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Hydrodeoxygenation of mono- and dimeric lignin model compounds on noble metal catalysts

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ABSTRACT

The influence of reaction conditions (temperature, acidity) on the catalytic performance of supported Pt, Pd and Ru catalysts for the aqueous phase hydrodeoxygenation (HDO) of lignin model compounds was systematically investigated. Phenol conversion proceeds via hydrogenation of the aromatic ring resulting in cyclohexanone, which is subsequently converted to cyclohexanol and cyclohexane. Although aromatic ring hydrogenation has a higher rate for Pt and Pd-based catalysts, the rate of hydrogenation of the polar C=O moiety in cyclohexanone is faster for Ru/C. The complete HDO of phenol to cyclohexane on noble-metal catalysts can only be achieved in the presence of a Brønsted acid co-catalyst. In guaiacol conversion, efficient demethoxylation and ring hydrogenation can be achieved within 0.5 h on Pt/C. Under acidic conditions, selectivity of nearly 90% to cyclohexane at a conversion of 75% was achieved in 4 h. To get an insight into the possibility to cleave covalent linkages between aromatic units in lignin under HDO conditions, the reactivity of dimeric model substances such as diphenyl ether, benzyl phenyl ether, diphenyl methane and biphenyl was investigated. Although dimeric oxygen-bridged model compounds such as benzylphenyl ether and diphenyl ether can be readily converted to monomeric species in the presence of noble metal catalysts, cleavage of C–C bonds in diphenyl methane and biphenyl was not observed. Plausible reaction mechanisms are proposed.

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1. Introduction

The efficient utilization of renewable biomass feedstock for fuel production is amongst others hampered by its composition and physico-chemical properties. Besides high water content, biomass usually contains significant amounts (15–40 wt% of its dry mass) oxygenated moieties [1–5]. Efficient deoxygenation of biomass represents one of the key challenges for the development of technologies to produce bio-liquids, whose components show sufficient thermal and chemical stability as well as high heating value and volatility necessary for utilization as liquid fuels in combustion engines [6].

A substantial fraction of lignocellulosic biomass (typically 15-30 wt%) is lignin, which is a poorly defined biopolymer composed of substituted oxygenated aromatic moieties, such as *p*-coumaryl, coniferyl and sinapyl alcohols [2,7]. An attractive route for removal of excessive oxygen from biomass derives from the established hydroprocessing of crude oil derived product streams

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to remove sulfur and nitrogen bound to organics using hydrogen [8]. The hydrodeoxygenation (HDO) of lignin has recently received widespread attention [1-3]. For example, HDO-type processes have been explored for upgrading of pyrolysis-oils by use of CoMo-based catalysts, which are traditionally employed in the petrochemical industry for hydrodesulfurization [9]. The principle possibility of upgrading bio-oils in the presence of such catalysts has been demonstrated using guaiacol as a model compound [4–6,10–12]. Nevertheless, the utilization of different molybdenum sulfide-containing catalysts (CoMoS, NiMoS or Mo₂N) for HDO of biomass-derived compounds requires high pressure and temperature [4–6,10–12]. In general, the activity of these catalysts is too low for efficient transformation of lignin and related compounds to gasoline-type fuels. In addition, the utilization of sulfide-based hydrotreating catalysts bring some important drawbacks such as enhanced coke formation, contamination of the upgraded bio-oil with sulfur and rapid catalyst deactivation [13].

The development of alternative more efficient catalytic systems for lignin HDO is an active area of research. The utilization of noblemetal containing heterogeneous catalysts offers an opportunity to strongly decrease the energy intensity of HDO by using relatively mild conditions. So far, a wide range of supported noble metal

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Fig. 1. Monomeric and dimeric lignin model compounds.

catalysts including Pd, Pt, Ru or Rh on SiO₂, amorphous silicaalumina, zeolites, ZrO₂, CeO₂, and activated carbons were investigated as potential HDO catalysts [14-19]. It is well established that hydrogenation of lignin model compounds over noble metal catalysts leads to complete hydrogenation of the aromatic rings, resulting in cyclic alcohols and cycloalkanes. However, complete removal of the oxygenated moieties is challenging. Zhao and co-workers [15] showed that deoxygenation of phenol can be achieved at moderate reaction temperature (423 K), when additional Brønsted acidity was added to the reaction mixture. Several authors concluded that the efficient deoxygenation of lignin model compounds can be achieved only when the transition metal hydrogenation functionality is combined with a mineral acid or acidic support to activate hydroxyl groups [7,15,16,20]. Fukuoka et al. [13] demonstrated that complete HDO of phenolic compounds over carbon-supported Pt catalysts under acid-free conditions is possible at substantially higher reaction temperature (553 K).

