University of Groningen

Decomposition of lignin model compounds by Lewis acid catalysts in water and ethanol

Guvenatam, Burcu; Heeres, Erik H. J.; Pidko, Evgeny A.; Hensen, Emiel J. M.

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2015

[Link to publication in University of Groningen/UMCG research database](#)
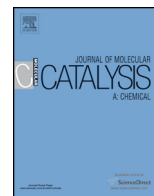
Decomposition of lignin model compounds by Lewis acid catalysts in water and ethanol

Burcu Güvenatam [a], Erik H.J. Heeres [b], Evgeny A. Pidko [a,c], Emiel J.M. Hensen [a,*]

[a] Laboratory of Inorganic Materials Chemistry, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[b] Institute for Technology and Management, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[c] Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ABSTRACT

The conversion of benzyl phenyl ether, diphenyl ether, diphenyl methane and biphenyl as representative model compounds for α–O_4, 5–O_4, α_1 (methylene bridges) and 5–5′ lignin linkages was investigated. We compared the use of metal chlorides and acetates. The reactions were studied in sub- and supercritical water and supercritical ethanol between 300 and 400 °C. At low temperature in water, Lewis acids mainly catalyzed condensation of hydrolysis products of the dimeric model compounds. At higher temperature, mono-aromatic products were formed. The yield of monomeric products was higher in ethanol than in water. The preference for ethanol is due to extensive alkylation of the mono-aromatic products, which inhibits their condensation into larger products. The highest yields of deoxygenated mono-aromatics were obtained using Lewis acid catalysts at 400 °C in supercritical ethanol. The preferred Lewis acid catalysts were Fe, Cu, Ni and Al chlorides.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Lignin is an amorphous three-dimensional biopolymer that makes up about a third of lignocellulosic biomass [1–3]. Its efficient valorization is pivotal in scenarios in which biomass serves as a renewable feedstock to fuels and chemicals. However, the structure of lignin is complex, as it is a polymer of three primary components, namely, *p*-coumaryl, coniferyl, and sinapyl alcohols, connected via different linkages [2]. For instance, the structure of hardwood and softwood lignin is dominated by α– and β–aryl ether bonds [1], among which β–O_4 constitutes nearly half of all linkages in lignin [2]. Due to its structural complexity, the use of model compounds that contain similar linkages as those found in lignin has become a common approach in identifying approaches to upgrade lignin [4–6]. A representative compound that contains the α—O_4 bond is benzyl phenyl ether (BPE) [3,7]. The C—O bond energy in BPE is 234 kJ/mol [3,7]. Diphenyl ether (DPE) bond is used as a model to represent the less common 5–O_4 linkage, in which the C—O bond is much stronger (330 kJ/mol) [3,7]. Experimental studies have confirmed that the cleavage of aryl—*O*—aryl bonds in lignin is much more difficult than the cleavage of alkyl—*O*—aryl bonds [8].

Among the many approaches that have already been explored for lignin depolymerization [2,8], Lewis acid salts have been only scarcely investigated. Hepditch and Thring [9] demonstrated that $NiCl_2$ and $FeCl_3$ facilitated the degradation of Alcell lignin in water at 305 °C into a mixture of low-molecular-weight products such as phenolics (syringols, guaiacols, catechols), aldehydes (syringaldehyde and vanillin) and phenolic ketones (acetoguaiacone and acetosyringone). This reaction in water yielded large amounts of insoluble reactor residue (~70 wt.%) in the presence of Lewis acids. Metal triflate salts such as indium triflate, scandium triflate, ytterbium triflate, and indium chloride have been recently used to catalyze the hydrolytic cleavage of C—O linkages in different lignin model compounds in water [6]. For example, the use of indium triflate as a catalyst allowed reaching a full conversion of benzyl phenyl ether at 225 °C after 3 h reaction. However, it was concluded that further improvement of these systems is needed to increase the yield of mono-aromatic products [6].

Lewis acidic salts have been studied much earlier as catalysts for coal liquefaction [10–12]. They were found to promote cleavage of CC bonds in aliphatic groups linking the aromatic units in coal, but not arylaryl linkages [11]. The activity of $ZnCl_2$ and $AlCl_3$ as representative Lewis acid catalysts in the conversion of such model compounds as biphenyl, diphenyl alkanes containing 1 to 4-carbon aliphatic linkages, as well as hydroxylated biphenyl and diphenyl methane was investigated by the Bell group [10–12]. $AlCl_3$ was

Table 1
Physicochemical properties of water as a function of temperature and pressure.[a]

	Normal water	Subcritical water	Supercritical water		Superheated steam
Temperature ($^{\circ}$C)	25	250	400	400	400
Pressure (MPa)	0.1	5	25	50	0.1
Density (g cm^{-3})	0.997	0.80	0.17	0.58	0.0003
Dielectric constant, ϵ	78.5	27.1	5.9	10.5	1
Ion dissociation constant, pK$_w$	14.0	11.2	19.4	11.9	–

[a] Ref. [13].

found to be more active in hydrogenation and cracking reactions of aryl—alkyl CC bonds than ZnCl$_2$ [11–12]. It has been proposed that the cleavage of CC and C—O—C bonds follows the carbonium ion mechanism, resulting in the formation of condensation products and tar [10]. Addition of molecular hydrogen improved the overall conversion but also led to enhanced tar formation [11]. This was caused by hydride-facilitated condensation of aromatic species via Scholl coupling reactions [11].

In the context of lignin model compounds, the use of metal chlorides has been explored for the conversion of guaiacol. The hydrolysis rate of guaiacol at 380 $^{\circ}$C in supercritical water (sc-water) was accelerated by metal chlorides such as NaCl, CaCl$_2$ and FeCl$_3$. The main products of these reactions were catechol and phenol [13]. However, similar to coal liquefaction studies, extensive tar formation occurred in the presence of Lewis acid catalysts [13].

The choice of solvent and its physical properties under reaction conditions are key factors that determine the efficiency of lignin depolymerization processes [2,8]. In the last decade, the use of water near or above its critical point (T_c = 374 $^{\circ}$C, P_c = 218 atm) has attracted considerable attention as a green and renewable alternative to organic solvents as a medium in synthetic fuel production, biomass processing, waste water treatment and material synthesis [14–16].

Table 1 summarizes the physical properties of water in different states. The ion product or dissociation constant of sc-water at high temperature and pressure is higher than that of water at ambient conditions. Accordingly, sc-water will contain more H$^+$ and OH$^-$ ions than liquid water, making dense high-temperature sc-water an effective medium for acid and base catalyzed organic reactions [15]. Water at pK$_w$ ≤ 14 has been argued to be a suitable medium for heterolytic reactions in which ionic mechanisms involving charged transition states and intermediates occur. On contrary, the use of water with pK$_w$ ≥ 14 is preferred for homolytic reactions, in which free radical mechanisms are usually important [17]. As temperature and pressure increase, the static dielectric constant of water at the critical point drops to a value of about 6 from 78.5 (at 258 $^{\circ}$C) because of the reduced number of hydrogen bonds at relatively low densities. The dielectric constant of a medium determines the solubility of molecules [16]. The advantage of sc-water over normal water under conventional conditions is that it behaves almost like a non-polar solvent allowing to efficiently dissolve various non-polar compounds such as alkanes and aromatics [15–16]. Also, gases are better miscible in sc-water. Thus, the use of sc-water as a solvent offers opportunities to effectively homogenize multiphase reactant systems and, accordingly, improve strongly its mass-transfer characteristics [10–11]. The specific heat capacity increases under supercritical conditions, which can be advantageous to reduce possible hot spot formation [16]. The density of sc-water strongly influenced the hydrolysis mechanism that led to C—O bond dissociation in DPE at high temperatures (415–480 $^{\circ}$C) [14]. At low density water (<0.3 g/cm^3) DPE conversion resulted in formation of various polycondensation products with low yield of mono-aromatics (<0.1%). At higher water densities (>0.4 g/cm^3) the rate of undesired condensation reactions paths was much lower and stoichiometric amounts of phenol were obtained [14].

