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Lewis acid-catalyzed depolymerization of soda lignin in supercritical ethanol/water mixtures

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ABSTRACT

The depolymerization of lignin model compounds and soda lignin by super Lewis acidic metal triflates has been investigated in a mixture of ethanol and water at 400 °C. The strong Lewis acids convert representative model compounds for the structure-forming linkages in lignin, namely α -O-4, 5-O-4 (C–O–C ether bridge), and α -1 (methylene bridge). Only the 5–5' C–C linkage in biphenyl was unaffected under the given reaction conditions. Full conversion of soda lignin was achieved without char formation. Lignin was converted into a wide range of aliphatic and aromatic hydrocarbons. Ethanol was involved in the alkylation of the lignin depolymerization products. These alkylation reactions increased the product yield by inhibiting repolymerization of the products. The resulting organic phase consisted of aliphatic hydrocarbons (paraffins and olefins), aromatic hydrocarbons (extensively alkylated non-oxygenated mono-aromatics, mainly alkylbenzenes as well as mono-aromatic oxygenates, mainly phenolics), condensation products (mainly naphthalenes) and saturated oxygenates (ketones and carboxylic acids). Although complete product analysis was not possible, the data suggest that the dominant fraction of lignin was converted into monomeric units with a small fraction with molecular weights up to 650 g/mol.

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1. Introduction

Lignin is one of the main constituents of abundant lignocellulosic biomass. This cheap and renewable feedstock has the potential to serve as a source of hydrocarbons for the production of liquid fuels and chemicals [1,2]. However, efficient conversion of lignin into value-added chemicals is challenging because of the high structural heterogeneity of lignin biopolymers and their recalcitrance to depolymerization.

In addition to conventional routes employing transition metal and Brønsted acid catalysts [3,4], reaction pathways catalyzed by Lewis acids are gaining increasing attention as promising and sustainable alternatives for the efficient depolymerization and deoxygenation of biomass constituents [5–7]. In particular, metal triflates can act as strong water-tolerant Lewis acids [7,8]. They retain substantial Lewis acidity not only in organic solvents but also in water. The use of water instead of organic solvents helps

to realize greener biomass conversion processes. An advantage of triflate catalysts is that $M(OTf)_n$ salts are typically only stable in water below 200 °C [7,8]. On the other hand, in some cases they have successfully been recovered from the reaction mixtures and reused without loss of activity [8]. The review of Kobayashi et al. discusses promising catalytic performance of rare-earth triflates in promoting a wide range of important organic reactions such as nucleophilic addition for C–C bond formation (aldol condensation, allylation, cyanation, Michael addition), cyclization (Diels–Alder reactions) and Friedel–Crafts acylation and alkylation [8]. It has also been reported that La, Ln, Yb and Sc triflates are effective catalysts in the Friedel–Crafts acylation and alkylation of aromatic derivatives using alcohols under mild conditions ($T < 100$ °C) [8,9]. These reactions require the use of an electrophile (e.g. alkyl halides, olefins), an aromatic nucleophile and Lewis or Brønsted acids [9]. The use of $M(OTf)_n$ salts (M = metal) in such processes provided good reaction rates and high selectivity towards the desired products at mild reaction conditions [7,8]. $Al(OTf)_3$ has also been reported to be effective to catalyze epoxide ring opening reactions at room temperature in polar solvents such as ethanol [10].

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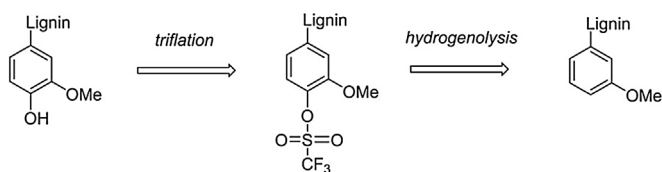


Fig. 1. Conceptual mechanism of triflate-assisted hydrogenolysis of lignin. Adopted from [23].

In previous studies, the use of triflic acid has also been investigated for comparison purposes against metal triflate catalysts. Significant differences have been found between the catalytic performances of metal triflates and triflic acid (TfOH); TfOH was less active for reactions such as Friedel–Craft alkylation, ring-opening of epoxides and cyclization of unsaturated alcohols [9–12].

The choice of the solvent plays an important role in determining the ability of a Lewis acidic salts to depolymerize lignin. In particular, previous studies evidence a very poor performance of metal acetates, chlorides and triflates when lignin upgrading is carried out in supercritical water [13,14]. Reactions in alcohol solvents and, in particular, in ethanol lead to a much deeper lignin depolymerization [13,15,16]. In catalysis by Lewis acids such as $\text{Al}(\text{OTf})_3$, the addition of small amounts of water to the organic solvent can result in significant improvements of the overall performance. For example, $\text{M}(\text{OTf})_n$ -catalyzed organic transformations can proceed via Lewis acid-assisted Brønsted acidity in the presence of water; the Brønsted acidity derives then from water [12]. The co-catalytic role of water likely helps to stabilize cationic intermediates. When water is added to organic solvents, the term “on water” has been frequently used in the literature. We speculate that carrying out biomass conversion reactions in ethanol/water mixtures might provide an alternative for aqueous phase reforming (APR) of biomass derived-products such as ethanol, sorbitol, glucose, glycerol to generate hydrogen and other products, for which also sometimes acidity is required [17,18]. $\text{M}(\text{OTf})_n$ salts are potential catalysts for such reactions. Previous studies evidence a beneficial effect of the use of water–ethanol [19–21] and water–methanol [22] media for the conversion of lignin. Besides the enhanced solubility of lignin in water–organic solvent mixtures, [19], such solvent systems effectively suppress char formation compared to the situation when the reactions are carried out in water.