Alternative non-noble transition metal catalysts based on Fe and Ni have also been explored for the HDO of lignin and lignin model compounds [21–23]. These catalysts are generally much less active than noble metal-based ones and require much higher reaction temperature (>623 K), which usually results in a wide range of undesired by-products.

The present work focuses on exploring the reactivity of different noble metal catalysts for aqueous phase HDO of lignin model compounds using hydrogen. Water is the solvent of choice in our HDO studies given the high water content of various types of bio-oils [8]. Aqueous-phase HDO has previously been advocated as an attractive route for lignin valorization [7,16]. Besides low cost and its abundance, water as a solvent offers the additional advantage of facile separation of the hydrocarbon products from the reaction medium [15]. The aim is to investigate the HDO reaction mechanism for various model compounds including phenol (PhOH), benzylphenyl ether (BPE), diphenylether (DPE), diphenylmethane (DPM), biphenyl (BPh) and guaiacol (GUA), which contain phenoxy, β -O-4, 4-O-5, β -1(methylene bridges), 5-5'-type and methoxy phenol linkages as also found in lignin (Fig. 1). The catalytic performance of Pt, Pd and Ru catalysts for the model compound HDO in water was investigated as a function of temperature, acidity and the type of support.

2. Experimental

2.1. Chemicals

Chemicals were purchased from Sigma-Aldrich, Merck and VWR. Noble metal-containing 5 wt% Pt/C (activated carbon), 5 wt% Pd/C (activated charcoal), 5 wt% Ru/C (activated charcoal), and 5 wt% Ru/Al₂O₃ catalysts were purchased from Sigma-Aldrich. Lignin model compounds, namely phenol (Merck, \geq 99%), guaiacol (Sigma-Aldrich, \geq 98%), benzylphenyl ether (Sigma-Aldrich, 98%), diphenyl ether (Sigma-Aldrich, 99%), diphenyl ether (Sigma-Aldrich, 99%), and biphenyl (Sigma-Aldrich, \geq 99%) were used as received. To acidify reaction mixtures, 85 wt% phosphoric acid in water (Sigma-Aldrich, \geq 99.999%) was used. To extract the organics from the water solvent, ethyl acetate (VWR, 99.5%) was used. *n*-Decane (Merck, \geq 99%) was employed as an internal standard for GC analysis.

2.2. Experimental setup and procedure

Stainless-steel autoclaves with an internal volume of 12 mL were used for all reactions. In a typical run, the amount of reactant was 1.6 and 0.8 mmol for monomeric and dimeric compounds, respectively. In each run, 5 mg of catalyst was used. The volume of solvent (water) was 6 mL. After the reactor was loaded with catalyst, reactant and solvent, it was flushed with H₂ for 3 times. Then, it was pressurized by H₂ to a total pressure 20 bar at room temperature. The autoclave was rapidly heated to 473 K (5 min) under stirring at 1000 rpm with a magnetic stirrer bar. After the reaction, the reactor was quenched in an ice bath. Acidified reaction mixtures were obtained by adding phosphoric acid such that the final concentration was 0.5 wt% (pH = 2.1).

2.3. Analysis

The reactor mixture was extracted by addition of an equivalent amount of ethyl acetate. The organic phase was analyzed by GC–MS and GC–FID. *n*-Decane was used as an internal standard and calibration solutions of reactants and products were used for quantification. GC–MS and GC–FID analysis were carried out with GC-17-A Shimadzu and Interscience Focus, respectively. In both cases, a Restek Rxi-5ms capillary column was used ($30 \text{ m} \times 0.25 \text{ mm}$ i.d and $0.25 \mu \text{m}$ film). The injector temperature was set at 523 K. The initial oven temperature was 313 K. The column was heated to 393 K at a rate of 10 K/min and held at this temperature for 5 min. Then, it was further heated to 553 K and held there for 10 min.