For the upgrading of lignin, another potential solvent that is green and renewable is ethanol [18]. It is currently already used as a bio-fuel. Ethanol can be produced from biomass via fermentation and, therefore, its production can be readily integrated in biorefinery concepts. The critical point of ethanol (T_c = 241 $^{\circ}$C, P_c = 6.14 MPa, ρ_c = 0.276 g/cm^3) is at lower temperature and pressure than that of water. Supercritical ethanol (sc-ethanol) is also less corrosive than sc-water [15–17]. Previous studies have demonstrated the beneficial effect of ethanol under near- and supercritical conditions as a solvent for separations and chemical reactions. Similar to water, ethanol becomes nearly non-polar under supercritical conditions and its dipolarity/polarizability ranges from gas-like to non-polar liquid with increasing temperature and pressure [19]. The main advantage of using sc-ethanol is that it maintains significant hydrogen-bond donating acidity under supercritical conditions [19]. On the other hand, the hydrogen-bond accepting basicity of ethanol becomes considerably weaker at elevated temperatures [19]. Several reactions of industrial significance such as catalytic etherification from tertiary alcohol, alkylation of toluene to produce *p*-ethyltoluene and non-catalytic hydrogen-transfer reductions of aldehydes and ketones have been successfully carried out in hot ethanol up to its critical temperature [19].

In this work, we investigate a range of inorganic salts as Lewis acid catalysts for the conversion of representative lignin model compounds in sub- and supercritical water and ethanol with the goal to assess their potential for lignin depolymerization. Benzyl phenyl ether, diphenyl ether, diphenyl methane and biphenyl were selected as representative model compounds for the α–O4 (aryl—alkyl bond), 5–O4 (arylaryl bond), α$_1$ (C(aryl)—C(alkyl) bond), 5–5′ (C(aryl)—C(aryl) bond) linkages in lignin. Chloride salts of Fe, Co, Cu, Ni and Al, acetate salts of Fe, Co, Cu, Ni and triflate salts of Sc and Al were evaluated as Lewis acid catalysts for conversion of these model compounds. For reasons of comparison, we employed metal triflates (M(OTf)$_n$, M = metal) as super Lewis acid catalysts. The reaction conditions such as temperature, solvent (water or ethanol) and solvent loading (density) were varied in order to understand their effect on the conversion and selectivity. On the basis of reactivity data, we discuss possible reaction mechanisms for the Lewis acid catalyzed conversion of the model compounds.

2. Experimental methods

2.1. Materials

Benzyl phenyl ether (Aldrich, 98%), diphenyl ether (ReagentPlus®, ≥99 %), diphenyl methane (Aldrich, 99%) and biphenyl (ReagentPlus®, 99.5%) were used as received. Deionized water and absolute ethanol (Sigma–Aldrich, ≥99.8%) were used as solvent. Iron(II) acetate (Aldrich, 95%), copper(II) acetate (Aldrich, powder, 98%), cobalt(II) acetate tetrahydrate (Merck, ≥98.0%), nickel(II) acetate tetrahydrate (Aldrich, 98%), iron(II) chloride tetrahydrate (Aldrich, ≥99.0%), copper(II) chloride dihydrate (Aldrich, ≥99.0%), cobalt(II) chloride (Aldrich, anhydrous, ≥98.0%), nickel(II) chloride (Aldrich, anhydrous, 98%), aluminum(III) chloride hexahydrate (Fluka, ≥99.0%), aluminum(III) triflate (Aldrich, 99.9%), scandium(III) triflate (Aldrich, 99%), copper(I) oxide

Table 2
Results of BPE hydrolysis in water at 300 °C (reaction time: 3 h).[a]

Catalyst	Selectivity of products, %						
	Aromatic monomers				Condensation products		
	Oxygenates						
	Benzyl alcohol	Phenol	Benzaldehyde	SUM	Di-aromatics	HMW[b]	SUM
Blank[1]	37	17	5	59	38	3	41
FeCl$_2$	–	32	–	32	62	6	68
CuCl$_2$	–	29	–	29	66	5	71
CoCl$_2$	–	24	–	24	71	5	76
NiCl$_2$	–	25	–	25	69	6	75
AlCl$_3$	–	31	–	31	62	7	69
Fe(OAc)$_2$	30	5	2	37	59	4	63
Cu(OAc)$_2$	32	11	8	51	45	4	49
Co(OAc)$_2$	34	14	9	57	41	2	43
Ni(OAc)$_2$	37	18	8	63	31	6	37
Al(OTf)$_3$	–	26	2	28	67	5	72
Sc(OTf)$_3$	–	27	–	27	67	6	73
Al$_2$O$_3$	47	15	2	64	32	4	36
CuO	34	14	5	53	43	4	47

[a] Complete BPE conversion in all cases except for the blank experiment (X = 98%).
[b] Higher molecular-weight products.

(Aldrich, ≥99.99% trace metals basis, anhydrous), alumina (Ketjen, *CK-300* high purity) were used without further purification. Ethyl acetate (VWR, 99.5%) was used as an extraction solvent. *N*-decane (Aldrich, anhydrous, ≥99%) and di-*n*-butyl ether (Aldrich, anhydrous, 99.3%) were used as external standards, respectively. Tetrahydrofuran (Aldrich, anhydrous, ≥99.9%) was used to dilute the samples prior to analysis.

2.2. Catalytic activity measurements

All the experiments were performed in stainless-steel batch reactors with an internal volume of 13 mL. Reactions were carried out in the temperature range of 300–400 °C with a reaction time of 3 h. The reactors were filled with either 8 mL of water or 6.5 mL of anhydrous ethanol. The reactant and catalyst concentrations were 0.1 mol/L and 0.025 mol/L, respectively. Reactions at 300 °C and 350 °C were carried out by placing the autoclaves in the oven of a gas chromatograph. Reactions at 400 °C were done in a pre-heated fluidized sand bath. After reaction, the reactors were quenched in an ice bath. The organic compounds were extracted from the water solvent by ethyl acetate in 1:1 volume ratio with water. In case of ethanol as solvent, this extraction step was not needed.

2.3. Product analysis

For the identification and quantification of the products, GC/MS-FID analyses were performed on a Shimadzu GC/MS-QP2010 SE series. The GC was equipped with a Restek Rtx-1701 capillary column (60 × 0.25 mm i.d. and 0.25 μm film thickness). The column flow was split in a 1:10 volume ratio to the MS and FID. The injector temperature was set at 250 °C. The oven temperature was kept at 45 °C for 4 min, followed by heating to 280 °C at a rate of 4 °C/min and then held at 280 °C for 5 min. Identification of products was done using the NIST11 and NIST11s libraries.

For product quantification in ethanol-mediated reactions, GC × GC analysis was performed on a Interscience Trace GC × GC equipped with a cryogenic trap system and two columns: 30 m × 0.25 mm i.d. and 0.25 μm film of Sol–gel (SGE-1MS) capillary column connected by a meltfit to a 150 cm × 0.1 mm i.d. and 0.1 μm film Restek Rtx-1701 column. An FID detector was used. A dual jet modulator was applied using carbon dioxide to trap the samples. Helium was used as the carrier gas (continuous flow 0.6 mL/min). The injector temperature and FID temperature were set at 250 °C. The oven temperature was kept at 40 °C for 5 min then heated to 250 °C at a rate of 3 °C/min. The pressure was set at 0.7 bar at 40 °C. The modulation time was 6 s.

Table 3
Results of BPE hydrolysis in water at 350 °C (reaction time: 3 h).[a]

Catalyst	Selectivity of products (%)									
	Aromatic monomers							Condensation products		
	Non-oxygenated			Aromatic oxygenates						
	Benzene	Toluene	SUM	Phenol	Benzaldehyde	Benzyl alcohol	SUM	Di-aromatics	HMW[b]	SUM
Blank	–	3	3	19	4	33	56	39	2	41
FeCl$_2$	2	3	5	52	2	–	54	28	13	41
CuCl$_2$	4	4	8	54	2	–	56	26	10	36
CoCl$_2$	3	2	5	54	2	–	56	29	10	39
NiCl$_2$	4	3	7	52	5	–	57	26	10	36
AlCl$_3$	3	4	7	54	3	–	57	27	9	36
Fe(OAc)$_2$	1	3	4	56	3	–	59	27	10	37
Cu(OAc)$_2$	2	3	5	52	19	1	72	20	3	23
Co(OAc)$_2$	1	4	5	52	8	4	64	24	7	31
Ni(OAc)$_2$	1	3	4	54	4	–	58	27	11	38
Al$_2$O$_3$	1	5	6	54	6	–	60	26	8	34

[a] Complete BPE conversion in all cases.
[b] Higher molecular-weight products.

The GC/FID analysis used to quantify mono- and di-aromatic products had error margins of 0.1% and 5%. The error margin in the quantification of higher-molecular weight (HMW) compounds was estimated at 10%.

