperature, and strong adsorption of phenol on carbon lead to cyclohexanol being the dominant product [25]. On the other hand, Pd/Al_2O_3, Pd/SiO_2, and Pd/ASA led to about 70% cyclohexanol and 30% cyclohexanone at 90% conversion under the identical conditions. Liu et al. found that Lewis acids such as $AlCl_3$, $ZnCl_2$, $InCl_3$, and $SnCl_2$ stabilized cyclohexanone intermediates in the presence of Pd/C [26], achieving a 100% cyclohexanone yield in dichloromethane solvent at low temperature (303 K) and hydrogen pressure (1 MPa). The present results qualitatively agree with the above suggestion, as over Lewis supports of Pd/Al_2O_3, Pd/SiO_2, and Pd/ASA catalysts, the cyclohexanone intermediate is stabilized, thus its yield reached up to 30%.

3.2.2. Effect of the pH value of aqueous solution

In neutral water, Pd/C yielded 98% cyclohexanol at 473 K. When a basic solution (80 ml of 0.05 wt.% NaOH solution, pH = 12) was added, the performance (conversion and selectivity) of the Pd/C catalyst was nearly unchanged by the presence of OH^- ions, leading to a yield of 97% cyclohexanol (see Table 2). However, when acetic acid was introduced, i.e., the main organic acid in crude bio-oil (up to 32 wt.%) [27], the product distribution was changed (Table 2). When using Pd/C with acetic acid (5 wt.%, pH = 2.6), 75% cyclohexane, 20% cyclohexanol, and 2% cyclohexanone were obtained. Small amounts of esters and ethers, i.e., 1% cyclohexyl acetate and 2% dicyclohexyl ether, were also catalytically produced with acetic acid. Applying a stronger mineral acid, such as phosphoric acid (0.5 wt.%, pH = 2.1), led to 85% cyclohexane selectivity with 99% phenol conversion, indicating that the acidity of the aqueous solution is the essential factor for cyclohexane formation.

By comparison, Pd/Al_2O_3, Pd/SiO_2, and Pd/ASA catalysts produced a 7:3 ratio of cyclohexanol to cyclohexanone at ca. 80% conversion in neutral water. When NaOH was added to the aqueous solution, the catalytic activity was drastically decreased by 10%, 32%, and 24%, respectively. This is attributed to the observed par-

Table 2
Aqueous-phase hydrodeoxygenation of phenol.[a]

Catalyst	*T* (K)	Solvent	Conv. (%)	Selectivity (C%)		
				Cyclo Hexane	Cyclo Hexanol	Cyclo Hexanone
Pd/C	473	H_2O	100	0	98	2
Pd/Al_2O_3	473	H_2O	82	0	72	28
Pd/SiO_2	473	H_2O	87	0	62	38
Pd/ASA	473	H_2O	96	0	73	27
Pd/C	473	NaOH–H_2O	100	0	97	3
Pd/Al_2O_3	473	NaOH–H_2O	72	0	69	31
Pd/SiO_2	473	NaOH–H_2O	55	0	53	47
Pd/ASA	473	NaOH–H_2O	72	0	64	36
Pd/C	473	CH_3COOH–H_2O	100	75	20	2
Pd/Al_2O_3	473	CH_3COOH–H_2O	88	20	20	56
Pd/SiO_2	473	CH_3COOH–H_2O	95	20	13	64
Pd/ASA	473	CH_3COOH–H_2O	100	21	24	53
Pd/C	423	H_3PO_4–H_2O	100	0	74	25
Pd/C[b]	423	H_3PO_4–H_2O	100	1	94	4
Pd/C	473	H_3PO_4–H_2O	99	85	10	4
Pd/C	523	H_3PO_4–H_2O	100	98	1	0
Pt/C	473	H_3PO_4–H_2O	100	86	13	0
Ru/C	473	H_3PO_4–H_2O	100	88	10	1
Rh/C	473	H_3PO_4–H_2O	100	92	7	0

[a] Reaction conditions: phenol (1.0 g, 0.0106 mol), H_2O (80 ml), H_3PO_4–H_2O (0.5 wt.%, 80 ml), CH_3COOH–H_2O (5 wt.%, 80 ml), NaOH–H_2O (0.05 wt.%, 80 ml), Pd/C (5 wt.%, 0.040 g), Rh/C (5 wt.%, 0.040 g), Ru/C (5 wt.%, 0.040 g), Pt/C (5 wt.%, 0.070 g), Pd/Al_2O_3 (2 wt.%, 0.10 g), Pd/SiO_2 (2 wt.%, 0.10 g), Pd/ASA (2 wt.%, 0.10 g), 5 MPa H_2, 0.5 h, stirred at 1000 rpm.

[b] Reaction time: 1 h.

tial dissolution of amorphous inorganic oxides in the aqueous basic solution at 473 K, and thus, the well-dispersed Pd particles aggregate, leading to less surface Pd atoms for the hydrogenation reaction [11]. In basic environment, the selectivity ratio of cyclohexanol to cyclohexanone remained approximately at 7:3. Additionally, ca. 20% of cyclohexane, 20% of cyclohexanol, and 55% of cyclohexanone were formed on Pd/Al_2O_3, Pd/SiO_2, and Pd/ASA with acetic acid. Severe dissolution of the amorphous silicon and aluminum oxides occurred after reaction with Brønsted liquid acids in water at 473 K. Approximately 20% cyclohexane was catalytically produced by acetic acid introduction. From the point of stability in non-neutral aqueous solutions, robust carbon supports are more practical for hydrodeoxygenation.

3.2.3. Effect of the metal sites

Besides Pd/C, other noble metal catalysts such as Rh/C, Ru/C, and Pt/C were explored. The results showed that these four catalysts exhibited similar activities (85% cyclohexane yields) in phenol conversion with H_3PO_4 at 473 K. The materials also performed quite similarly in neutral and basic water solution, yielding ca. 100% cyclohexanol (Table S1). Because of the slight difference in activities, Pd/C was selected as the typical catalyst to perform the following experiments. For this reason, these three metals (Rh, Ru, Pt) will not be discussed in detail in the discussion section.