The conversion and selectivity were determined for each batch experiment. The conversions and the selectivities were calculated from the analyzed organic phase. The conversion of reactant ($X_{reactant}(\%)$) was calculated from the initial and final amounts (mol) of reactant (Eq. (1)). The unreacted part was not included in the calculation of the product selectivities (S_i (mol%)) (Eq. (2)). In Eqs. (1) and (2), n represents the moles of the reactant or product.

$$X_{\text{reactant}}(\%) = \frac{n(\text{reactant})_{\text{in}} - n(\text{reactant})_{\text{out}}}{n(\text{reactant})_{\text{in}}} \times 100$$
(1)

$$S_i(\%) = \frac{n(\text{product})_i}{\sum_{i=1}^m n(\text{product})_i} \times 100$$
(2)

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3. Results and discussion

3.1. HDO of phenol

Fig. 2 shows the conversion and selectivity for PhOH hydrogenation over Pt/C as a function of reaction time. Under acid-free conditions (Fig. 2a and b), PhOH is converted to cyclohexanol (CyOH) via intermediate formation of cyclohexanone (CyO=). The conversion rates of PhOH and CyO= strongly increase when increasing the temperature from 423 K (Fig. 2a) to 473 K (Fig. 2b). In line with previous studies [7], the combination of acidic conditions and elevated reaction temperature resulted in almost complete deoxygenation of PhOH to CyH (cyclohexane) with 90% selectivity (Fig. 2d). Comparison of results presented in Fig. 2c and d suggests that hydrogenation of the CyO= intermediate is inhibited at 423 K and low pH. Deoxygenation of CyOH is not catalyzed at this low temperature resulting in accumulation of CyO= at intermediate reaction times (see Fig. 2c). In line with previous findings [15], our results demonstrate the necessity of Brønsted acidity for phenol HDO and that high selectivity can be achieved at the elevated temperature (473 K).

Zhao et al. [7] reported that Pd/C, Pt/C, Ru/C and Rh/C show similar activity and selectivity in PhOH conversion at 473 K and a H₂ pressure of 50 bar. However, the present results obtained at lower H₂ pressure (20 bar) point to pronounced differences in the catalytic behavior of noble metal catalysts (Table 1, Figs. S1-S3). While the reaction over Ru/C proceeds via CyOH formation (Fig. S2) similar to Pt/C, for Pd/C CyO= is identified as a major reaction intermediate under acid-free as well as acidic conditions (Fig. S1). The high intermediate yield of CyO= observed in the course of the reaction under acid-free conditions points to low activity of Pd/C toward hydrogenation of the polar carbonyl group in CyO=. This conclusion also follows from the observation that when the reaction is carried out under acidic conditions the hydrogenation of CyO= over Pd/C is much slower than dehydroxylation of CyOH (Fig. S1). For Ru/C, on the other hand, the dehydroxylation of the CyOH is slow, even at elevated temperature and under acidic conditions. After 2 h of reaction, a lower PhOH conversion to CyOH is achieved for Ru/C (Table 1, entry 10) as compared to Pt/C (Table 1, entry 5). It is important to note that in the former case the selectivity to the CyO= intermediate is much lower, suggesting faster hydrogenation of the polar C=O moiety by Ru/C than by Pt/C and Pd/C (see supporting information). Wildschut et al. [24] also showed that Ru/C promotes fast hydrogenation of CyO=, which was not observed as an intermediate component in the conversion of PhOH to CyH at relatively high temperature and pressure (523 K, 200 bar).

Ru/C is the only catalyst for which the product of direct deoxygenation of PhOH was observed under acidic conditions. Nearly 7% selectivity to benzene was obtained after 4 h reaction at 473 K (Fig. S2(b)). The results are however different when Ru is supported on γ -alumina (Ru/Al₂O₃). The conversion of PhOH was very low for this catalyst and did not depend on the pH. This may be due to structural transformation of the support under hydrothermal reaction conditions [25]. A substantial amount (~20%) of 1-methyl cyclopentane was produced (Table 1, entry 12). 1-Methylcyclopentane formation under acidic condition on Ru/Al₂O₃ can be explained via ring–contraction and proton transfer isomerization of CyH. Such a reaction sequence requires metallic and acidic sites [7,26]. Its reversibility [26] explains the decrease in selectivity of 1-methylcylopentane and increase of CyH for prolonged reaction times (Fig. S3b).

