



Foundational techniques for catalyst design in the upgrading of biomass-derived multifunctional molecules



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ABSTRACT

The production of fuels and chemicals from renewable lignocellulosic biomass resources has been a major research focus in the last few decades. The most efficient method for synthesizing value-added chemical products from sustainable feedstocks is direct catalytic conversion, however, the multifunctional and highly oxygenated biomass-derived substrates are significantly different from petroleum-based feedstocks. Thus, systematic development of new catalytic materials is required to take advantage of the only substantial source of renewable carbon. In this review, we discuss the foundational methodologies that enable rational catalyst design through the investigation of surface-adsorbate interactions and the elucidation of descriptors for selectivity control. Molecular spectroscopies, efficient and predictive computational modeling, rigorous kinetic investigations, and highly controlled materials synthesis have generated fundamental insights leading to general catalyst design principles in biomass upgrading processes. The application of each technique in biomass research is discussed in the context of several case studies, with a focus on the unique insights available from each technique. Moreover, the interplay among multiple techniques, particularly between experimental and computational methods, is also highlighted. Despite the impressive progress made in the biomass field, major roadblocks still exist due to the complexity in the composition and structure of both substrates and catalysts. We share our perspectives regarding future needs in selective catalytic conversions of multifunctional substrates and methods for accelerating catalyst development.

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Contents

1. Introduction	2
2. Spectroscopic techniques	3
2.1. Spectroscopic investigations of reactions at solid-gas interfaces	4
2.1.1. Hydrodeoxygenation of furanics over metal and metal carbide catalysts	4
2.1.2. Support effects in hydrodeoxygenation of furanics and phenolics	5
2.1.3. Methyl lactate dehydration to acrylates over NaY	6
2.2. Spectroscopic investigations of reactions at solid-liquid interfaces	7
3. Computational techniques	8
3.1. Mechanistic insights from computational simulations of model surfaces	8
3.1.1. Hydrogenolysis of cyclic ethers over metal-metal oxide composite catalysts	8
3.1.2. Hydrogenation and deoxygenation of furanics over metal surfaces	9
3.2. Multi-scale modeling for catalyst design	11

Abbreviations: 1,2-PDO, 1,2-propanediol; 1,3-PDO, 1,3-propanediol; 2-MF, 2-methylfuran; ALD, atomic layer deposition; A&AEM, alkali & alkaline earth metals, ATR-FTIR, attenuated total reflectance-Fourier transform infrared spectroscopy; BAS, Brønsted acid site; BEP, Brønsted-Evans-Polanyi Relation; CBE, carbon binding energy; CTH, catalytic transfer hydrogenation; DFT, density functional theory; DMF, 2,5-dimethylfuran; DRIFTS, diffuse reflectance infrared Fourier-Transform spectroscopy; EG, ethylene glycol; FAL, furfural; FPSEM, first principles semi-empirical model; FOL, furfuryl alcohol; FTIR, Fourier-Transform infrared spectroscopy; GA, group additivity; HBE, hydrogen binding energy; HDO, hydrodeoxygenation; HMF, 5-hydroxymethylfurfural; HREELS, high-resolution electron energy-loss spectroscopy; KIE, kinetic isotope effect; LSR, linear scaling relation; ML, monolayer; MSM, multi-scale modeling; NMR, nuclear magnetic resonance; OBE, oxygen binding energy; QM, quantum mechanical; RLS, rate-limiting step; SEIRAS, surface-enhanced infrared absorption spectroscopy; SERS, surface-enhanced Raman spectroscopy; TSS, transition state scaling; XAS, X-ray absorption

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4.	Reaction kinetics.....	12
4.1.	Development and parameterization of kinetic models for reaction optimization.....	12
4.1.1.	2,5-dimethylfuran ring-opening to 2-hexanone over Pt/C.....	12
4.1.2.	Methyl levulinate hydrogenation to γ -valerolactone over Lewis acidic zeolites.....	12
4.2.	Kinetic investigations for mechanistic insights.....	13
4.2.1.	Hydrogenolysis of cyclic ethers and glycerol over metal-metal oxide composite catalysts.....	14
4.2.2.	Synthesis of aromatics from furanics over zeolites.....	15
5.	Synthesis of catalysts with tailored composition and structure.....	16
5.1.	Molecular-level control of active sites.....	16
5.1.1.	Controlled heteroatom incorporation in zeotype materials.....	16
5.1.2.	Atomic layer deposition for controlled catalyst synthesis.....	17
5.2.	Active site accessibility control.....	18
5.2.1.	Hierarchical zeotype materials.....	18
5.2.2.	Metal surface modification.....	19
5.3.	Multi-domain catalysts.....	19
5.3.1.	Emulsion-stabilizing materials.....	19
5.3.2.	Micellar and organosiliceous materials.....	19
5.4.	Deactivation-resistant catalysts.....	20
6.	Perspective.....	21
	Supplementary materials.....	22