3.2.4. Effect of temperature

With the Pd/C and H_3PO_4 combination, different temperatures (423, 473, 523 K) were applied for phenol conversion. Cyclohexane was not formed at 423 K after 0.5 and 1 h, cyclohexanol and cyclohexanone being the main products. The different reaction routes for phenol conversion are determined by the hydronium ion concentration of the aqueous solution, but the reaction temperature needs to be sufficiently high to catalyze the more demanding dehydration to cyclohexene at appreciable rates. Thus, increasing the reaction temperature to 473 and 523 K led to 85% and 98% cyclohexane yields over Pd/C and H_3PO_4 catalysts, respectively (Table 1). Note that the yields of cyclohexane achieved are far higher than those achieved with the most active CoMo-sulfided catalysts, producing approximately 34% benzene and 4% cyclohexane from phenol at 673 K in a fixed bed reactor at comparable residence times [28].

3.2.5. Hydrodeoxygenation reaction pathway for phenol conversion

The mechanism for gas-phase phenol conversion to cyclohexane with heterogeneous sulfide catalysts has been proposed in Refs. [7,29]: (i) direct hydrogenolysis to benzene ($\Delta H^{\Theta} = -62\ \mathrm{kJ\ mol^{-1}}$), followed by benzene hydrogenation ($\Delta H^{\Theta} = -206\ \mathrm{kJ\ mol^{-1}}$), and (ii) hydrogenation to cyclohexanol ($\Delta H^{\Theta} = -190\ \mathrm{kJ\ mol^{-1}}$), followed by direct cyclohexanol hydrogenolysis ($\Delta H^{\Theta} = -78\ \mathrm{kJ\ mol^{-1}}$). However, in the present aqueous-phase process with Pd/C, phenol and cyclohexanol were unequivocally shown not to follow the classical hydrogenolysis route. Thus, the overall hydrodeoxygenation route does not follow the hydrogenation/hydrogenolysis sequential mechanism.

In our previous work [15], it was shown that phenol was hydrogenated to cyclohexanone over Pd/C in the first step. It was concluded to have actually been formed by fast isomerization of cyclohexenol (cyclic keto/enol transformation) [30,31]. Then, cyclohexanone was gradually hydrogenated to cyclohexanol with the hydrogenation catalysts. Pd/C does not catalyze the (structure sensitive) hydrogenolysis of phenol, and thus, Pd as well as Pt-, Ru-, and Rh-based catalysts favor phenol hydrogenation to cyclohexanol in neutral water (Table S1).

Table 3
Aqueous-phase dehydration of cyclohexanol.[a]

T (K)	Catalyst	Solvent	Conv. (%)	Selectivity (C%)	
				Cyclohexene	Cyclohexanone
473	–	H_2O	0	0	0
473	Pd/C	H_2O	1.2	0	100
473	Pd/C	H_3PO_4–H_2O	98	99.9[b]	0.1
373	–	H_3PO_4–H_2O	0	0	0
393	–	H_3PO_4–H_2O	0.1	62	38
423	–	H_3PO_4–H_2O	1.2	69	31
433	–	H_3PO_4–H_2O	2.3	83	17
453	–	H_3PO_4–H_2O	8.6	95	5.0
473	–	H_3PO_4–H_2O	95	99.9	0.1
473[c]	–	H_3PO_4–H_2O	93	100	0

[a] Reaction conditions: cyclohexanol (1.06 g, 0.0106 mol), Pd/C (5 wt.%, 0.04 g), H_2O (80 ml), H_3PO_4–H_2O (0.5 wt.%, 80 ml), 5 MPa H_2 (ambient temperature), 0.5 h, stirred at 1000 rpm.

[b] Cyclohexane selectivity.

[c] Repeat of the experiment carried out with H_3PO_4 at 473 K.

The intermediate product, cyclohexanol, was not hydrogenolyzed to cyclohexane over Pd/C at 473 K in water either, but was dehydrogenated to 100% cyclohexanone at 1.2% conversion. With the mineral acid H_3PO_4 at 373 K, cyclohexanol was stable with zero conversion in water solvent (Table 3). From 393 to 453 K, the dehydration conversion of cyclohexanol over H_3PO_4 increased from 0.1% to 8.6%. The apparent activation energy, calculated from the data presented in Table 3 for the aqueous-phase cyclohexanol dehydration with H_3PO_4, was $120\ \mathrm{kJ\ mol^{-1}}$. At 473 K, cyclohexanol was quantitatively dehydrated to cyclohexene within half an hour in the presence of H_3PO_4 (Table 3). In previous studies, cyclohexanol was dehydrated to cyclohexene with 80% yield over Lewis acid alumina at 603–623 K [32], or it was dehydrated by Brønsted liquid acids, such as sulfuric acid and phosphoric acid, and by solid acids in the liquid phase at 403–473 K in the absence of solvents [33,34]. In the aqueous phase, water as solvent inhibits cyclohexanol dehydration with respect to the chemical equilibrium, because it is also a reaction product. Thus, the reaction temperature has to be increased to 473 K in water compared to 403 K with sulfuric acid without a solvent. Catalyzed by the Pd/C and H_3PO_4 dual-functional components, phenol was rapidly and quantitatively hydrodeoxygenated to cyclohexane (Table 3). In summary, cyclohexane formation from phenol requires dual-functional catalysis, i.e., the presence of hydronium ions for dehydration at appropriate temperatures, and a metallic function able to hydrogenate in the presence of water.

The overall reaction pathway for the aqueous-phase hydrodeoxygenation of phenol to cyclohexane proceeds via an initial metal-catalyzed aromatic ring hydrogenation and naphthenic alcohol dehydration and then metal-catalyzed cycloalkene hydrogenation (Fig. 1) [15].