The conversion of reactant ($X(\%)$) was calculated from the initial and final amounts (mol) of the substrate (Eq. (1)). The selectivities (S_i (mol%)) of each product was calculated according to Eq. (2).

$$X(\%) = \frac{\text{initial mol of reactant} - \text{final mol of reactant}}{\text{initial mol of reactant}} \times 100 \tag{1}$$

$$S_i(\%) = \frac{\text{mol of product } i \text{ formed (calc. from GC} - \text{FID)} \times \text{number of C atoms}}{\text{total mol of products (calc. from GC} - \text{FID)} \times \text{number of C atoms}} \times 100 \tag{2}$$

For the reactions in water, the response factors were obtained via calibration using commercially available mono- and di-aromatic compounds. When specific di-aromatic or HMW components were not available, a representative response factor (RF) was calculated as an average of the response factors of BPE, DPE, DPM and biphenyl. For the reactions in ethanol, alkylated products were summed and the corresponding response factors of the parent product were used.

3. Results and discussion

3.1. Benzyl phenyl ether conversion in water

We first carried out BPE conversion reactions in water at different temperatures in the presence of Fe, Cu, Co, Ni or Al chloride or acetate salts. A blank experiment was also performed. The results of the catalytic reactions at 300, 350 and 400 °C are summarized in Tables 2–4.

Already at 300 °C, BPE is almost completely converted within 3 h in all cases (Table 2). In the blank reaction, the conversion was 98%, and benzyl alcohol, phenol and benzaldehyde were formed in addition to di-aromatics and some higher molecular-weight (HMW) products. For metal chlorides (MCl_n), the main monomer product was phenol (Fig. S1). For metal acetates ($M(OAc)_n$), phenol, benzylic alcohol and benzaldehyde were the monomeric products. In all catalytic experiments, di-aromatics, mainly isomers of hydroxy-DPM (2-benzyl phenol and 4-benzylphenol), and HMW products were formed similar with blank reaction. The use of MCl_n decreased the monomer yield compared to the blank. This is mainly due to the formation of more substantial amounts of di-aromatic products. The anionic part of the metal salt affected the product distribution more than the cationic part. Co- and Ni-acetates produced nearly similar yields of monomers as in the blank experiment.

The low monomer yield in water at 300 °C is due to the high rate of condensation of reactive intermediates formed during BPE hydrolysis. There are pronounced selectivity differences in the catalytic effect of chloride and acetate salts. We hypothesize that the nature of the anion determines the stability of the metal site against hydrolysis and, therefore, the effective Lewis acidity of the catalyst [20–22]. To verify this hypothesis, additional measurements were carried out using water-tolerant $Sc(OTf)_3$ and $Al(OTf)_3$ super Lewis acids [23].

We also used bulk Al_2O_3 and CuO oxides as models to mimick the possible products of hydrolysis of the metal salts that can produce oxides. The results of these catalytic tests are also given in Table 2. BPE was fully converted with all of these catalysts. With $M(OTf)_n$, phenol and hydroxy-DPM were the main products formed, and roughly speaking, the yields correspond to those seen for the MCl_n catalysts. It supports the conclusion that high Lewis acidity promotes condensation of reactive intermediates, leading to CC linked products such as substituted DPM. When Al_2O_3 and

CuO were used, the product distributions were similar to those for the blank and $M(OAc)_n$ catalyzed experiments. Note, however, that in the presence of Al_2O_3 the highest yield of monomer products was obtained (64%) with benzyl alcohol as the dominant product formed at a selectivity of 47%. The yield of di-aromatics was the lowest (~30%) for Al_2O_3. The reaction selectivities with CuO were identical to those obtained with the $Cu(OAc)_2$ catalyst, suggesting that Cu–acetate decomposed during reaction. High-temperature hydrolysis has been earlier reported for $Pd(OAc)_2$–catalyzed Heck coupling reactions in sc-water at 400 °C [24]. Therefore, we propose that the higher Lewis acidity of MCl_n catalysts compared with that of $M(OAc)_n$ is most likely due to the decomposition of the latter into less reactive oxides/hydroxide compounds under the conditions of the catalytic reaction. At low temperature and in the presence of the strong Lewis acidity of MCl_n and $M(OTf)_n$, condensation products of BPE hydrolysis are strongly favored and only very low monomer yields can be obtained.

As condensation reactions may be suppressed at higher temperature, we evaluated BPE conversion at 350 °C and 400 °C (Table 3 and 4). Expectedly, BPE conversion was complete in all cases. In addition to oxygen-containing aromatic monomers (mono-aromatic oxygenates) and oligomeric products, non-oxygenated aromatic monomers (mono-aromatics) were observed in the product mixture. In the blank reaction, toluene was the only mono-aromatic product. In the presence of MCl_n, $M(OAc)_n$ and Al_2O_3, small amounts of benzene was also formed. The highest selectivity to mono-aromatics was obtained with Cu, Ni and Al chlorides.

Except for the formation of toluene, the product compositions of the blank experiments were similar at 300 and 350 °C. The main monomer products were benzyl alcohol (33%), phenol (19%) and benzaldehyde (4%). For all catalysts, the main product at 350 °C was phenol (selectivity 54 ± 2%). Only small amounts of benzyl alcohol were observed for $Cu(OAc)_2$ and $Co(OAc)_2$, very different from the results obtained at 300 °C, where benzyl alcohol was the main monomer for Al_2O_3 and $M(OAc)_n$. In most catalytic experiments, small amounts of benzaldehyde were observed. Especially, $Cu(OAc)_2$ promoted benzaldehyde formation. Previously, the aqueous-phase benzyl alcohol oxidation to benzaldehyde has been shown to occur via hydride abstraction from benzyl alcohol [25–27].

The selectivity patterns for MCl_n, $M(OAc)_n$ and bulk Al_2O_3 were similar. This means that the hydrolyzed metal species either did not form or that they were dissociated again. As expected, less condensation products formed at higher temperature. The most pronounced decrease was seen for the MCl_n catalysts, where the condensates yield decreased by almost 50%. $Cu(OAc)_2$ produced the least condensation products among the catalysts evaluated at 350 °C.

At 400 °C, phenol is the main reaction product in all of the cases (Table 4). Note that the yield of non-oxygenated mono-aromatics formed at 400 °C with MCl_n is higher than that obtained at a lower temperature of 350 °C. The highest non-oxygenated mono-aromatic yield was reached by using $AlCl_3$. The phenol selectivity ranged between 40 and 53% in the presence of Lewis acidic catalysts. For Al_2O_3, the phenol selectivity dropped to 17%. Benzyl alcohol is totally degraded at 400 °C, which resulted in high yields of condensation (di-aromatics and HMW) products. Especially, Al_2O_3 promoted this condensation path. At 400 °C and high water loading (8 mL), the carbon balance was between 70 and 80% depending on the catalyst type. When the solvent loading was 4 mL, only 40–60% of the carbon was found back in the products. At low density water,

Table 4
Results of BPE hydrolysis in water at 400 °C at high density or low density water (reaction time: 3 h).[a]

Catalyst	$T = 400\,°C$, $V_{solvent}$: 8 mL:			Selectivity of products, %		$T = 400\,°C$, $V_{solvent}$: 4 mL:			Selectivity of products, %	
	Monomers			Condensation Products		Monomers			Condensation products	
	Benzene	Toluene	Phenol	Di-aromatics	HMW[b]	Benzene	Toluene	Phenol	Di-aromatics	HMW[b]
Blank	2	13	46	35	4	12	5	74	2	7
FeCl$_2$	7	11	45	33	4	2	22	60	5	11
CuCl$_2$	7	11	52	25	5	6	30	59	2	3
CoCl$_2$	4	8	42	40	6	3	21	66	2	8
NiCl$_2$	9	10	48	29	4	11	21	62	4	2
AlCl$_3$	8	17	48	24	3	10	23	55	5	7
Fe(OAc)$_2$	2	12	40	39	7	3	10	76	1	10
Cu(OAc)$_2$	5	16	53	19	7	3	6	79	3	9
Co(OAc)$_2$	2	15	48	31	4	5	18	69	3	5
Ni(OAc)$_2$	3	18	53	23	3	1	7	81	1	10
Al$_2$O$_3$	4	14	17	56	9	n/d	n/d	n/d	n/d	n/d

[a] Complete BPE conversion in all cases.
[b] Higher molecular-weight products.

the selectivity of di-aromatics was below 5% while the selectivity to HMW products was below 10% during the blank reaction and below 20% when catalysts were used. This may suggest that unidentified products with much higher molecular weights were formed. The same trend was previously observed in base-catalyzed conversion of BPE when the water density decreased [26]. Thus, phenol was the main product with high selectivity for the blank reaction (74%) and also for the M(OAc)$_n$ catalysts. In this case, the highest degree of deoxygenation was obtained with the MCl$_n$ catalysts with combined benzene and toluene selectivities as high as 36% for CuCl$_2$. In brief, when the temperature is increased above 300 °C, mono-aromatics can be obtained by BPE hydrolysis. Both MCl$_n$ and M(OAc)$_n$ catalysts are active in the deoxygenation at 400 °C. However, even at these elevated temperatures, condensation reactions cannot be fully prevented in water.