1. Introduction

Motivated by concerns about anthropogenic climate change, major advances have been made in the last decade-plus toward the synthesis of fuels and commodity chemicals from non-edible lignocellulosic biomass, which is the only substantial source of renewable carbon [1–14]. Abundant and transportable petroleum-derived hydrocarbons have been used to synthesize fuels and chemicals for the last century, and heterogeneous catalytic research has historically been performed in the context of upgrading these fossil carbon resources [15–19]. Industrial processes and catalytic materials that efficiently mediate the selective oxidation of hydrocarbons have been established and improved over decades to synthesize partially oxidized platform chemicals and monomers [20–22]. Replacing polluting fossil carbons with renewable biomass-based raw materials entails the development of new production methods that account for the substantial differences in the chemical composition between the two types of feedstocks (particularly the oxygen content, which is 0.05–1.5 wt% in fossil hydrocarbons vs. 30–50 wt% in biomass feedstocks), and the resulting contrasts in physicochemical properties such as thermal stability and polarity [16,23–25]. Selective reduction and deoxygenation, rather than oxidation, are required for the synthesis of drop-in platform chemical substitutes from biomass feedstocks [3,9,10,26,27]. Efficient heterogeneous catalysis is necessary to upgrade biomass on the industrial scale, but new fundamental understanding is first required to develop the novel catalytic materials and systems that will facilitate renewable chemicals production [7,14,26,28–33]. In this review, we discuss the application of key research strategies used to gain molecular-level insights into the catalytic chemistry of biomass valorization, and how those insights are applied to the design of active, selective, and durable catalysts (Fig. 1.1).

While multiple strategies have been proposed for upgrading biomass resources to fuels and specialty chemicals, direct catalytic transformation is the most promising approach because it has the potential to meet the stringent technical, economic, and sustainability targets [9,13,14,28,34–37]. Lignocellulosic biomass has three main constituent parts: hemicellulose (25–35 wt%) and cellulose (40–50 wt%) are composed of polymerized sugars, and lignin (15–20 wt%) is an amorphous polymer consisting of methoxylated phenylpropane units [1,2,23,38,39]. Early valorization proposals focused on complete gasification or pyrolysis of raw biomass to produce syngas for established petrochemical processes such as the Fischer–Tropsch and the alcohol synthesis processes [40–46]. This

approach deconstructs the starting material through complete C–H and C–C bond cleavage followed by inefficient molecular-level reassembling of the most basic building blocks (synthesis gas) in capital-intensive chemical plants. Due to high transportation costs, widely distributed biomass resources are not well-suited to the centralized processing required for upgrading through gasification and pyrolysis. These processes also destroy the potentially valuable structural units of lignocellulose [3,36,37,47–49]. By contrast, direct catalytic transformations utilize these molecular building blocks to synthesize value-added chemicals and monomers, and can be performed in a modular and distributed manner [1,9,24,50]. Upstream processing steps such as fractionation and depolymerization are applied to generate a variety of oxygenated platform molecules, e.g., short-chain polyols/carboxylic acids, substituted furanics, and phenolics [6,51–55]. These multifunctional molecules can be converted to polymer precursors such as alkylated furans, aromatics, and α,ω -diols through selective hydrodeoxygenation (HDO) and/or dehydration, accompanied by hydrogenation, hydrogenolysis, cycloaddition, or isomerization steps as needed to attain the final product [3,12,27,32,56–58]. This review focuses on these downstream transformations, particularly the challenges of upgrading multifunctional molecules, as well as developing multifunctional catalytic materials that enable these processes.

The most significant challenge in direct conversions of multifunctional biomass-derived platform molecules is selectivity control. Selectivities for critical reactions have substantially improved in recent years as a direct result of improved mechanistic understanding. Targeting specific functional groups in multifunctional molecules for reduction or deoxygenation typically requires catalysts with tailored combinations of active sites [27,31,50,59–63]. The complexity of these materials poses challenges in establishing clear structure-activity relations and gaining insight into reaction mechanisms, both of which are prerequisites for catalyst design. Rather than a comprehensive review of the biomass upgrading field, this article aims to provide the authors' perspective on the central methodologies utilized in mechanistic investigations of biomass-to-chemicals reactions, and how the insights gained aid in the rational development of active, selective, and durable catalysts for upgrading biomass-derived feedstocks. We focus on the application of: (1) spectroscopic techniques; (2) multi-scale computational methods; (3) rigorous kinetic investigations; and (4) controlled materials synthesis methods (Fig. 1.1). Readers interested in more general surveys of biomass conversion are referred to recent review articles [10,12,13,27,31,32,49,55,56,64–69].

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