3.3. Hydrodeoxygenation of phenolic monomers

After optimizing the reaction conditions on such aqueous system (Table S2), phenol and substituted phenols including catechol and 4-*n*-propylphenol were quantitatively converted to cyclohexane at 523 K and 5 MPa H_2 in half an hour over Pd/C and H_3PO_4 catalysts (Table 4). Five guaiacols, 4-methylguaiacol, 4-ethylguaiacol, 4-*n*-propylguaiacol, 4-allylguaiacol, and 4-acetonylguaiacol, were fully converted to cycloalkanes, methanol, and intermediates. About 80% yields of cycloalkanes, 8–10% methanol, and 12–18% intermediates (cycloalkanol or cycloalkanone) were produced from guaiacols. Promoted by acid catalysis, cycloalkanes undergo carbon skeletal isomerization at the extent of 6–10%. The most complex lignin-derived compound syringol (4-allyl-2,6-dimethoxyphenol) was also tested, achieving a yield of 67% cycloalkanes and 12% methanol. These results suggest that the new catalytic approach

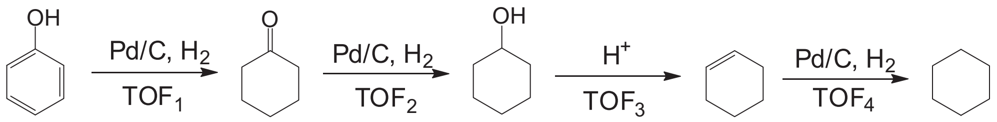
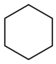
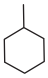
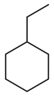
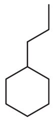
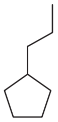
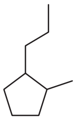
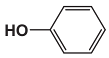
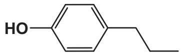
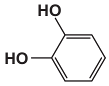
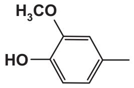
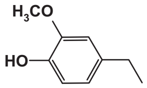
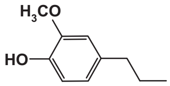
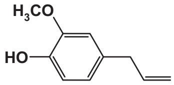
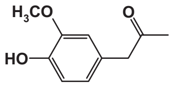
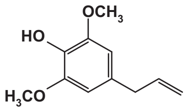


Fig. 1. Reaction pathway for aqueous-phase phenol of hydrodeoxygenation on dual-functional catalysts of Pd/C and H_3PO_4 at 473 K.

Table 4
Aqueous-phase hydrodeoxygenation of bio-derived phenolic monomers with Pd/C and H_3PO_4 catalysts at 523 K.[a]

Reactant	Conv. (%)	Selectivity (C%)							
								CH_3OH	Cycloalcohol/ketone
	100	98	–	–	–	–	–	–	1.3
	100	–	–	–	96	–	–	–	3.6
	100	87	–	–	–	–	–	–	12
	100	–	78[b]	–	–	–	–	10	10
	100	–	–	80[c]	–	–	–	10	9.2
	100	–	–	–	66	3.0	6.7	7.2	17
	99	–	–	–	65	3.5	5.0	7.4	18
	100	–	–	–	71	3.1	5.2	8.2	12
	92	–	–	–	58	3.1	5.6	12	21

[a] Reaction conditions: phenol (1.0 g, 0.0106 mol) or other phenolic monomers (0.0106 mol), Pd/C (5 wt.%, 0.040 g), H_3PO_4-H_2O (0.5 wt.%, 80 ml), 5 MPa H_2 (ambient temperature), 0.5 h, stirred at 1000 rpm.

[b] Includes isomerization products: methylcyclopentane (selectivity: 1.8%) and 1,2-dimethylcyclopentane (selectivity: 4.6%).

[c] Includes isomerization products: ethylcyclopentane (selectivity: 2.2%) and 2-methyl-1-ethylcyclopentane (selectivity: 7.6%).

can be effectively applied in the hydrodeoxygenation of the diverse substituted phenolic monomers in bio-oil upgrading.

The hydrodeoxygenation of a phenolic mixture was tested over Pd/C and H_3PO_4. Phenolic monomers (4-*n*-propylphenol, 2-methoxy-4-*n*-propylphenol, 4-hydroxy-3-methoxyphenylacetone, and 4-allyl-2,6-dimethoxyphenol) were mixed in equal molar amounts to simulate the bio-oil mixture (Table 5). As expected, the substitute bio-oil was effectively hydrodeoxygenated at conditions 523 K, 5 MPa H_2, and 0.5 h, maintaining a high rate of the overall reaction. The conversions of the components ranged from 82% to 100%, with selectivities of 70% in cycloalkanes and 8.0% in methanol.

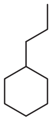
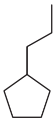
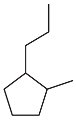
Moreover, to test for catalyst recyclability, a batch of Pd/C catalyst was repeatedly used on the substitute bio-oil mixture at 523 K and 5 MPa H_2 for 2 h (Table 5). The first run reached 100% conversion and selectivities of 89% cycloalkanes and 9.0% methanol after 2 h testing. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of the organic phase and the aqueous solution after each cycle did not show even traces of leached Pd (detection limit: 1 μg/mL). Nearly quantitative conversions and very high selectivities (ca. 80% cycloalkanes and 8% methanol) were also obtained in the two subsequent recycle experiments (Table 5). The stable catalyst recycle performance indicates that the Pd active sites have not changed (no changes in the Pd dispersion or Pd leaching).

4. Discussion

4.1. Kinetics of the phenol hydrodeoxygenation network

The elementary reactions for the aqueous-phase phenol hydrodeoxygenation network are divided into four processes (Fig. 1), (i) phenol hydrogenation to cyclohexanone on Pd/C, (ii) cyclohexa-

Table 5
Hydrodeoxygenation of phenolic mixture and catalyst recycle.