A mechanism of PhOH hydrodeoxygenation is proposed in Fig. 3. The first reaction step is rapid hydrogenation of the aromatic ring over the noble metal resulting in the CyO= intermediate. In fact, CyO= can be formed via fast isomerization of the cyclic keto/enol transformations pathway between cyclohexenol and CyO= [7]. It may be that cyclohexenol is converted directly to CyO=. This intermediate has not been observed in our experiments. The subsequent hydrogenation of the keto-group to the main reaction product, CyOH, is slow, especially over Pd/C. This step is inhibited at low temperature, even in the presence of an acid and might be the rate-determining step for HDO of PhOH. The acid promoter, however, is required to deoxygenate the alcohol product toward CyH. Only under acidic conditions, complete HDO of PhOH to CyH was achieved. CyH= (cyclohexene) is typically considered as an intermediate product in CyOH conversion to CyH under acidic conditions [4,5,7,25]. Our study further supports this proposition. Small amounts of CyH= were observed during PhOH (Fig. 2c and d) as well as CyOH conversion on Pt/C under acidic conditions at 473 K (see supporting information, Table S1). For most of the other catalysts, the hydrogenation of CyH= was so fast that it was not possible to detect this intermediate compound.

3.2. HDO of guaiacol

We further considered HDO of guaiacol, which is a more realistic model compound for lignin, over the carbon-supported Pt, Pd and Ru catalysts. The main results of the catalytic tests are summarized in Fig. 4. Similar to PhOH conversion, the main reaction products are due to fast hydrogenation of the aromatic ring. The highest hydrogenation activity under acid-free conditions was observed for Pt/C resulting in a conversion of 75% after 2 h. For Ru/C a reaction time of 4 h was needed to reach this conversion level (Fig. 4c). Pd/C was the least active catalyst. Only 50% guaiacol conversion was reached after 4 h reaction time with Pd/C (Fig. 4b). Guaiacol HDO over Pt/C is strongly enhanced in the presence of H_3PO_4 (Fig. 4d). In this case, the maximum 75% conversion of guaiacol was reached already within 0.5 h reaction time. In all cases, the conversion of guaiacol was lower than for HDO of phenol. The lower reactivity of guaiacol has previously been attributed to the electron-donating hydroxyl group that stabilizes the transition state carbocation decreasing the hydrolysis rate of the methoxy group [7].

The main reaction products include products from aromatic ring hydrogenation, demethylation, demethoxylation and dehydroxylation of guaiacol. The reaction selectivity strongly depends on the nature of transition metal catalyst and the presence of the Brønsted acid promoter (Fig. 4). Under acid-free reaction conditions, substantial selectivity toward the ring hydrogenationproduct, methyl-1,2-cylohexanediol, is observed for all catalysts. This product is formed by ring hydrogenation and methyl group transfer reactions of guaiacol [27]. When the reaction is performed under acid-free conditions over Pt/C catalyst, the main product is CyOH formed with a selectivity of around 70%. The selectivity to the second most abundant product, methyl-1,2-cylohexanediol, is ca. 25%. In addition, minor amounts of PhOH, CyO= and cyclohexylmethyl ether were observed as intermediates (see supporting information, Fig. S4). It is important to note that although guaiacol conversion over Pt/C steadily increased from nearly 40% to 80% from the beginning of the reaction (0.5 h) till the end (4 h), the product distribution remained largely unchanged. This suggests that the main reaction products, methyl-1,2-cyclohexanediol and CyOH, are formed over Pt/C via different reaction routes.