We propose that BPE is converted according to the mechanism shown in Fig. 1. The acidity of water itself strongly increases with temperature [27], explaining the high BPE conversion in sc-water. Reactions between Lewis acidic metal ions with water result in the generation of acidic protons. BPE will undergo the acid-catalyzed hydrolysis of the ether bond to form phenol and benzyl alcohol, which are the main monomer products at 300 °C These reactive products can further undergo various transformations including self- and cross-condensation [5]. Benzyl alcohol can undergo dehydrogenation at elevated temperatures in sc-water, resulting in the formation of benzaldehyde and molecular H$_2$ [28]. All these mono-aromatic oxygenated products are prone to condensation reactions and form di-aromatic and HMW components. Benzyl

alcohol readily reacts with phenol to form di-aromatic components such as 2-benzylphenol and 4-benzylphenol (hydroxy-DPM) [26]. The reaction of these di-aromatic species with the mono-aromatic oxygenates may proceed towards tri-nuclear aromatics and further HMW products. The small amount of toluene detected at 350 °C can be formed via slow hydride abstraction from the media by the benzyl cation [11], while benzene is likely the product of the hydrodeoxygenation of phenol or decarbonylation of the benzaldehyde intermediate [28]. We speculate that cleavage of ether cross-links was favored above 350 °C via radical pathways. It was previously shown that there is always competition between radical and ionic reaction pathways during thermal hydrolysis of ethers in water [25]. The ionic mechanism is the more relevant one at lower temperatures [8].

To summarize, full conversion of BPE in water can be achieved at temperatures in the range of 300–400 °C. Both the catalytic and non-catalytic reactions were always accompanied by the formation of dimeric and higher molecular weight products. It was observed that higher reaction temperatures promoted deoxygenation resulting in an increase of the yields of benzene and toluene. At the highest temperature of 400 °C and high water density, the use of AlCl$_3$ afforded more non-oxygenated mono-aromatics than the blank reaction.

3.2. Conversion of benzyl phenyl ether in ethanol

We investigated in a similar manner BPE conversion in ethanol. The results for sc-ethanol reactions at 300, 350 and 400 °C are summarized in Tables 5 and 6. Unlike for the sc-water-mediated reaction, the conversion of BPE in ethanol at 300 °C is not complete after 3 h. Without catalyst, the conversion was 72%. The product composition was also very different from the experiments done in sc-water. Without catalyst, the monomer products were toluene and phenol with selectivities of 27 and 53%, respectively. In the presence of Lewis acids, the product distribution depended more on the anionic than on the cationic part. It was found that ethanol was reactive under the chosen reaction conditions. In addition to phenol and toluene, substantial amounts of alkylated benzyl alcohol (alkyl-BzOHs) and alkylated phenols (alkyl-PhOHs) were observed (Fig. S2). The products of ethanol conversion include 1,1-diethoxyethane and diethyl ether as major products as well as acetaldehyde and butenes (Fig. S2).

The use of M(OAc)$_n$ led to much lower BPE conversion compared with the blank reaction. The selectivities to phenol, toluene and alkyl-PhOHs were in the range of 42–52%, 20–27%, and 3–9%, respectively, for M(OAc)$_n$. In addition, alkyl-BzOHs were only formed in trace amounts for Fe(OAc)$_2$ and Cu(OAc)$_2$. The

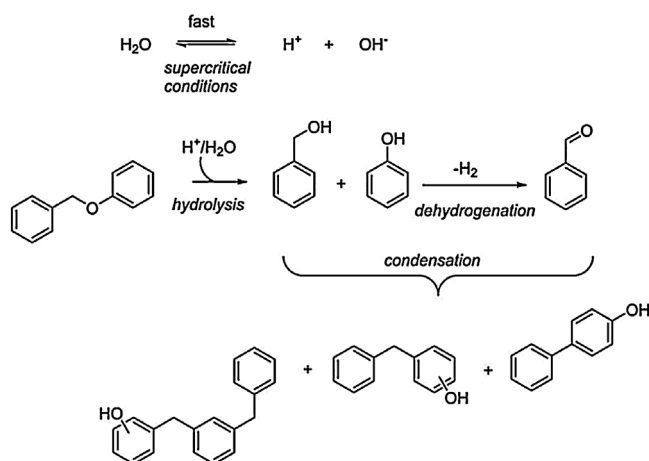**Fig. 1.** Proposed reaction mechanism for BPE conversion in water.

Table 5
Results of BPE alcoholysis in ethanol at 300 °C (reaction time: 3 h).

| Catalyst | X, % | Selectivity of products, % | | | | | | | |
| | | Monomers | | | | | Condensation products | | |
		Toluene	Phenol	Alkyl-BzOHs	Alkyl-PhOHs	SUM	Di-aromatics	HMW[a]	SUM
Blank	72	27	53	–	–	53	11	9	20
FeCl$_2$	94	21	55	11	6	72	5	2	7
CuCl$_2$	90	23	51	15	4	70	6	1	7
CoCl$_2$	80	19	50	17	4	71	9	1	10
NiCl$_2$	83	22	55	10	4	69	8	1	9
AlCl$_3$	90	24	46	20	3	69	5	2	7
Fe(OAc)$_2$	50	21	50	1	5	56	22	1	23
Cu(OAc)$_2$	46	27	49	1	3	53	18	2	20
Co(OAc)$_2$	50	24	42	–	9	51	23	2	25
Ni(OAc)$_2$	52	20	52	–	7	59	19	2	21
Al$_2$O$_3$	74	17	36	25	1	62	20	1	21
CuO	84	37	45	–	1	46	16	1	17

[a] Higher molecular weight products.

mono-aromatic oxygenates selectivity and the ratio of phenol and alkyl-PhOHs were only slightly influenced by the nature of the cation. The reaction with Co(OAc)$_2$ resulted in the highest selectivity to alkyl-PhOHs (9%) and, accordingly, the lowest phenol selectivity (42%). This indicates that Co(OAc)$_2$ is a good alkylation catalyst at 300 °C. Fe and Ni acetates showed slightly lower alkylation activity, resulting in very similar selectivities to phenol (50 and 52%, respectively) and alkyl-PhOHs (5 and 7%, respectively). In the presence of Cu(OAc)$_2$ catalyst, the selectivity towards alkylated products was the lowest (~3%).

MCl$_n$ catalysts strongly promoted BPE conversion in sc-ethanol. FeCl$_2$ was able to nearly fully convert BPE within 3 h at 300 °C. CuCl$_2$ and AlCl$_3$ gave slightly lower BPE conversions (90%), while CoCl$_2$ and NiCl$_2$ converted, respectively, 80 and 83% of BPE. All MCl$_n$ catalysts gave very similar monomer selectivities. The combined selectivities to mono-aromatic oxygenate compounds was around 70%. The stronger Lewis acid MCl$_n$ led to higher yields of the alkylation products (14–23%) compared to use of M(OAc)$_2$. Interestingly, almost all Lewis acid catalysts considered here decreased the toluene selectivity compared to the blank experiment.

The condensation products were mainly di-aromatics such as diphenyl methane (DPM), hydroxy-DPM, 1,2-diphenylethane, and ethyl-hydroxy-DPM as well as HMW products, mainly tri-nuclear aromatics with molecular weights higher than 258 g/mol. The formation of DPM and 1,2-diphenylethane might suggest radical-type condensation reactions of toluene. M(OAc)$_2$ produced more condensed products than MCl$_n$.

For Al$_2$O$_3$, the conversion of BPE was 74%, similar to the value for the blank reaction. However, the product composition was very different. The mono-aromatic oxygenates selectivity of 62% was higher than for M(OAc)$_2$ and lower than for MCl$_n$. Alkylation of mono-aromatic oxygenates was strongly promoted in the presence of Al$_2$O$_3$, resulting in the highest selectivity towards alkyl-BzOHs (25%). The toluene selectivity was only 17% which may relate to the promotion of radical condensation paths leading to di-aromatic and HMW products. CuO gave a BPE conversion of 84% with substantial amounts (37%) of toluene and less mono-aromatic oxygenates (46%). With CuO alkylation of mono-aromatic oxygenates was not possible (<1%). In addition, condensation reactions led to the formation of mainly hydroxy-DPM and DPM type of di-aromatic components (~16%). Thus, the catalytic results of Al$_2$O$_3$ and CuO did not correspond to the behaviour of the corresponding Lewis acidic salts in sc-ethanol at 300 °C as they did in sc-water.