	Conv. (%)	Selectivity (C%)				
					CH_3OH	Cycloalcohol/ketone
HDO of phenolic mixture[a]	4-*n*-Propylphenol: 100 2-Methoxy-4-*n*-propylphenol: 92 4-Hydroxy-3-methoxyphenylacetone: 100 4-Allyl-2,6-dimethoxyphenol: 82	64	3.0	3.2	8.0	20
Catalyst recycle (the reaction was carried out at 523 K for 2 h)						
Run 1	4-*n*-Propylphenol: 100 2-Methoxy-4-*n*-propylphenol: 100 4-Hydroxy-3-methoxyphenylacetone: 100 4-Allyl-2,6-dimethoxyphenol: 95	80	3.6	5.0	9.0	1.7
Run 2	4-*n*-Propylphenol: 100 2-Methoxy-4-*n*-propylphenol: 98 4-Hydroxy-3-methoxyphenylacetone: 100 4-Allyl-2,6-dimethoxyphenol: 87	73	2.5	3.1	8.4	12
Run 3	4-*n*-Propylphenol: 100 2-Methoxy-4-*n*-propylphenol: 88 4-Hydroxy-3-methoxyphenylacetone: 95 4-Allyl-2,6-dimethoxyphenol: 79	67	1.7	1.7	7.5	21

[a] Reaction conditions: the phenolic monomer mixture (3.4 g) contains 2-methoxy-4-*n*-propylphenol (0.83 g, 0.005 mol), 4-*n*-propylphenol (0.68 g, 0.005 mol), 4-hydroxy-3-methoxyphenylacetone (0.90 g, 0.005 mol), and 4-allyl-2,6-dimethoxyphenol (0.97 g, 0.005 mol), Pd/C (0.080 g, 5 wt.%), H_3PO_4-H_2O solution (80 ml, 0.5 wt.%), 523 K, 5 MPa H_2 (ambient temperature), 0.5 h, stirred at 1000 rpm.

Table 6
Turnover frequencies for aqueous-phase phenol hydrodeoxygenation network.

TOF_1 for phenol hydrogenation (h^{-1})	TOF_2 for cyclohexanone hydrogenation (h^{-1})	TOF_3 for cyclohexanol dehydration (h^{-1})	TOF_4 for cyclohexene hydrogenation (h^{-1})
6.2×10^3	1.2×10^4	15	$>9 \times 10^6$

none hydrogenation to cyclohexanol on Pd/C, (iii) cyclohexanol dehydration to cyclohexene with H_3PO_4, and (iv) cyclohexene hydrogenation to cyclohexane on Pd/C.

Cyclohexanone was found to be the dominant product (>95% selectivity) (see Fig. 2a) for phenol hydrogenation ($\Delta H^{\circ}_{(473K)} = -130$ kJ mol^{-1}) at 473 K on Pd/C at low conversions (lower than 10%). The TOF of phenol hydrogenation on Pd/C was 6.2×10^3 mol$_{phenol}$ mol$^{-1}_{surf.Pd}$ h^{-1} (see Table 6). For the further cyclohexanone hydrogenation to cyclohexanol ($\Delta H^{\circ}_{(473K)} = -74$ kJ mol^{-1}), the TOF of the ketone hydrogenation on Pd/C at 473 K was 1.2×10^4 mol$_{cyclohexanone}$ mol$^{-1}_{surf.Pd}$ h^{-1} (Fig. 2b), a higher value than that of the phenol hydrogenation.

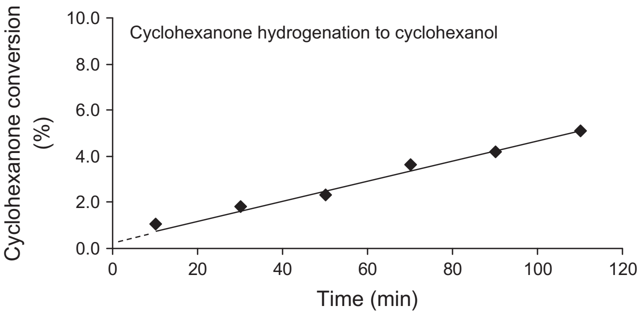


Fig. 2b. Aqueous-phase hydrogenation of cyclohexanone to cyclohexanol as a function of time. Reaction conditions: cyclohexanone (60 g), Pd/C (1 wt.%, 0.020 g), 473 K, 5 MPa H_2, stirred at 1000 rpm.

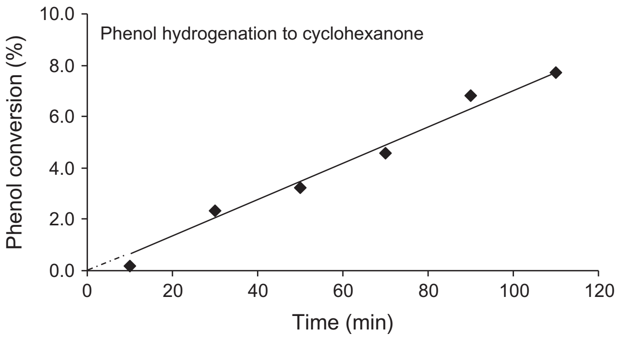


Fig. 2a. Aqueous-phase hydrogenation of phenol to cyclohexanone as a function of time. Reaction conditions: phenol (12.5 g), Pd/C (1 wt.%, 0.020 g), 473 K, 5 MPa H_2, stirred at 1000 rpm.

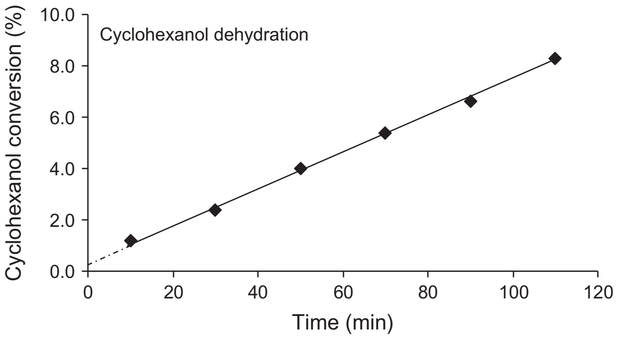


Fig. 2c. Aqueous-phase dehydration of cyclohexanol to cyclohexene as a function of time. Reaction conditions: cyclohexanol (140 g), H_3PO_4-H_2O (0.5 wt.%, 80 ml), 473 K, 5 MPa N_2, stirred at 1000 rpm.