In spite of the potential of the catalytic chemistry of super Lewis acidic metal triflate salts ($\text{M}(\text{OTf})_n$; $\text{M} = \text{Al}, \text{Cu}, \text{Ni}, \text{Sc}$ etc.) described above, only very few studies have used metal triflates as catalysts for the conversion of lignin. Hu et al. studied the triflate-assisted hydrogenolysis reaction for the hydrodeoxygenation of phenolics as lignin model compounds [23]. Fig. 1 shows that triflation of lignin by triflate anhydride ($\text{CF}_3\text{SO}_2)_2\text{O}$ proceeds in a similar manner as the acetylation of lignin by acetic anhydride. The reaction is promoted by the exchange of the hydroxyl group of phenol by the strongly electron-withdrawing $-\text{OTf}$ group [23,24]. To selectively cleave the resulting aryl– OTf bonds by hydrogen transfer, coordination to Pd^{2+} was required. In this example, triethylammonium formate ($\text{HCO}_2\text{NHEt}_3$) was used as the hydrogen donor. As a result of hydrogenolysis of the aryl– OTf bond, deoxygenated products were obtained. Similar approaches have been applied to the waste from the pulp and paper industry to reduce the strength of paper. This can make hydroxyl sites of cellulose more accessible for further processing [23]. Recently, Yang et al. investigated the catalytic effect of such water-tolerant Lewis acids as indium triflate, scandium triflate, ytterbium triflate, and indium chloride on the hydrolysis of lignin model compounds in aqueous solutions [14]. In the presence of $\text{In}(\text{OTf})_3$ a complete conversion of benzylphenyl

ether was achieved already at 225 °C after 3 h reaction, whereas the hydrolysis of more stable model compounds such as guaiacol and diphenyl ether required much higher reaction temperatures [14].

In this study, we discuss the use of Lewis acid triflate catalysts in ethanol/water solvent mixtures for the depolymerization of lignin. We first evaluated the performance of $\text{Al}(\text{OTf})_3$ for the conversion of model compounds such as phenol, benzyl phenyl ether, diphenyl ether, diphenyl methane and biphenyl in ethanol/water mixtures. We found that ethanol is also converted into a wide range of liquid hydrocarbons products as well as H_2 . With this knowledge, we also examined the conversion of soda lignin by metal triflates. The results of these reactivity studies are compared to those of our earlier study on the use of $\text{M}(\text{OTf})_n$ salts in which ethanol was the solvent [13].

2. Experimental methods

2.1. Materials

De-ionized water and/or absolute ethanol (Sigma–Aldrich, $\geq 99.8\%$) were used as reaction solvents. Aluminum (III) chloride hexahydrate (Fluka, $\geq 99.0\%$), aluminum (III) triflate (Aldrich, 99.9%), copper (II) triflate (Aldrich, 98%), nickel (II) triflate (Aldrich, 96%), scandium (III) triflate (Aldrich, 99%) were used as received. N-decane (Aldrich, anhydrous, $\geq 99\%$) and di-n-butyl ether (Aldrich, anhydrous, 99.3%) were used as external standards during GC analysis. Protobind 1000 lignin, which is obtained from wheat straw by soda pulping, was used as received from GreenValue (Switzerland).

The chemicals were diluted in tetrahydrofuran (Aldrich, anhydrous, $\geq 99.9\%$) 10 times prior to GC \times GC analysis. Chloroform-D (Cambridge Isotope Laboratories Inc, D, 99.8% stabilized with silver foil) was used as a solvent in ^1H - ^{13}C HSQC NMR analysis.

2.2. Catalytic activity measurements

All the experiments were performed in stainless-steel batch reactors with an internal volume of 13 mL. The reactors were filled with either 6.5 mL of anhydrous ethanol or 3.5 mL ethanol/3 mL water. In a typical run, a solution of 0.025 mol/L Lewis acidic salt containing 150 mg lignin was loaded into the reactor. For model experiments, 150 mg of a model compound was used. The reactors were sealed by Swagelok O-rings. The reactors were loaded under ambient atmosphere. The reactions were carried out at 400 °C with a reaction time of 4 h by placing the reactors in a pre-heated fluidized sand bath that allowed for rapid heating to the desired reaction temperature. The estimated autogeneous pressure under the reaction conditions in water–ethanol solvent system was between 375 and 400 bars. In our system, 10 parallel reactions could be run at the same time. After the reaction was completed, the reactors were quenched in an ice bath. After cooling, reactors were opened and the reaction solution was collected. When lignin residue was present, the solids were separated from the liquid products. The liquid phase consisted of two layers: an organic layer and an aqueous layer. The aqueous and organic layers were separated by decantation and separately weighed. Further analyses of the liquid organic phase were carried out by GC/MS-FID, GC \times GC, GPC and MALDI-TOF-MS and ^1H - ^{13}C HSQC NMR analysis methods.

The yields of organic products were calculated as:

$$\begin{aligned} \text{Yield of product}_i(\text{in mg}) &= \text{wt. of organic phase} \\ &\quad \times \text{Conc. of product}_i(\text{calc. from GC} \\ &\quad \times \text{GC – FID}) \end{aligned} \quad (1)$$

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