BPE conversion was complete at a reaction temperature of 350 °C and 400 °C (Table 6). The mono-aromatics selectivity, mainly toluene, increased substantially at the expense of mono-aromatic oxygenates. In the non-catalytic alcoholysis of BPE, toluene (39%) and phenols (42%) were almost obtained in equimolar ratio at 350 °C. Alkylation of phenol led to the formation of small amounts of alkyl-PhOHs (3%). In addition, ethanol products such as acetaldehyde, diethyl ether, 2-butanol and 1,1-diethoxyethane were observed. In the presence of catalyst, more alkylated mono-aromatic oxygenates were found. Alkylation of mono-aromatics was much slower than alkylation of mono-aromatic oxygenates. The mono-aromatics yield was the highest (45%) with Cu(OAc)$_2$.
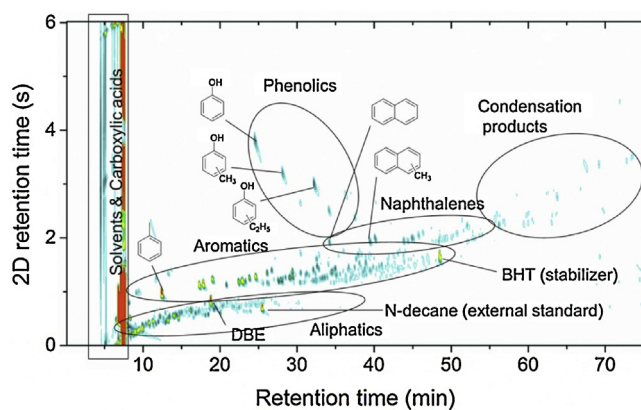
Table 6
Results of BPE alcoholysis in ethanol at 350 °C and 400 °C (reaction time: 3 h).[a]

| Catalyst | T = 350 °C: Selectivity of products, % | | | | | | | T = 400 °C: Selectivities, % | | | |
| | Monomers | | | | | Condens. products | | Monomers | | Condens. products | |
	Toluene	Alkyl-aromatics	Phenol	Alkyl BzOHs	Alkyl–PhOHs	Di-aromatics	HMW[b]	Non-oxygenated	Oxygenates	Naphthalenes	Di-aromatics
Blank	39	–	39	–	3	18	1	40	52	5	3
FeCl$_2$	34	1	41	10	6	7	1	58	13	21	8
CuCl$_2$	38	2	35	5	10	9	1	60	13	22	5
CoCl$_2$	34	2	32	8	13	9	2	59	20	15	6
NiCl$_2$	40	2	33	4	9	9	3	58	18	18	6
AlCl$_3$	34	2	34	8	7	14	1	58	19	17	6
Fe(OAc)$_2$	35	1	45	–	2	15	2	43	18	25	14
Cu(OAc)$_2$	43	2	33	–	6	14	2	38	28	21	13
Co(OAc)$_2$	40	3	32	–	10	13	2	26	44	12	18
Ni(OAc)$_2$	41	1	37	–	7	13	1	43	29	21	7
Al$_2$O$_3$	29	2	33	11	4	18	3	n/d	n/d	n/d	n/d
CuO	40	–	34	–	8	15	3	n/d	n/d	n/d	n/d

[a] Complete BPE conversion in all cases.
[b] Higher molecular weight products.

Fig. 2. GC × GC chromatogram of the products of BPE alcoholysis in sc-ethanol in the presence of CuCl$_2$ at 400 °C after a reaction time of 3 h.

Fig. 3. Proposed reaction mechanism for BPE alcoholysis in ethanol.

Similar with the results at 300 °C, the mono-aromatic oxygenates fraction consisted of phenol, alkyl-BzOHs and alkyl-PhOHs for MCl$_n$.

At 350 °C, the use of bulk catalysts had a significant influence on the selectivity towards alkylated products compared to the blank reaction. Catalytic activity of Al$_2$O$_3$ was comparable with the corresponding chloride salts AlCl$_3$, while CuO exhibited similar behaviour with the corresponding acetate salt Cu(OAc)$_2$. Al$_2$O$_3$ catalyzed the formation of alkyl-BzOHs. These products did not form with CuO. In ethanol, a better mass balance closure was observed than in water, for most experiments above 85%.

At 400 °C, ethanol conversion was strongly increased. As a result, the composition of the product mixture was very different from that obtained at lower temperatures. As the product mixtures were complex, we combined results of GC/MS-FID and GC × GC. Fig. 2 shows a representative GC × GC chromatogram for the reaction of BPE with CuCl$_2$ in ethanol at 400 °C. Ethanol products such as butenes, acetaldehyde, ethyl ethers and carboxylic acids (acetic, propanoic and butanoic acid) were observed. A wide range of aliphatic products (mainly alkanes and some alkenes) were formed as well as alkylated mono-aromatics bearing alkyl side chains. Alkylation of aromatics was possible at the meta-, para- and ortho-positions. Mono-aromatic oxygenates were mainly present as alkylated-PhOHs (Fig. 2). Naphthalenes might be formed via oligomerization reactions of monomeric products. They can be also likely formed via cyclization of hexyl-alkylated aromatics. Condensation further results in formation of di-aromatic components.

The reaction data obtained at 400 °C are also collected in Table 6. At elevated temperature, deoxygenation became more prominent, as follows from the much higher yield of mono-aromatics, when MCl$_n$ was the catalyst. Comparatively, the blank reaction and the use of M(OAc)$_n$ produced less mono-aromatics and more mono-aromatic oxygenates. The product distribution did not vary much for the MCl$_n$ catalysts. As an example, the main products with CuCl$_2$ were alkylated mono-aromatic, di-aromatic, mono-aromatic oxygenate, naphthalene and di-aromatic products formed with selectivities of 60%, 13%, 22% and 5%, respectively. With M(OAc)$_n$, selectivities for mono-aromatics and naphthalenes amounted to ~41% and ~22%, respectively. Co(OAc)$_2$ displayed the lowest deoxygenation activity and the highest di-aromatics selectivity. MCl$_n$ produced less undesired condensation products than M(OAc)$_n$ at 400 °C. This is in line with the results for the reactions at lower temperatures (300 °C and 350 °C). Interestingly, in the absence of catalysts, the selectivity to di-aromatics and naphthalenes was very low, suggesting a crucial role of Lewis acid catalysts for the condensation reactions. Furthermore, the conver-
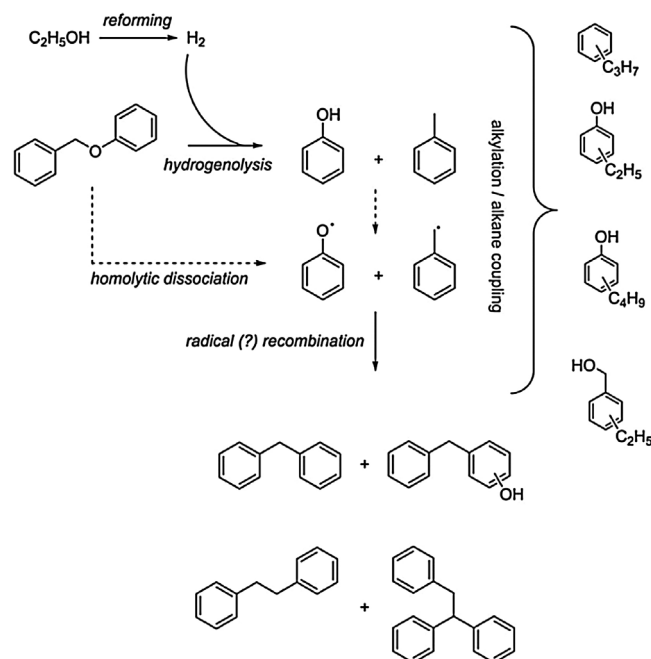
sion of ethanol was much less pronounced in the blank reaction compared to catalytic experiments.