With Pd/C, the predominant reaction product formed with selectivity of ca. 60% is methyl-1,2-cyclohexanediol (Fig. 4b). Although the selectivity toward CyOH increases in the course of the reaction, it reached only 25% after 4 h. The saturated ketone product of guaiacol hydrogenation (2-methoxycyclohexanone) appears to be an important reaction intermediate. Whereas a selectivity of 45% to 2-methoxycyclohexanone is observed after 0.5 h of reaction, this intermediate is completely converted, most likely to CyOH, via demethoxylation and hydrogenation during the reaction. CyO=, PhOH and methylcyclohexyl ether (Fig. 5) were also observed in



Fig. 2. Evolution of phenol conversion (*X* (%), **——**) and selectivities (1) to CyOH (cyclohexanol); (2) to CyO= (cyclohexanone); (3) to CyH (cyclohexane); (4) to CyH= (cyclohexene) in the presence of Pt/C catalyst under acid-free conditions ((a) 423 K, (b) 473 K) and acidic conditions ((c) 423 K, (d) 473 K).

small amounts as intermediate products during guaiacol conversion over Pd/C. These findings are in line with previous reports on the activity of Pd/C in the conversion of biomass-derived aromatics [15]. It has been demonstrated that the demethoxylation reaction over Pd/C requires much higher reaction temperature and pressure (523 K, 50 bar H₂) than those employed in this study. Among the catalysts considered, Pd/C showed unique reactivity toward methyl-1,2-cylohexanediol that was formed with a substantially higher selectivity than CyOH, which in turn is the predominant product over Pt/C and Ru/C. The low activity of Pd/C catalyst in HDO of guaiacol is in line with the results by Ohta et al. [13] on the conversion of 4-propylphenol over different noble metal-containing different carbon supports at 553 K and 40 bar H₂. On the other hand, the results reported by Gutierrez et al. [18] evidenced a substantially higher deoxygenation activity of zirconia-supported Pd compared to Pt in guaiacol conversion at 573 K and 80 bar H₂. This apparent disagreement is due to the use of different support material. As shown by Lee et al. [19] metal catalysts supported on acidic oxides (like Ru/ZrO₂) show enhanced activity in hydrodeoxygenation of guaiacol.

Guaiacol HDO over Ru/C (Fig. 4c) resulted in predominant formation of CyOH. The reaction proceeds via PhOH and CyO= intermediates (Fig. S4c). This suggests that the reaction is initiated by demethoxylation of guaiacol, followed by ring hydrogenation,

Table 1

Overview of results for the HDO of phenol after 2 h reaction at 473 K using carbon-supported Pt, Pd and Ru ca	italysts.
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Number	Catalyst	Solvent	X (%)	S (%)					
				\bigcirc	OH		\bigcirc		\triangleleft
1	Pt/C ^a	H ₂ O	100	_	100	-	_	_	_
2	Pt/C ^a	H ₂ O-H ₃ PO ₄	99	11	89	-	-	-	-
3	Pt/C ^b	H ₂ O	82	1	61	35	5	-	-
4	Pt/C	H ₂ O	99	1	98	-	1	-	-
5	Pt/C	$H_2O-H_3PO_4$	100	94	4	2	-	-	-
6	Pd/C	H ₂ O	100	-	98	2	-	-	-
7	Pd/C	H ₂ O-H ₃ PO ₄	100	62	3	35	-	-	-
8	Ru/C ^b	H ₂ O	44	-	84	16	-	-	-
9	Ru/C	H ₂ O	100	-	100	-	-	-	-
10	Ru/C	$H_2O-H_3PO_4$	91	72	21	-	-	7	-
11	Ru/Al_2O_3	H ₂ O	25	-	65	28	7	-	-
12	Ru/Al_2O_3	$H_2O-H_3PO_4$	24	24	14	36	-	-	11

^a temperature is 423 K

^b reaction time was 0.5 h.

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Fig. 3. Reaction network for phenol conversion on Pt, Pd and Ru on carbon.

in a similar fashion as the reaction sequence for PhOH. The selectivity toward methyl-1,2-cyclohexanediol was about 20% in the course of the reaction. The results presented in Fig. 4c further confirm our proposition that the formation of CyOH and methyl-1,2-cyclohexanediol proceed via different reaction channels. The latter path involves the intermediate formation of 2-methoxycyclohexanone, which was observed in low concentrations during the reaction. Selectivity to other products such as benzene and CyH did not exceed 2%.