The TOF rate of the acid-catalyzed alcohol dehydration at 473 K ($\Delta H^{\circ}_{(473\mathrm{K})} = 26\ \mathrm{kJ \cdot mol^{-1}}$) was as low as 15 $\mathrm{mol_{cyclohexanol}\ mol_{H^+}^{-1}\ h^{-1}}$ (Fig. 2c, Table 6). This indicates that the aqueous-phase dehydration is the key step in the overall hydrodeoxygenation reaction, which is also in line with its high apparent activation energy.

The rate of cyclohexene hydrogenation was very high, so that the conversion reached 87% at 473 K on Pd/C after 5 min (for the reaction conditions see Section 2.5.2), thus the TOF value for cyclohexene hydrogenation ($\Delta H^{\circ}_{(473\mathrm{K})} = -119\ \mathrm{kJ\ mol^{-1}}$) on Pd/C exceeded 9×10^6 $\mathrm{mol_{cyclohexene}\ mol_{surf.Pd}^{-1}\ h^{-1}}$ (Table 6). The extremely high intrinsic consumption rate of cyclohexene and the phase separation also shift the equilibrium of the dehydration reaction, allowing nearly quantitative cyclohexane production.

4.2. Kinetics of anisole, catechol, and guaiacol hydrodeoxygenation

To probe the stepwise aqueous-phase conversion of various substituted groups at the aromatic ring, i.e., a methoxy group, two adjacent hydroxyl groups, and adjacent hydroxyl and methoxy groups on Pd/C and H_3PO_4, anisole, catechol, and guaiacol were selected.

Anisole (methyl phenyl ether) was reacted on Pd/C at 423 K and 5 MPa H_2 with H_3PO_4 and the conversion and selectivity of products are displayed in Fig. 3a as a function of reaction time. The primary product ($t = 0$, selectivity = 80%) was cyclohexanone originating from phenol hydrogenation. This implies that under the selected conditions, hydrolysis of anisole to phenol is the dominating reaction. The TOF for anisole hydrolysis on H_3PO_4 at 423 K was 2.8 $\mathrm{mol_{anisole}\ mol_{H^+}^{-1}\ h^{-1}}$. This hydrolysis rate is much lower than the phenol hydrogenation rate (6120 $\mathrm{h^{-1}}$), thus the phenol intermediate is not detected and cyclohexanone appears to be the primary product. Ratton also showed that anisole was 100% hydrolyzed to phenol at 473 K in water with 3 wt.% acetic acid [35]. The increasing cyclohexanol selectivity was accompanied by a decreasing cyclohexanone selectivity (see Fig. 3a), which suggests that after the rapid hydrolysis of anisole and the partial hydrogenation of phenol, the hydrogenation of cyclohexanone was somewhat slower. Note that the high selectivity to cyclohexanone indicates a higher adsorption constant of the aromatic rings compared to the saturated cyclic compounds. The other independent primary product was the directly hydrogenated methoxycyclohexane ($t = 0$, selectivity ≈ 10%). As the selectivity to methoxy-cyclohexane and methanol was approximately constant at 30% and 10% from 10 to 190 min, respectively, the ratio of the aromatic ring hydrogenation to the ether hydrolysis is concluded to be constant. This indicates that the hydrogenation of the aromatic ring and methoxy hydrolysis take place as parallel reaction routes. Moreover, the ratio of the selectivities of cyclohexanone and cyclohexanol to methanol was 6:1, which coincides with the carbon molar ratio of aromatic ring to methoxy group in anisole. The TOF for initial anisole hydrogenation on Pd/C at 423 K exceeded

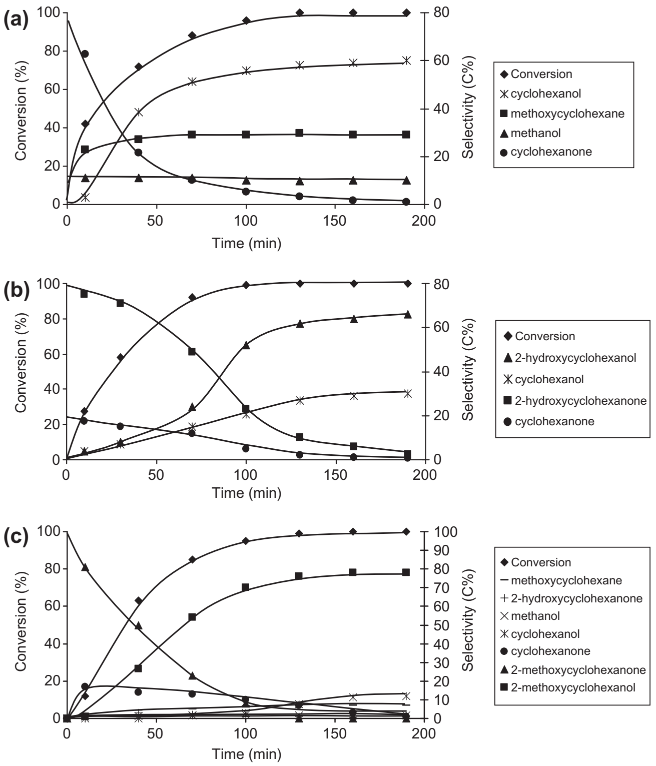


Fig. 3. Product distribution after hydrogenation of phenolic monomers (a) anisole, (b) catechol, and (c) guaiacol. Reaction conditions: reactant (0.0106 mol), Pd/C (5 wt.%, 0.020 g), H_3PO_4-H_2O (0.5 wt.%, 80 ml), 423 K, 5 MPa H_2 (ambient temperature), stirred at 1000 rpm.