Summarizing, at 300 °C condensation reactions in sc-ethanol are slower than in sc-water. MCl$_n$ catalysts gave the lowest yield of condensation products. However, the condensation reactions towards stable C–C linked di- and tri- aromatic compounds could not be completely suppressed by the higher reaction temperature. At 350 °C, in addition to complete conversion of BPE, the increased yields of mono-aromatics (up to 45 mol%) showed that the deoxygenation paths became strongly favored. Results indicated that BPE was converted via different reaction mechanisms in sc-ethanol and sc-water. In ethanol, the formation of phenol and toluene at 300 and 350 °C points to alcoholysis of BPE involving molecular hydrogen formed via ethanol dehydrogenation (Fig. 3). The formation of hydrogen is consistent with the observation of acetaldehyde in the product mixture. An alternative explanation is homolytic cleavage of the ether bond, resulting in phenoxy and benzyl radicals that lead to phenol and toluene upon recombination with ethanol solvent. Phenol is more susceptible to alkylation than benzene, which explains the predominant formation of alkylated mono-aromatic oxygenates at low temperature. At temperatures below 400 °C, the transformation of ethanol was limited to dehydrogenation and alkylation of mono-oxygenate species. However, at 400 °C ethanol conversion became more extensive and resulted in a wide range of aliphatic hydrocarbons (alkanes and alkenes). In fact, in the presence of Lewis acid catalysts, ethanol was involved in alkane coupling reactions to form aliphatic products and to alkylate all types of alcoholysis products. Furthermore, the radical nature of the reaction resulted in increased selectivity to condensation products at the higher temperature. Condensation products were mainly produced by combination of phenol, benzyl alcohol and toluene. The isomers of hydroxy-DPM were the principle di-aromatic products. Other abundant types of condensation products obtained at 400 °C were DPM, 1,2-diphenylethane, ethyl-hydroxy-DPM. Formation of HMW components was limited at 400 °C in ethanol. Only trace amount of tri-nuclear aromatics with molecular weights higher than 258 were detected. Naphthalenes were the main condensation products at 400 °C.
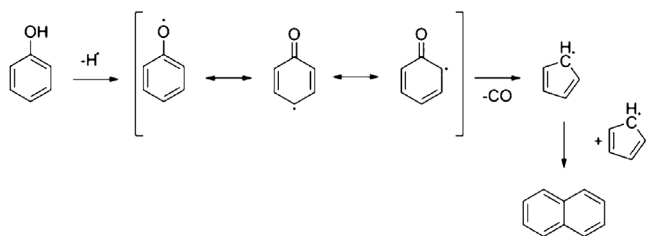
Fig. 4. Proposed reaction mechanism of naphthalene formation from phenol in sc-ethanol (adopted from Ref. [25]).

The proposed reaction mechanism for naphthalene formation is shown in Fig. 4 where phenol, as a monomer product of alcoholysis of BPE, is converted to naphthalene. Previously, naphthalene formation was reported in pyrolysis studies of anisole [29]. It was proposed that the reaction is initiated by the formation of phenoxy radicals that undergo decarbonylation reaction to yield cyclopentadienyl (C_5H_5) radicals [29]. Being the main precursor of naphthalene and polycyclic aromatic hydrocarbons, C_5H_5 radicals undergo self-recombination towards naphthalene [29]. Consistent with this, the catalyst that showed the highest yield of mono-aromatic oxygenates (mainly phenols), i.e. Co(OAc)$_2$ showed the lowest naphthalene selectivity.

3.3. Conversion of diphenyl ether

We also examined the effect of Lewis acid salts on the decomposition of DPE, the model compound for the 5–O$_4$ ether aryl—O—aryl lignin linkage. Previously, it was reported that cleavage of aryl—O—aryl ether bond in sc-water is much more difficult than that of alkyl—aryl ether bond [8]. As we hypothesized that relatively high reaction temperatures and strong Lewis acid catalysts are necessary to cleave the 5–O$_4$ ether bond, reactions were only carried out at 350 and 400 °C in sc-water and sc-ethanol.

Without catalyst, DPE was not converted at 350 °C in sc-water and only trace amounts of phenol were observed (Table S1). DPE conversion was also very low for all Lewis acids considered here. The highest conversion (8%) was for Co(OAc)$_2$ with 4-hydroxy biphenyl as the main reaction product. In all other cases, phenol was the dominant product. At 400 °C, DPE conversion was higher (Table S1). In the blank reaction, the phenol selectivity was 54 %, and various condensation products including 4-hydroxy biphenyl were also formed. For MCl$_n$, no condensation products were observed. The main products were phenol (87% ± 3%) and benzene (13% ± 3%). NiCl$_2$, however, gave more benzene, showing its high deoxygenation activity. For M(OAc)$_n$, the DPE conversion was higher than for MCl$_n$, but it led to a higher yield of condensed products at the expensive of the phenol selectivity. Again, Co(OAc)$_2$ gave almost exclusive formation of 4-hydroxy biphenyl (95%) with phenol as the only other product.

Previously, it has been shown that DPE hydrolysis can be catalyzed by the strong BF$_3$ Lewis acid at 380 °C. Four equivalents of BF$_3$ hydrolyzed 58% DPE to phenol in water (at 380 °C, 30 min) [30]. When the BF$_3$ concentration was lowered four times, the phenol yields decreased to 12%. Varga et al. [30] compared the catalytic activities of BF$_3$ (strong Lewis acid) with HBF$_4$ (Brønsted acid) on DPE hydrolysis and illustrated that BF$_3$ is nearly twice as effective as HBF$_4$. Accordingly, we surmise that the relatively low DPE conversion in the present study is due to the low Lewis acid loading.

We propose the following reaction mechanism for the hydrolysis of DPE in water (Fig. 5). Acid-catalyzed hydrolysis of DPE leads to the formation of two phenol molecules. The reaction proceeds via highly unstable phenyl-cation species. The recombination of these species with water is the predominant path at 350 °C, resulting in the exclusive formation of phenol [14]. At elevated tempera-
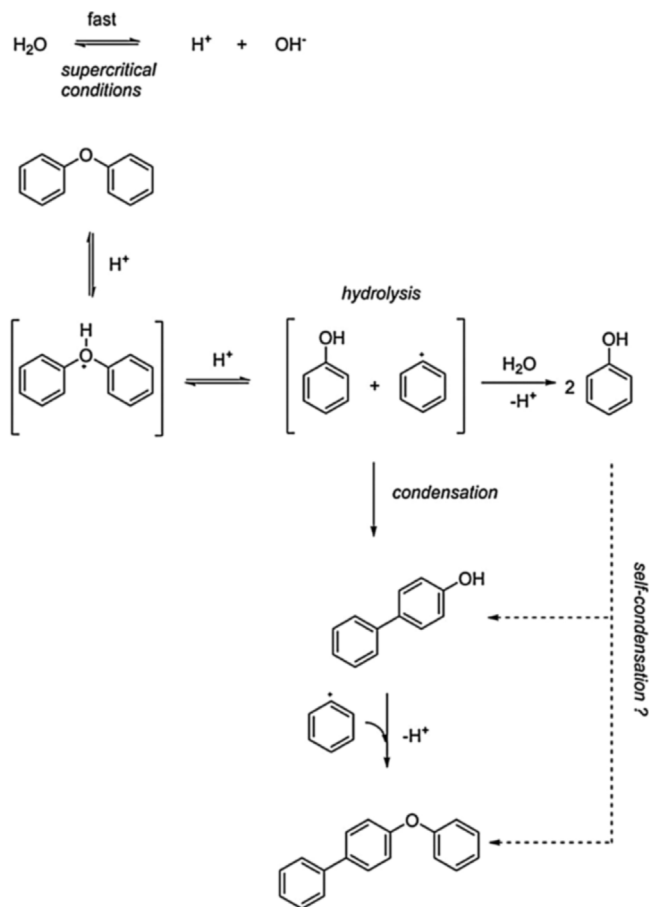

Fig. 5. Proposed reaction mechanism for DPE hydrolysis in water.

tures or in the presence of specific catalysts such as Co(OAc)$_2$, the recombination of these activated monomer species towards 4-hydroxy biphenyl becomes preferred. Interestingly, no oligoaromatics formed for MCl$_n$ at 400 °C. Also benzene was observed in some cases, and especially NiCl$_2$ was active in the deoxygenation of phenol.

