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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

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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.

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

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* Corresponding author.
E-mail address: e.j.m.hensen@tue.nl (E.J.M. Hensen).

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

	Normal water	Subcritical water	Supercritical water		Superheated steam
Temperature (°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 °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 ($T_c = 374\,°C$, $P_c = 218$ 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 $pK_W \leq 14$ 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 $pK_W \geq 14$ 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 °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 °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 ($T_c = 241\,°C$, $P_c = 6.14$ MPa, $\rho_c = 0.276\,g/cm^3$) 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–O_4 (aryl—alkyl bond), 5–O_4 (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