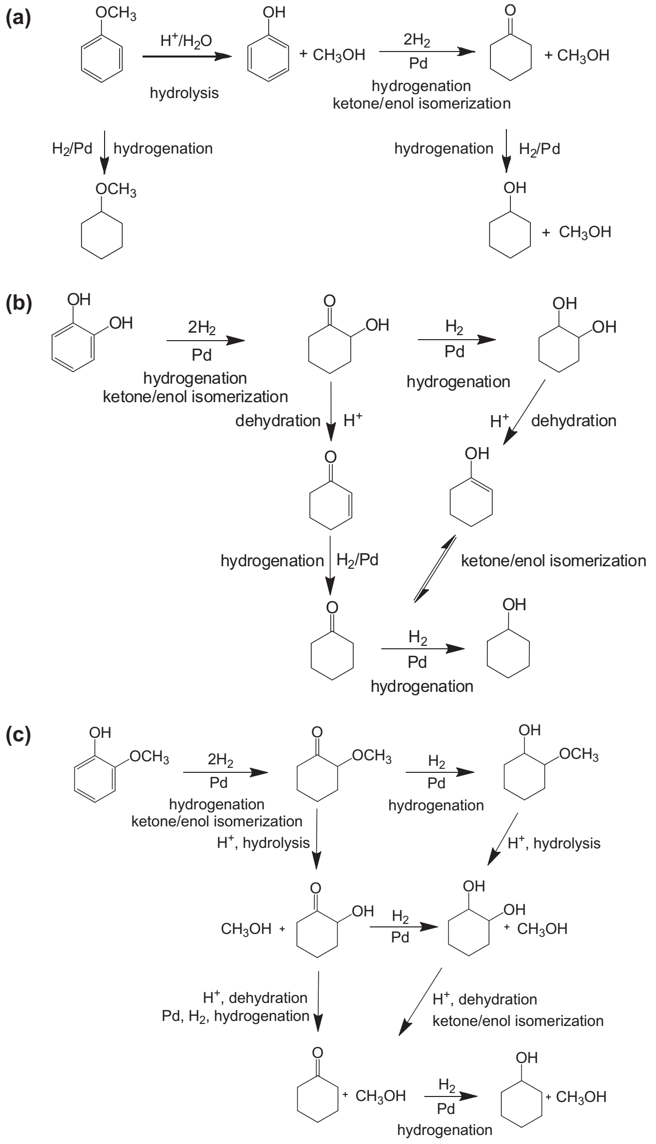


Fig. 4. Proposed reaction pathway for aqueous-phase conversion of bio-derived phenolic monomers (a) anisole, (b) catechol, and (c) guaiacol to cyclohexanol with Pd/C catalyst and H_3PO_4 component.

1100 $mol_{anisole}$ $mol^{-1}_{surf.Pd}$ h^{-1}. The results also imply that the alkyl C-O bond of an aryl alkyl ether (anisole) is much easier to hydrolyze than that of a dialkyl ether (methoxy-cyclohexane), which is in line with the findings of the hydrolysis of benzyl phenyl ether [36] and diphenyl ether [37]. Hence, with a single methoxy group at the aromatic ring, anisole can be catalytically hydrolyzed and directly hydrogenated at the same time on the dual-functional catalyst system Pd/C and H_3PO_4 (Fig. 4a).

Catechol having two adjacent hydroxyl groups on the aromatic ring is an important constituent from lignin depolymerization and also an intermediate in the guaiacol or syringol conversion. When Pd/C and a mineral acid were jointly used as catalysts for catechol hydrodeoxygenation, it was rapidly hydrogenated at the aromatic ring leading to 2-hydroxycyclohexanone ($t = 0$, selectivity = 80%) (Fig. 3b). The TOF for catechol hydrogenation on Pd/C at 423 K exceeded 3500 $mol_{catechol}$ $mol^{-1}_{surf.Pd}$ h^{-1}. Subsequently, 2-hydroxycyclohexanone was rapidly converted to cyclohexanone ($\tau = 0$, selectivity = 20%) via two parallel routes of sequential alcohol dehydration/alkene hydrogenation (minor pathway) and ketone hydrogenation/alcohol dehydration (major pathway) (Fig. 4b). It was shown in a separate experiment that 1,2-cyclohexanediol was dehydrated to cyclohexanone at 92% yield at 523 K with Pd/C and H_3PO_4 in 10 min (Table S3). Note that the dehydration rate of 1,2-cyclohexanediol was significantly lower at 423 K. It was shown from Fig. 3b that cyclohexanone was then slowly hydrogenated to cyclohexanol, eventually reaching nearly 30% selectivity. Thus, the catechol conversion proceeds in the first step via hydrogenation, as initial metal-catalyzed partial aromatic hydrogenation to form 2-hydroxycyclohexanone, and then, it was subsequently converted to cyclohexanone via two parallel pathways: one via dehydration followed by hydrogenation and the other via hydrogenation followed by dehydration. This dual pathway may explain why cyclohexanone behaves as a primary product. Cyclohexanone is in turn hydrogenated to cyclohexanol (Fig. 4b). Note that we cannot rule out, however, that in a first step, only one double bond of catechol is hydrogenated and that this diol undergoes acid-catalyzed elimination of water to phenol, which subsequently is then partially hydrogenated to cyclohexanone [38].

Hydrogenation of the most representative phenolic monomer, guaiacol, with adjacent methoxy and hydroxy functional groups at the aromatic ring led to a variety of products including cycloalkanone, cycloalkanol, aromatics, and methanol at 423 K (Fig. S2). The primary product was the intermediately hydrogenated 2-methoxycyclohexanone ($t = 0$, selectivity = 100%) (Fig. 3c). Also, in this case, the fastest step is the metal-catalyzed hydrogenation of the aromatic ring and not the acid-catalyzed hydrolysis of the methoxy group. The initial TOF for guaiacol hydrogenation on Pd/C at 423 K exceeded 1500 $mol_{guaiacol}$ $mol^{-1}_{surf.Pd}$ h^{-1}. In comparison with anisole, which has only a single methoxy group and which is easily hydrolyzed at 423 K in water, the lower rate of the methoxy group hydrolysis of guaiacol may be caused by the stabilization of the carbocation transition state through electron donation by the adjacent hydroxyl groups, preventing its further hydrolysis to methanol. Note that Kanetake et al. reported that under more drastic conditions, i.e., in supercritical water at 653–673 K, guaiacol can be hydrolyzed and pyrolyzed to catechol, methanol, phenol, and char [39].