DPE conversion in sc-ethanol at 350 °C and 400 °C are summarized in Table S2. DPE conversion at 350 °C was very low for all catalysts (3–10 %). There was only little influence of the presence of the type of catalyst. The only product observed was 4-hydroxy biphenyl. DPE conversion was higher at 400 °C (Table S2). The conversion of ethanol led to hydrocarbons with up to 20C atoms. A representative GC × GC chromatogram of the reaction mixture formed by the alcoholysis of DPE with CuCl$_2$ in ethanol is shown in Fig. 6. The reaction products consisted of mono-aromatics, aliphatics and carboxylic acids. Importantly, a substantial amount of deoxygenated mono-aromatic products were formed. These products were also alkylated by the solvent. The extensive alkylation of mono-aromatics hampers subsequent condensation reactions. This may explain the relatively low selectivity to HMW products [31]. In the blank reaction, DPE conversion was very low and alkyl-aromatics (86%), phenol (9%) and alkyl-PhOHs (5%) were obtained. The product of ethanol conversion in the absence of Lewis acidic salts was limited to light aliphatics. Nevertheless, it is important to note that, even without catalyst, high selectivity towards alkylated mono-aromatic products was obtained at 400 °C. In the presence of the Lewis acid catalysts, formation of mono-aromatics increased. Deoxygenation led to the formation of water and also alkylated mono-aromatic products. As a result,
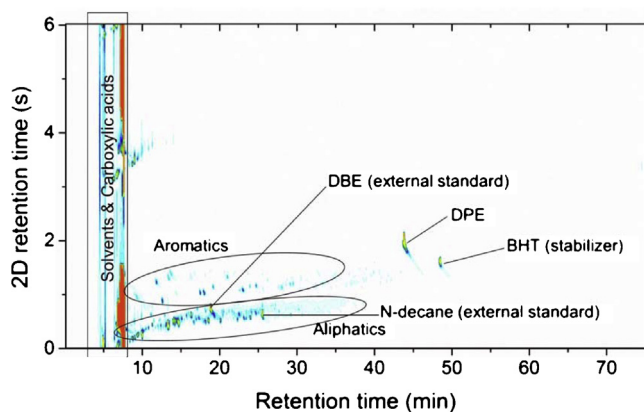
Fig. 6. GC × GC chromatograms of the products of DPE alcoholysis in sc-ethanol in the presence of CuCl$_2$ at 400 °C after a reaction time of 3 h.
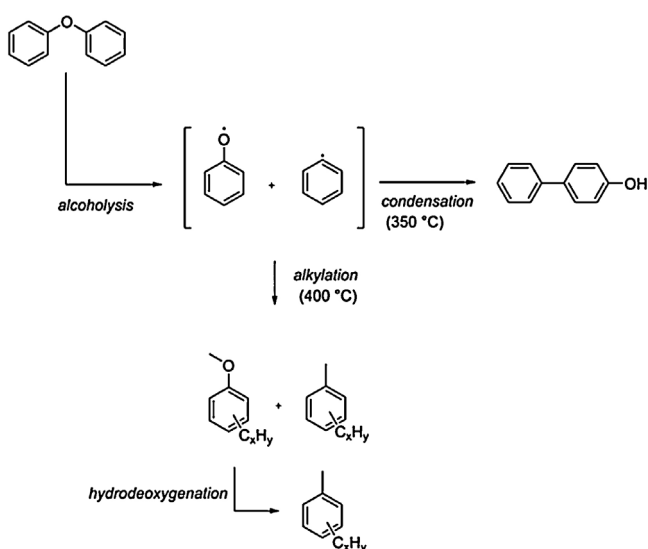

Fig. 7. Proposed reaction mechanism for DPE alcoholysis in ethanol.

phase separation of the reaction mixture occurred. In the presence of MCl$_n$ and M(OAc)$_n$, DPE conversion was much higher. The products are extensively alkylated mono-aromatics. By using CuCl$_2$, a conversion of 48% could be reached with a selectivity of 94% to mono-aromatics. Very similar results were obtained with AlCl$_3$.

We propose for DPE conversion the reaction mechanism depicted in Fig. 7. Homolytic dissociation of DPE produces phenyl and phenoxy radicals in ethanol. At 350 °C, radicals cannot be stabilized and underwent recombination reactions to form the sole product 4-hydroxy biphenyl. At 400 °C, ethanol was converted to aliphatic hydrocarbons and it was very reactive for the alkylation of the DPE alcoholysis products. Alkylation and in-situ generation of hydrogen are expected to stabilize these radicals. As a result, extensively alkylated mono-aromatics and alkyl phenyl ethers were formed. Aryl—alkyl ether bonds formed in the course of reaction were easily hydrodeoxygenated to form alkyl-aromatics and aliphatics (alkanes and alkenes). More importantly, in the presence of Lewis acidic salts, it was possible to reach nearly complete deoxygenation which resulted in high yields of mono-aromatic products.

We briefly discuss the influence of the solvent by using the concept of donor number for reactants and solvents. The donor number (DN) can be determined calorimetrically as the negative value of the standard enthalpy change for the 1:1 adducts formation between compound solvent and antimony pentachloride (SbCl$_5$) in 1,2-dichloroethane at 25 °C [32]. DPE and phenol have donor numbers (DN) of 6 and 11, respectively [30]. However, the donor numbers for water and ethanol are much higher at 18 (gas) and 33 (liquid) and 32, respectively [32]. Previously, the combination of strong Lewis acid and very low donicity solvents was considered necessary to hydrolyze DPE at lower temperatures (250 °C) [30]. The advantage of ethanol as a solvent in our system might be that its conversion to higher hydrocarbons at 400 °C resulted in the formation of a solvent media with much lower DN numbers (e.g., DN$_{hexane}$ = 0). This might be the reason for the higher conversion of DPE in ethanol at 400 °C. It has also been reported that H$_2$ was required for both hydrolysis and hydrogenolysis reaction of DPE catalyzed by Ni/SiO$_2$ in water [33], where C—O bond cleavage was reported as a rate determining step instead of ring hydrogenation. In our studies, ethanol also acts as hydrogen donor solvent, especially at 400 °C, accelerating the conversion of DPE.

In summary, we showed that the cleavage of 5–O$_4$ type of ether bond was much more difficult than the α–O$_4$ cleavage, even at 400 °C in the presence of Lewis acid catalysts. DPE reactions proceeded at much lower rates in sc-water than in sc-ethanol. This is the oppositive of what was observed for BPE conversion. At 400 °C in sc-ethanol, DPE was converted in high yield to monomer products that additionally underwent deoxygenation reactions and extensive alkylation by ethanol. It is argued that both the deoxygenation and alkylation protects the products from condensation reactions.

3.4. Conversion of diphenyl methane

We also investigated the reactivity of Lewis acid catalysts towards the cleavage of DPM as a model for the cleavage of aryl—alkyl CC α$_1$–type lignin linkages. This reaction was only done at 350 °C in sc-water and sc-ethanol.

In water, DPM conversion was low (max 18% for Cu(OAc)$_2$ and AlCl$_3$) and the products in decreasing order of yield were condensation products (mostly HMW products) > mono-aromatic oxygenates (benzaldehyde and phenol) > aromatics (mostly benzene) (Table S3). With MCl$_n$, the benzene yield was the highest. The conversion of DPM in water was dominated by condensation reaction paths. Tri-nuclear aromatics were formed in higher yields than di-aromatics. In sc-ethanol, DPM was not converted at all, except when CuCl$_2$ was the catalyst. In this case, DPM conversion was 5% with 99% selectivity to toluene.

Fig. 8 depicts the proposed reaction mechanism for the high-temperature conversion of DPM in water. It has been shown previously that a direct oxygen supply from sc-water is necessary for the hydrolysis of DPM [34]. We propose that hydroxyl radicals first attack to the methylene carbon and form diphenyl methanol (benzhydrol), which is very reactive and unstable in sc-water [34]. Subsequently, diphenyl methanol is converted to DPM and benzophenone [34]. Benzophenone can be formed in sc-water as the first stable product from DPM [34–35]. In sc-water, decomposition of benzophenone into benzoic acid has also been reported [34]. We speculate that benzophenone is further converted to the phenyl radical and benzoic acid via homolytic cleavage. The radical can be converted to benzene via H• radicals from water or form phenol by directly reacting with water. On the other hand, benzoic acid can be converted to benzaldehyde via dehydroxylation. The ketone group can easily undergo hydrogenation reactions to form benzyl alcohol, which is further hydrodeoxygenated to toluene. However, in our studies, intermediate products such as benzhydrol, benzoic acid and benzyl alcohol were not detected. Benzophenone was observed only in very small quantities.
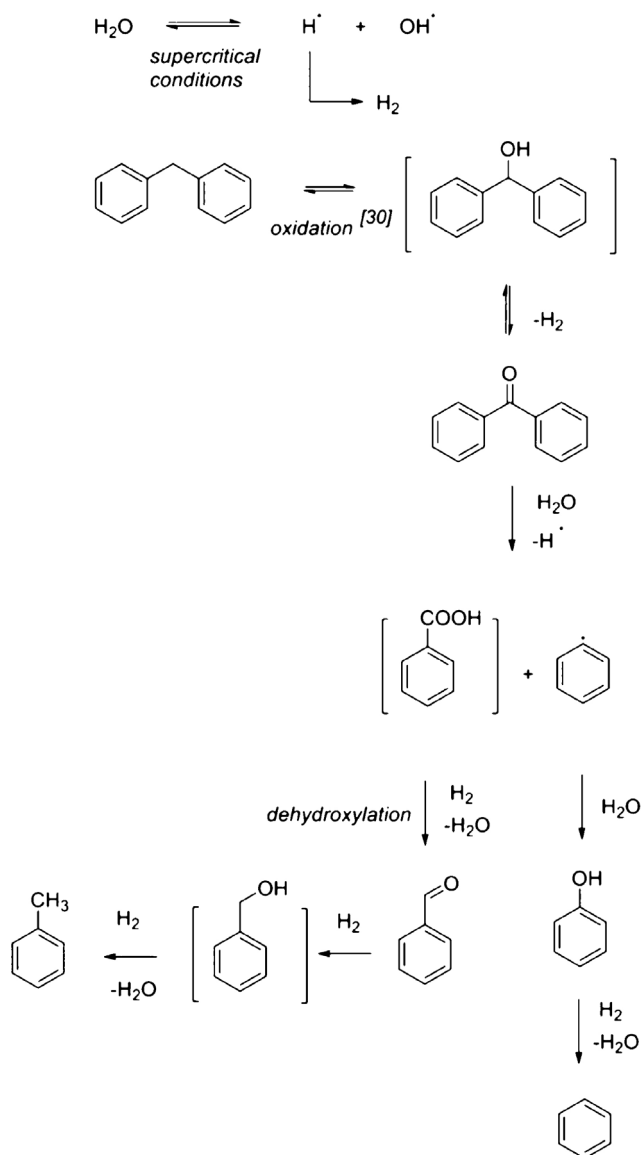
Fig. 8. Proposed reaction mechanism for DPM hydrolysis in sc-water at 350 °C ([H_2] equivalent).

