

Theoretical and Experimental Approach to Hydrogenolysis and Hydrogenation of Lignin and Catalyst Design

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(リグニンの水素化・水素化分解ならびに触媒設計に対する理論的および実験的アプローチ)

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論文内容の要旨

Lignin accounts for almost 30% of the organic part of biomass. It has become a center of interest for worldwide scientists and industries, as the lignin, of which more than half of that carbon is aromatic, provides alternative and attractive new sustainable platforms of fuels, chemicals, and materials. Depolymerization is a prerequisite for efficient utilization of lignin because it is a randomly polymerized material forming a complex three-dimensional macromolecular structure. Catalytic hydroprocessing is a major approach to upgrading of lignin. Designing highly active catalyst is thus a critical subject to the efficient hydroprocessing of lignin. In this thesis, theoretical and experimental approaches are applied comprehensively to design highly dispersive heterogeneous nickel catalysts, and catalytic hydroprocessing of lignin monomers and kraft lignin.

In Chapter 1, the current situations of lignin utilization are first introduced. Various approaches to prepare heterogeneous catalysts are then summarized and compared, and chemical reduction is regarded as the best. In order to have a deep insight into the mechanism of catalyst formation, and that of hydroprocessing of lignin, density functional theory (DFT) is widely used in this study. The developments and performances of DFT are summarized in Chapter 1 as well.

Chapter 2 first reports complete arene hydrogenation of phenolic compounds as lignin monomers over a non-noble metal catalyst supported by a general material. A type of nano-sized Ni catalyst was prepared in ethanol and *in-situ* supported by a ZSM-5 zeolite through general borohydride reduction of Ni^{2+} to Ni^0 , but with application of a simple ligand, pyridine. This catalyst showed an activity so high as to completely or near completely hydrogenate the aromatic rings of phenol and its twelve derivatives as potential lignin monomers at 180°C. The activity was clearly higher than that of another type of conventional Ni catalyst prepared in the absence of pyridine. Analyses of the catalysts by TEM/EDS, XPS, XAFS and others demonstrated that pyridine had crucial roles for selective formation of nano-sized Ni and maintenance of its activity by appropriate interaction with the support. This chapter also shows our theoretical approach to the mechanism of the borohydride reduction. First-principles calculations on the basis of DFT revealed the reaction pathway from Ni^{2+} to Ni^0 and the role of pyridine, which was validated by some experimental facts. The DFT calculations also explain the variety of reactivities of the lignin monomers, which are strongly influenced by their molecular electrostatic and steric natures.

In Chapter 3, DFT is employed to investigate the initial hydrogenolytic cleavages of recognized five different types of

inter-aromatic unit linkages of lignin, with assuming the presence of hydrogen free radicals. The relative free energies of reactant complexes, reaction free energy changes, and rate constants for candidate reactions are calculated comprehensively at 298–538 K. Based on the results of calculation and a rapid equilibrium hypothesis, the major reaction channel is decided for each linkage, and its kinetics is assessed. It is concluded that the hydrogenolysis occurs at β -O-4 ether, diphenylether 4-O-5', and β -1' diphenylmethane linkages instantaneously if these are accessible to hydrogen free radicals, while β -5 phenylcoumaran and β - β' pinoresinol linkages are virtually inert to hydrogenolysis.

In Chapter 4, inspired by results of calculation on the basis of DFT and a semi-empirical method, the author found an easy, robust, and efficient approach to solve the problem of folded lignin macromolecules, which is a key factor for impeding their breakdown into monomers by hydrogenolysis. Oxidation and hydrogenolysis, which appear to be independent and contradictory of each other in many past studies, were combined and successively performed in this study. Hydrogen peroxide was used to damage the strong intramolecular hydrogen bonds of Kraft lignin efficiently, transforming the folded three-dimensional geometries of the lignin macromolecules into stretched ones in an alkaline aqueous medium. Following the pretreatment of stretching lignin molecules, catalytic hydrogenolysis was performed in the presence of a Ni catalyst supported by ZSM-5 zeolite, reported by the authors. Because of more chemisorption sites of the stretched lignin macromolecules onto the catalyst surface and the remission of lignin re-polymerization/self-condensation, conversion of the kraft lignin into oil reached 83 wt%-lignin, 91 wt% which was accounted for by nine types of monomers. This chapter has thus demonstrated high yield monomer production from lignin dissolved in aqueous media.

In Chapter 5, general conclusions of this study are proposed. First, on the basis of the borohydride reduction stoichiometry of $2\text{Ni}^{2+} + 4\text{BH}_4^- + 6\text{EtOH} = 2\text{Ni} + 8\text{H}_2 + \text{B}_2\text{H}_6 + 2\text{B}(\text{OEt})_3$, the addition of Py to the ethanol solution of $\text{Ni}(\text{NO}_3)_2$ prior to the Ni^{2+} to Ni^0 reduction with BH_4^- realizes selective formation and deposition of Ni particles with sizes around 4 nm without coarser particles. The new type Ni catalyst has a sufficiently high activity as to completely or near completely hydrogenate phenol and its twelve derivatives with one or more alkyl, alkoxy or hydroxyl substituents at 180°C. Second, regarding the five typical types of inter-aromatic linkages of lignin, diphenyl ether, β -O-4 ether, and diphenyl methane types are cleaved most rapidly as well as completely as far as $\text{H}\cdot$ radicals are available. Cleavages of β -5 phenylcoumaran and β - β' pinoresinol are extremely slow and difficult. This is arisen from difficulty of complete cleavages of mono- or di-condensed hydrofuranyl rings that connects two aromatic rings. These rings could be opened, but the resulting aliphatic chains hardly undergo cleavage unless $\text{H}\cdot$ radicals are available at high concentration. Third, the hydrogenolysis of kraft lignin is successfully performed in alkaline water with the new type Ni catalyst. Both theoretical and experimental studies prove that a lignin macromolecule, of which alcoholic hydroxyl groups had been oxidized to a sufficient degree, is stretched well in the alkaline water due to the loss of original intramolecular hydrogen bonds and the repulsion among the abundant negative charge. The oxidation thus improved the accessibility of reactive sites of the macromolecule to the catalyst surface, and in addition, suppressed re-polymerization and self-condensation during the hydrogenolysis. The conversion of hydrogenolysis of Kraft lignin and that into monomers are thus increased largely.