The present findings show that Pt/C is the most active and selective catalyst for guaiacol conversion to CyOH. Therefore, this catalyst was further considered in the investigation of the effect of Brønsted acidity on the HDO of guaiacol. The catalytic results are summarized in Fig. 4d. Addition of phosphoric acid substantially enhances the catalytic performance of Pt/C. The conversion was ca. 70% within 0.5 h of reaction. The predominant product is CyH via CyO= and CyOH intermediates. At the end of the reaction, the main

products are CyH and PhOH formed with selectivities of 85% and 8%, respectively. Previously, the possibility of the direct dehydroxylation of guaiacol has been demonstrated by Bykova et al. [22]. Our catalytic experiments with Pt/C catalyst evidence the formation of anisole (methoxybenzene) and benzene (<3%), which do not form under acid-free conditions (see supporting information, Fig. S4).

The results presented so far allow us to propose a plausible mechanism of guaiacol HDO (Fig. 5) for different noble metals. Pt/C and Ru/C were found to predominantly promote demethoxylation of guaiacol to phenol, which opens a path toward selective formation of CyOH (Fig. 5/Route 1). In the presence of mineral acid, the latter is readily converted to cyclohexane. Demethoxylation and ring hydrogenation steps are much faster over Pt/C than over Ru/C. Methanol produced by demethoxylation of guaiacol is detected in the liquid phase by GC analysis. An alternative route involves the direct hydrogenation of the aromatic ring prior to deoxygenation, resulting in an intermediate product, 2-methoxycyclohexanone,



Fig. 4. Evolution of guaiacol conversion (*X* (%), —) and selectivities to major products at 473 K under acid-free conditions on ((a) Pt/C, (b) Pd/C, (c) Ru/C) and under acidic condition ((d) Pt/C). (Selectivities to minor products (<10%) are shown in Fig. S4 in supporting information).

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Fig. 5. Reaction network for guaiacol conversion on noble metal catalysts at 473 K.

which is further isomerized and hydrogenated to methyl-1,2cyclohexanodiol (Fig. 5/Route 2). The contribution of this path for Pt/C and Ru/C does not exceed 20%. However, it is dominant for Pd/C, whose selectivity to methyl-1,2-cyclohexanediol reaches up to 60%. The low demethoxylation activity of Pd/C is further apparent from the observation of a slow decrease of selectivity to methyl-1,2-cyclohexanediol at longer reaction times concomitant with increasing CyOH yield (Fig. 4 (b)). Interestingly, this was not observed for Pt/C and Ru/C. In both cases the selectivity to methyl-1,2-cyclohexanodiol remained constant (ca. 25–30%) during the reaction, independently of changes in selectivity to the main product CyOH. This implies that transformation of methyl-1,2-cyclohexanediol to CyOH under acid-free conditions (cyclohexanol in Fig. 5) is a unique feature of the Pd/C system. Thus, an almost complete HDO of guaiacol to CyH can be achieved by Pt/C in the presence of an acid at 473 K. The reaction proceeds through initial demethoxylation and dehydroxylation of the substrate to phenol. Our findings are quite different from those recently reported by Lee et al. on guaiacol conversion over different supported noble-metal catalysts in *n*-decane [19]. It was proposed that the HDO reaction is initiated by ring hydrogenation to 2-methoxycyclohexanol. No phenol was observed in the reaction mixture. This points to a strong solvent effect on the reaction mechanism of guaiacol HDO. In studies using metal sulfide catalysts, guaiacol is typically converted to catechols by direct demethylation [4–6,12,25]. In our studies, guaiacol conversion via HDO route on noble metal catalysts leads to PhOH and CyOH via combined ring hydrogenation and demethoxylation. Under acidic conditions, CyH is formed via dehydroxylation of CyOH.

Table 2

Evolution of BPE conversion (X, %) and selectivities (S, %) on Pt/C catalyst in time under acid-free condition 473 K.

