



Review

From models to lignin: Transition metal catalysis for selective bond cleavage reactions



Peter J. Deuss, Katalin Barta*

Stratingh Institute for Chemistry, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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ABSTRACT

In the coming decades major changes are expected in the chemical industry regarding the utilized raw material inputs. Depleting fossil resources will gradually be replaced by renewable feedstocks wherever possible. Because of this transition, new and efficient methodologies are required that enable depolymerization and defunctionalization of these complex, highly oxygenated biopolymers. Additionally, utilization of all components of lignocellulose is of great importance. In particular, depolymerization of lignin into its aromatic subunits or defined aromatic platform chemicals has proven challenging.

* Corresponding author. Tel.: +31 50 363 4232; fax: +31 50 363 4296.
 E-mail address: k.barta@rug.nl (K. Barta).

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Various approaches to overcome these difficulties have been attempted and resulted in new and exciting developments in many fields. In this review we will give an overview of bond cleavage strategies relevant for lignin depolymerization using homogeneous catalysts, focusing especially on reductive and hydrogen transfer methods.

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1. Introduction

1.1. Motivation and scope of this review

Devising and implementing strategies, which would enable the production of bulk and fine chemicals [1,2] or fuels [3] from sustainable biomass materials, especially from agricultural or municipal waste resources that do not compete with food supply [4], is one of the grand challenges in sustainable chemistry [5]. To successfully address this challenge, a paradigm shift in chemical catalysis is necessary. New methods are desired that allow for depolymerization and defunctionalization of complex and highly oxygenated bio-derived polymers or platform chemicals derived therein [6–8]. Because conventional petroleum-based chemistry primarily adds functionality to simpler structures, novel scientific insights are of major importance to enable such methods [9].

In order to allow for the utilization of all lignocellulose components, particular attention has to be devoted to the depolymerization of lignin, which has proven particularly difficult. In this review we will provide an overview of the different approaches taken to tackle this problem and will primarily focus on the design of transition metal complexes for the selective cleavage of specific bonds in model compounds. The compatibility of these systems with the use of real lignin will also be discussed.

1.2. Why lignin?

Lignocellulose consists of about 30–50% cellulose, 20–35% hemicellulose and 20–35% lignin [10]. While established routes exist for the conversion of the cellulose fraction of biomass and derived platform chemicals [11–17], there is a general lack of efficient processes for the utilization of lignin, which is the most important renewable source of aromatics on the planet [18]. The successful implementation of the biorefinery concept in which lignocellulose is fractionated into its main components, requires efficient chemical or catalytic valorization routes for all fractions. This includes lignin, which is currently simply burned to provide heat for other processes [19–21]. Moreover, a large volume of lignin waste is produced annually by the paper industry and this amount is expected to increase with the introduction of second-generation bioethanol [22,23]. Considering these factors, it has become highly desirable to develop efficient methods for the conversion of lignin especially to aromatic chemicals [18,24,25]. Additionally important is that, besides various other approaches to take care of the increased energy demand, shale gas has emerged as an alternative to petroleum. Considering the implementation of shale gas, a shortage of aromatic chemicals is a serious prospect [26].

A plethora of research directions have been initiated for lignin valorization, predominantly in the past decade. Very important are thermal approaches [27], especially pyrolysis and gasification, which can be used for the production of syngas or pyrolysis oils from lignocellulose or lignin [3,28,29,30]. By now lignin conversion has touched a number of scientific disciplines. New methods have emerged for enzymatic [31,32] mechanochemical [33,34] hydrothermal [27,35] electrochemical [36] or microwave assisted [37] lignin depolymerization. Exciting developments have taken place in the field of chemical catalysis [10]. Heterogeneous catalysts

historically developed for the petrol industry have been applied also in lignin upgrading and new catalysts were designed [38]. A summary of different approaches is given in a variety of excellent reviews [39–43]. Importantly, lignin depolymerization to a selected set of desired products requires selective cleavage of specific bonds (see also Section 1.4). This initiated new research questions and the search for novel catalysts structures also in the field of homogeneous catalysis [44]. We have recently summarized the latest advances in this field in a perspective, which also addressed other biomass-derived materials such as sugars and fatty acids [45]. In the current contribution we will focus entirely on research relevant for lignin conversion in more depth and include a large number of new results, which appeared in recent literature. Oxidation has already been reviewed [10,46–50] therefore this review will primarily focus on reductive approaches using transition metal catalysts. Although not strictly related to coordination chemistry, the discussion will include acid and base catalysis, as well as selected examples of heterogeneous systems where appropriate. Within this, a separate section will address the formidable advances made in the Ford laboratory regarding the reductive depolymerization of lignin and lignocellulose via hydrogen transfer from supercritical methanol [9].

1.3. Structural considerations and challenges

Due to its high aromatic content, lignin could be an ideal source of simple aromatic or fine chemicals in the future [8,10,11,18,41,45]. However, the selective conversion of lignin to well defined chemicals is very challenging. This is perhaps no surprise, considering that nature designed lignin to be robust, and to provide structural stability to plants. In nature, lignin is biosynthesized from three simple aromatic building blocks: coniferyl, sinapyl and coumaryl alcohol (Fig. 1) [51–54]. These monolignans are randomly coupled via radical processes, to result in a stable, heterogeneous, 3-dimensional biopolymer that is particularly resistant towards chemical degradation. In Fig. 1, all positions in the corresponding monolignans that are potentially involved in bond forming reactions are depicted. This demonstrates that a large number of variations are possible and shows why there is no generally accepted, precise description of the lignin structure.

Nonetheless, a lignin of known origin (e.g. plant type, hardwood vs softwood) can be described by several common characteristics. These are the guaiacyl/syringyl ratio, representative structure, aliphatic vs aromatic free –OH content, the molecular weight and the abundance of the most common linkages. Indeed, lignin chemistry dates back to the 30–40s when main efforts focused on structural elucidation of the native lignin structure [55–59]. The development of new analytical procedures for structural characterization of lignin and product mixtures obtained, for example by 2D NMR spectroscopy, will have great relevance for understanding catalytic conversion pathways [60–62]. A further difficulty, primarily caused by the amorphous structure of lignin, is its relatively high molecular weight, and limited solubility in most common organic solvents at ambient temperature. To this end, alternative reaction media such as supercritical solvents [63,64] or ionic liquids have emerged as an important advance [65,66]. The nature of the bond cleavage reactions desired for selective

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