Moreover, in the presence of MCl_n, both stabilization of phenyl radical by H• radicals and hydrodeoxygenation of benzaldehyde were promoted. On the contrary, $M(OAc)_n$ promoted recombination of phenyl cations resulting in di-aromatic products such as biphenyl. In addition, condensation of mono-aromatic oxygenates formed hydroxy-DPM and tri-nuclear aromatic products.

In summary, it is only possible to cleave the α_1 CC bond in DPM in sc-water. Oxygenation of the α_1 bond in sc-water led to formation of monomers but also to extensive condensation reactions in the presence of Lewis acid catalysts. The use of sc-ethanol as solvent did not lead to conversion of DPM.

3.5. Conversion of biphenyl

Biphenyl was not converted in sc-water or in sc-ethanol with or without catalysts in the temperature range of 300–400 °C. The recalcitrance of biphenyl is well known [8], and it is due to the high bond strength of the 5–5′ C–C linkage. This suggests that phenyl–phenyl linkages of lignin will be very difficult to break down into smaller aromatic units, even in the presence of Lewis acidic salts.

4. Conclusions

The catalytic effect of Lewis acidic salts on the cleavage of different types of lignin linkages in representative di-aromatic model compounds was investigated. Full conversion of benzyl phenyl ether (α–O_4) can be achieved in water and ethanol solvents at the temperatures between 300 and 400 °C. The main reaction products are phenol, toluene and benzyl alcohol. Condensation reactions towards higher molecular weight products occurred at higher rates in water than in ethanol. Higher Lewis acidity also promoted these condensation reactions. The conversion of diphenyl ether (5–O_4 model) was low, even at 400 °C. In ethanol, the conversion was substantially higher, especially with metal chloride catalysts. At 400 °C deoxygenation of the monomeric products was almost complete. Ethanol was involved as reactant in the alkylation of the aromatic products of lignin model compound decomposition. It was found that dissociation of the α_1 bond in diphenyl methane was only possible in water. This reaction most likely involves the oxidation of the bridging methylene group to benzophenone. Although benzaldehyde, benzene, phenol and toluene were formed in the course of diphenyl methane conversion, condensation reactions led to formation of high-molecular weight products. Biphenyl representing the most stable 5–5′ lignin linkage could not be converted into mono-aromatic molecules under the studied reaction conditions.

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.molcata.2015.09.007.

References

[1] Lignin and Lignans: Advances in Chemistry, in: D. Dimmel, C. in, D.R. Heitner, J.A. Schmidt Dimmel (Eds.), CRS, Press, Boca Raton, FL, 2010, pp. 1–11.
[2] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev. 110 (2010) 3552–3599.
[3] E. Dorrestijn, L. Laarhoven, I. Arends, P. Mulder, J. Anal. Appl. Pyrolysis 54 (2000) 153–192.
[4] C. Zhao, J.A. Lercher, Angew. Chem. 124 (2012) 6037–6042.
[5] J. He, L. Lu, C. Zhao, D. Mei, J.A. Lercher, J. Catal. 311 (2014) 41–51.
[6] L. Yang, Y. Li, P.E. Savage, Ind. Eng. Chem. Res. 53 (2014) 2633–2639.
[7] W. Scheppingen, E. Dorrestijn, I. Arends, P. Mulder, J. Phys. Chem. A 101 (1997) 5404–5411.
[8] C. Zhao, J.A. Lercher, The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals, in: K. Triantafyllidis, A. Lappas, M. Stocker (Eds.), Elsevier, 2013, 2015, pp. 289–320.
[9] M.M. Hepditch, R.W. Thring, Can. J. Chem. Eng. 78 (2000) 226–231.
[10] D.P. Mobley, A.T. Bell, Fuel 58 (1979) 661–666.
[11] N.D. Tayler, A.T. Bell, Fuel 59 (1980) 499–506.
[12] S.S. Salim, A.T. Bell, Fuel 161 (1982) 745–754.
[13] G.L. Huppert, B.C. Wu, S.H. Townsend, M.T. Klein, S.C. Paspek, Ind. Eng. Chem. Res. 28 (1989) 161–165.
[14] J.M.L. Penninger, R.J.A. Kersten, H.C.L. Baur, J. Supercrit. Fluids 16 (1999) 119–132.
[15] P.E. Savage, Chem. Rev. 99 (1999) 603–621.
[16] D. Bröll, C. Kaul, A. Krämer, P. Krammer, T. Richter, M. Jung, H. Vogel, P. Zehner, Angew. Chem. Int. Ed. 38 (1999) 2998–3014.
[17] X. Xu, C. De Almeida, M.J. Antal Jr., J. Supercrit. Fluids 3 (1990) 228–232.
[18] R. Ma, W. Hao, X. Ma, Y. Tian, Y. Li, Angew. Chem. 126 (2014) 7438–7443.
[19] J. Lu, E.C. Boughner, C.L. Liotta, C.A. Eckert, Fluid Phase Equilib. 198 (2002) 37–49.
[20] T. Okuhara, Chem. Rev. 102 (2002) 3641–3666.
[21] F. Fringuelli, F. Pizzo, L. Vaccaro, Tetrahedron Lett. 42 (2001) 1131–1133.
[22] P.G. Jessop, J. Supercrit. Fluids 38 (2006) 211–231.

[23] S. Kobayashi, M. Sugiura, H. Kitagawa, W.W.-L. Lam, Chem. Rev. 102 (2002) 2227–2302.

[24] A. Kruse, E. Dinjus, J. Supercrit. Fluids 39 (2007) 362–380.

[25] M. Siskin, G. Brons, S.N. Vaughn, Energy Fuels 4 (1990) 488–492.

[26] V. Roberts, S. Fendt, A.A. Lemonidou, X. Li, J.A. Lercher, Appl. Catal. B 95 (2010) 71–77.

[27] G. Gonzalez, D. Montane, AIChE J. 51 (2005) 971–981.

[28] C.C. Tsao, Y. Zhou, X. Liu, T.J. Houser, J. Supercrit. Fluids 5 (1992) 107–113.

[29] M. Nowakowska, O. Herbinet, A. Dufour, P.-A. Glaude, Combust. Flame 161 (2014) 1474–1488.

[30] T.R. Varga, Z. Fazekas, Y. Ikeda, H. Tomiyasu, J. Supercrit. Fluids 23 (2002) 163–167.

[31] X. Huang, T.I. Korányi, M.D. Boot, E.J.M. Hensen, ChemSusChem 8 (2014) 2276–2288.

[32] K. Izutsu, Properties of solvents and solvent classification, in: Electrochemistry in Nonaqueous Solutions, Wiley-VCH, 2009, 2015, pp. 1–24.

[33] J. He, C. Zhao, D. Mei, J.A. Lercher, J. Catal. 309 (2014) 280–290.

[34] H. Tagaya, Y. Suzuki, T. Asou, J. Kadokawa, K. Chiba, Chem. Lett. 27 (1998) 937–938.

[35] C.-W. Chen, A.-N. Ko, J. Chin. Chem. Soc. 58 (2011) 1–11.