Time (h)	X(%)	S (%)								
		OH	OH		\bigcup	OH	OH	Dimerics	Trimers	
0.5	81	10	21	30	10	2	0	27	10	
1	95	12	18	29	11	0	0	24	6	
2	100	20	16	25	14	2	3	13	7	
4	100	29	0	20	25	0	5	11	10	

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Fig. 6. Reaction network for BPE conversion on Pt/C catalyst under acid free and acidic condition.

3.3. HDO of dimeric model compounds

We further investigated the ability of the most active Pt/C catalyst in the presence and in the absence of mineral acid to catalyze the hydrogen-assisted cleavage of different

representative structural linkages in lignin. Conversion of benzylphenyl ether (BPE), diphenyl ether (DPE), diphenylmethane (DPM) and biphenyl model compounds for, respectively, β -O-4, 4-O-5, β -1(methylene bridges), 5–5'-type lignin linkages was considered.



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Table 3

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Time (h)	X (%)	S (%)									
		\bigcirc	OH	OH		\bigcirc	ОН	ОН	Dimerics	Trimers	
0.5	95	0	13	37	0	34	3	6	3	3	
1	99	0	17	30	4	32	3	7	7	-	
2	99	6	11	27	7	33	4	9	3	-	
4	100	23	3	15	7	42	3	5	1	1	

Tables 2 and 3 report the main results of BPE conversion under acid-free and acidic conditions, respectively. The noble metalcatalyzed hydrogenolysis of BPE is very fast. Conversion of 81% is achieved already after 0.5 h at 473 K and conversion is nearly complete after 1 h of reaction. The main products are CyOH, PhOH, PhCH₃ and CyCH₃. The selectivities to the unsaturated products decrease in the course of the reaction. Taking into account that Pt/C is very active in guaiacol demethoxylation, we propose that the conversion of BPE mainly proceeds via the hydrogenolysis of the sp^3 –C–O ether bond followed by the hydrogenation of the aromatic rings of the resulting monomeric species. It is important to note that, while selectivity to PhOH decreases from 20% after 0.5 h to almost 0% after 4 h reaction, the selectivity to toluene (PhCH₃) changes from 30% to 20%. Substantial amounts of methylenebridged saturated dimeric and trimeric compounds was observed. We attribute their formation to the Pt-catalyzed recombination of (partially) hydrogenated monomeric species. Previously, bicyclic formation during catalytic hydrogenation of PhOH over acidic zeolite was explained via two different pathways, namely via aldol condensation of CyO= and electrophilic aromatic substitution of PhOH to CyOH [28]. In the presence of phosphoric acid, the BPE conversion is 95% conversion after 0.5 h (Table 3). The reaction predominantly yields CyCH₃ (42%), CyH (23%) and PhOH (15%). Selectivities to other products such as PhCH₂OH, CyCH₂OH and PhCH₃ as well as various dimeric and trimeric compounds are low. It appears that the presence of the acid promoter inhibits recombination side-reactions leading to higher molecular-weight products.

Fig. 6 shows a proposed reaction network for BPE hydrogenolysis over Pt/C under acidic and acid-free conditions. Cleavage of the ether linkage can take place either via the acid-catalyzed hydrolysis or Pt-catalyzed hydrogenolysis route. The promotion of the former path in the presence of the mineral acid is evidenced by the increased selectivity to CyCH₃ and CyCH₂OH products. The mechanism of further transformation of the monomeric compounds is similar to that postulated for the respective model compounds. We tentatively attribute the formation of higher molecular-weight compounds to conversion paths involving (partially) hydrogenated alkylated monomers over the Pt/C catalyst. The exact mechanism of these transformations is not clear yet.

Similarly, hydrogenolysis of aryl-O-aryl bond in DPE can be efficiently carried out with Pt/C under acid-free as well as acidic conditions (Fig. 7). In contrast to BPE, the hydrogenation of aromatic moieties in diphenyl ether (DPE) prior to the hydrogenolysis of the ether linkage is evident from the pronounced selectivity to dicyclohexyl ether (Cy_2O) at intermediate reaction times. Under acid-free conditions, subsequent cleavage of the aliphatic ether bond is slow. An alternative path involves hydrogenolysis followed by ring hydrogenation of the resulting monomeric species yielding CyH and CyO=. The latter is then rapidly hydrogenated to CyOH (Fig. 7a). In the presence of acid, CyOH is dehydrated and hydrogenated to CyH, allowing for nearly quantitative conversion to cyclohexane (Fig. 7b). No stable higher molecular weight products were observed in this case supporting our hypothesis that the recombination reactions require the presence of alkylated hydrocarbons in the reaction mixture.