The hydrogenated intermediate 2-methoxycyclohexanone is converted to cyclohexanone and methanol via two routes (Fig. 4c). One is based on sequential methoxy hydrolysis followed

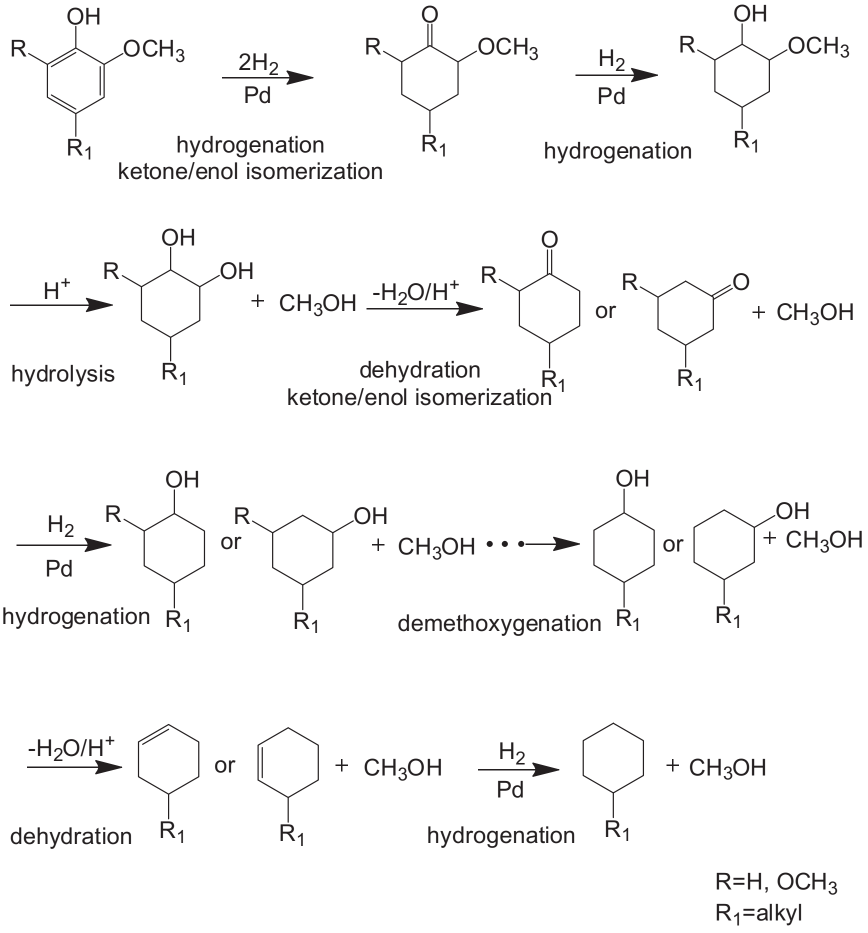


Fig. 5. Proposed overall reaction pathway for hydrodeoxygenation of bio-derived phenolic monomers to cycloalkanes with Pd/C catalyst and H_3PO_4 component [15].

by alcohol dehydration and alkene hydrogenation and the other route is based on sequential ketone hydrogenation followed by hydrolysis, diol dehydration, and ketone/enol isomerization. As shown (Fig. 3c), 2-methoxycyclohexanone was mainly hydrogenated to 2-methoxycyclohexanol, eventually achieving an 80% yield. Note that at 523 K, 2-methoxycyclohexanol was converted to cyclohexanone and methanol with 85% yield on Pd/C and H_3PO_4 catalysts in 10 min (Table S3). The primary reaction pathway for methoxycyclohexanol conversion is speculated to be the acid-catalyzed hydrolysis to methanol and 1,2-cyclohexanediol, followed by the acid-catalyzed dehydration of the latter product and the keto/enol isomerization to cyclohexanone. The pathway to the rapid initial formation of cyclohexanone is unclear to us at present. Independent of the pathway by which it is formed, cyclohexanone is in turn gradually hydrogenated on Pd/C to cyclohexanol at 423 K (Fig. 4c).

4.3. Overall hydrodeoxygenation reaction pathway for conversion of phenolic monomers to cycloalkanes

Combining the results from phenolic molecules to the cycloalkanol (Figs. 1–4) and cycloalkanol to cycloalkane through dehydration (Table 3), the overall reaction pathway for converting phenolic monomers to cycloalkanes is summarized in Fig. 5 [15]. Under appropriate conditions, phenolic monomers such as methoxy-substituted phenols are first hydrogenated on the aromatic ring on the metal site to form 2-methoxycyclohexanone and subsequently hydrogenated at 2-methoxycyclohexanone to 2-methoxycyclohexanol. The reaction sequence continues with the acid-catalyzed hydrolysis of the cyclohexanol methyl ether to form the cyclohexan-1,2-diol, which is in turn dehydrated to cyclohexanone. Subsequent hydrogenation of cyclohexanone leads to cyclohexanol. Acid-catalyzed cyclohexanol dehydration and metal-catalyzed cyclohexene hydrogenation finally lead to the targeted cyclohexane. This highly integrated stepwise aqueous-phase hydrodeoxygenation pathway of phenolic monomers is based on dual-functional catalysis, i.e., coupling metal-catalyzed hydrogenation and acid-catalyzed hydrolysis and dehydration. It differs drastically from the C–O bond hydrogenolysis pathway proposed for sulfided catalysts [25].

4.4. Acid-catalyzed isomerization of cycloalkanes

Catalyzed by acids, cycloalkanes undergo carbon skeletal isomerization to the extent of 6–10%. For example, *n*-propylcyclohexane was isomerized to *n*-butylcyclopentane via ring contraction and proton transfer and to 2-methylpropylcyclopentane via 1,3-carbon backbone transformation.