The proposed reaction network for DPE HDO over Pt/C is depicted in Fig. 8. We propose that the direct hydrogenolysis toward CyO= and CyH is in competition with direct hydrogenation of the aromatic moieties toward Cy₂O, which can then undergo either an acid-catalyzed hydrolysis or Pt-catalyzed hydrogenolysis reaction resulting in CyOH and CyH. Complete deoxygenation of the CyOH product requires the acid promoter, which allows for 100% selectivity of hydrodeoxygenation of DPE over Pt/C at 473 K.

For BPE conversion, significant selectivity toward dimeric methylene-bridged higher molecular weight compounds was observed. Similar unsaturated molecular units can also be found in lignins. We therefore investigated the activity of Pt/C toward cleavage of the respective -CH₂- linkage using diphenylmethane (DPM) as a model compound. The reaction in this case led only to complete and rapid hydrogenation of the aromatic rings. Complete DPM conversion to almost exclusively dicyclohexyl methane was achieved within the first 0.5 h (Fig. S5). Biphenyl was also converted to totally saturated dimer, bicyclohexyl, under similar conditions (Fig. S6). Introduction of Brønsted acidity does not affect the reaction selectivity and conversion rate for DPM and biphenyl. Zhao et al. [29] showed this trend in their studies where oxygencontaining groups like hydroxyl, methoxy, ketone, alkyl-O-aryl and aryl-O-aryl were likely to be cleaved in the combined catalytic route over Pd/C and HZSM-5. However, C-C connectivities between aromatic moieties could not be hydrolyzed [29]. Thus, in line with results for BPE conversion, C-C bonds cannot be cleaved by Pt/C. The lower yield of higher molecular weight products observed upon the acid-promoted HDO of BPE is likely due to inhibition of the condensation reactions at low pH. As noted by Gosselink [30], competition between lignin depolymerization and recondensation of formed fragments exists even under acidic conditions.



Fig. 8. Reaction network for DPE conversion on Pt/C catalyst.

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4. Conclusions

Noble metal catalysts promote hydrogenation of aromatic rings in lignin model compounds (phenol, guaiacol, benzylphenyl ether, diphenyl ether, diphenyl methane and biphenyl). The removal of the oxygenated functionalities can be achieved in the presence of a mineral acid. Besides activating C–O bonds, Brønsted acidity also enhances the hydrogenation activity of the noble-metal catalyst. Substantial activity differences of supported Pt, Pd and Ru catalysts were observed for the conversion of monomeric lignin model compounds. Pd/C exhibited the lowest HDO activity for PhOH and guaiacol reactants. This is attributed to low activity for the hydrogenation of polar carbonyl moieties of intermediates resulting in the high selectivity of ketonic products when the reaction is performed over Pd/C catalyst. Similar compounds are also formed over Pt/C and Ru/C. However, in these cases they are rapidly hydrogenated to the respective alcohols and in the presence of a Brønsted acid promoter dehydroxylated and hydrogenated further to the final alkane product. Ru/C is particularly active in the conversion of CyO= to CyOH. Nevertheless, its activity is generally substantially lower than that of Pt/C.

Pt/C catalyst shows optimal reactivity in hydrogenation, dehydroxylation and demethoxylation reactions allowing to efficiently hydrodeoxygenate different aromatic model compounds to the respective saturated hydrocarbons. A complete hydrodeoxygenation of both monomeric and dimeric model compounds was achieved in the presence of Pt/C catalyst at 473 K and low pH. Although such conditions are suitable for the cleavage of the ethertype lignin linkages represented by BPE and DPE models resulting in saturated cycloalkanes, the C–C structure-forming units represented by DPM and biphenyl cannot be activated under the HDO conditions over Pt/C. Thus, implication of noble metal catalysts in lignin conversion processes might be a possibility to produce cyclic products which can be used as an additive in diesel-like fuels to increase the combustion efficiency.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2013. 12.011.

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