5. Conclusions

The reaction pathways of (substituted) phenols such as phenol, anisole, catechol, and guaiacol are described together with the principal kinetic pathways to outline the elementary catalytic steps in dual-functional hydrodeoxygenation. Phenol is concluded to be converted to cyclohexane by sequential phenol hydrogenation, cyclohexenol transformation, cyclohexanone hydrogenation, cyclohexanol dehydration, and cyclohexene hydrogenation. The more complex guaiacol is first hydrogenated to 2-methoxycyclohexanol, followed by the hydrolysis of the methoxy group to cyclohexane-1,2-diol, and then dehydration to cyclohexenol/cyclohexanone. The subsequent series of steps transform cyclohexanone via hydrodeoxygenation to cyclohexane as discussed above.

The dual-functional catalysis for hydrodeoxygenation requires a metal function for hydrogenation and an acid function for hydrolysis, dehydration, and isomerization. The balance between these functions determines the observed catalytic chemistry. The turnover frequencies of the acid-catalyzed dehydration reactions are at least two orders of magnitude lower than the rates of metal-catalyzed hydrogenation. This causes the acid-catalyzed steps to determine the overall hydrodeoxygenation reaction, and high concentrations of hydronium ions are required to efficiently catalyze it. A balanced dual-functional catalyst allows to convert phenol-based bio-oils to the mixture of cyclic alcohols or alkanes depending on the chosen reaction conditions.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.02.001.

References

[1] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411.
[2] S. Czernik, A.V. Bridgwater, Energy Fuels 18 (2004) 590.
[3] D. Mohan, C.U. Pittman, P.H. Steele, Energy Fuels 20 (2006) 848.
[4] K. Sipilä, E. Kuoppala, L. Fagernäs, A. Oasmaa, Biomass Bioenergy 14 (1998) 103.
[5] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Biomass Bioenergy 31 (2007) 222.
[6] T.-R. Viljava, R.S. Komulainen, A.O.I. Krause, Catal. Today 60 (2001) 83.
[7] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.
[8] R.D. Cortright, R.R. Davda, J.A. Dumesic, Nature 418 (2002) 964.
[9] G.W. Huber, J.W. Shabaker, J.A. Dumesic, Science 300 (2003) 2075.
[10] N. Yan, C. Zhao, C. Luo, P.J. Dyson, H. Liu, Y. Kou, J. Am. Chem. Soc. 128 (2006) 8714.
[11] C. Zhao, W.J. Gan, X.B. Fan, Z.P. Cai, P.J. Dyson, Y. Kou, J. Catal. 254 (2008) 244.
[12] T. Wang, C.X. Xiao, L. Yan, L. Xu, J. Luo, H. Shou, Y. Kou, H. Liu, Chem. Commun. (2007) 4375.
[13] N. Yan, C. Zhao, P.J. Dyson, C. Wang, L. Liu, Y. Kou, ChemSusChem 1 (2008) 626.
[14] C.X. Xiao, Z.P. Cai, T. Wang, Y. Kou, N. Yan, Angew. Chem. Int. Ed. 47 (2008) 746.
[15] C. Zhao, Y. Kou, A.A. Lemonidou, X.B. Li, J.A. Lercher, Angew. Chem. Int. Ed. 48 (2009) 3987.
[16] C. Zhao, Y. Kou, A.A. Lemonidou, X.B. Li, J.A. Lercher, Chem. Commun. 46 (2010) 412.
[17] M.F. Williams, B. Fonfé, C. Sievers, A. Abraham, J.A. van Bokhoven, A. Jentys, J.A.R. van Veen, J.A. Lercher, J. Catal. 251 (2007) 485.
[18] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[19] Y.Z. Chen, C.W. Liaw, L.I. Lee, Appl. Catal. A 177 (1999) 1.
[20] N. Mahata, V. Vishwanathan, J. Catal. 196 (2000) 262.
[21] S. Scire, S. Minico, C. Crisafulli, Appl. Catal. A 235 (2002) 21.
[22] E. Díaz, A.F. Mohedano, L. Calvo, M.A. Gilarranz, J.A. Casas, J.J. Rodríguez, Chem. Eng. J. 131 (2007) 65.
[23] G. Yuan, M.A. Keane, Ind. Eng. Chem. Res. 46 (2007) 705.
[24] S. Velu, M.P. Kapoor, S. Inagaki, S. Suzuki, Appl. Catal. A 245 (2003) 317.
[25] G. Neri, A.M. Visco, A. Donato, C. Milone, M. Malentacchi, G. Gubitosa, Appl. Catal. A 110 (1994) 49.
[26] H. Liu, T. Jiang, B. Han, S. Liang, Y. Zhou, Science 326 (2009) 1250.
[27] K. Takanabe, K. Aika, K. Seshan, L. Lefferts, J. Catal. 227 (2004) 101.
[28] D.C. Elliott, Energy Fuels 21 (2007) 792.
[29] E. Furimsky, Appl. Catal. A 199 (2000) 147.
[30] R.A. Correa, P.E. Lindner, D.M. Lemal, J. Am. Chem. Soc. 116 (1994) 10795.
[31] P.E. Lindner, R.A. Correa, J. Gino, D.M. Lemal, J. Am. Chem. Soc. 118 (1996) 2556.
[32] C.E. Parish, US Patent 3 275 698, 1966, to Signal Oil and Gas Company.
[33] F. Eschard, US Patent 2 957 034, 1960, to Institut Francais du Petrole.
[34] H. Aizawa, A, Kuroda, M. Minaga, K. Ohnishi, S. Matsuhisa, US Patent 3 974 232, 1976, to Toray Industries, Inc.
[35] S. Ratton, US 4 473 713, 1984, to Rhone-Poulenc Specialites Chimiques.
[36] V.M. Roberts, S. Fendt, A.A. Lemonidou, X. Li, J.A. Lercher, Appl. Catal. B 95 (2010) 71.
[37] V.M. Roberts, R.T. Knapp, X. Li, J.A. Lercher, ChemCatChem 2 (2010) 1407.
[38] J.S. Kudavalli, D.R. Boyd, D. Coyne, J.R. Keeffe, D.A. Lawlor, A.C. MacCormac, R.A.M. O'Ferrall, S.N. Rao, N.D. Sharma, Org. Lett. 12 (2010) 5550.
[39] W.T. Kanetake, M. Sasaki, M. Goto, Chem. Eng. Technol. 30 (2007) 1113.