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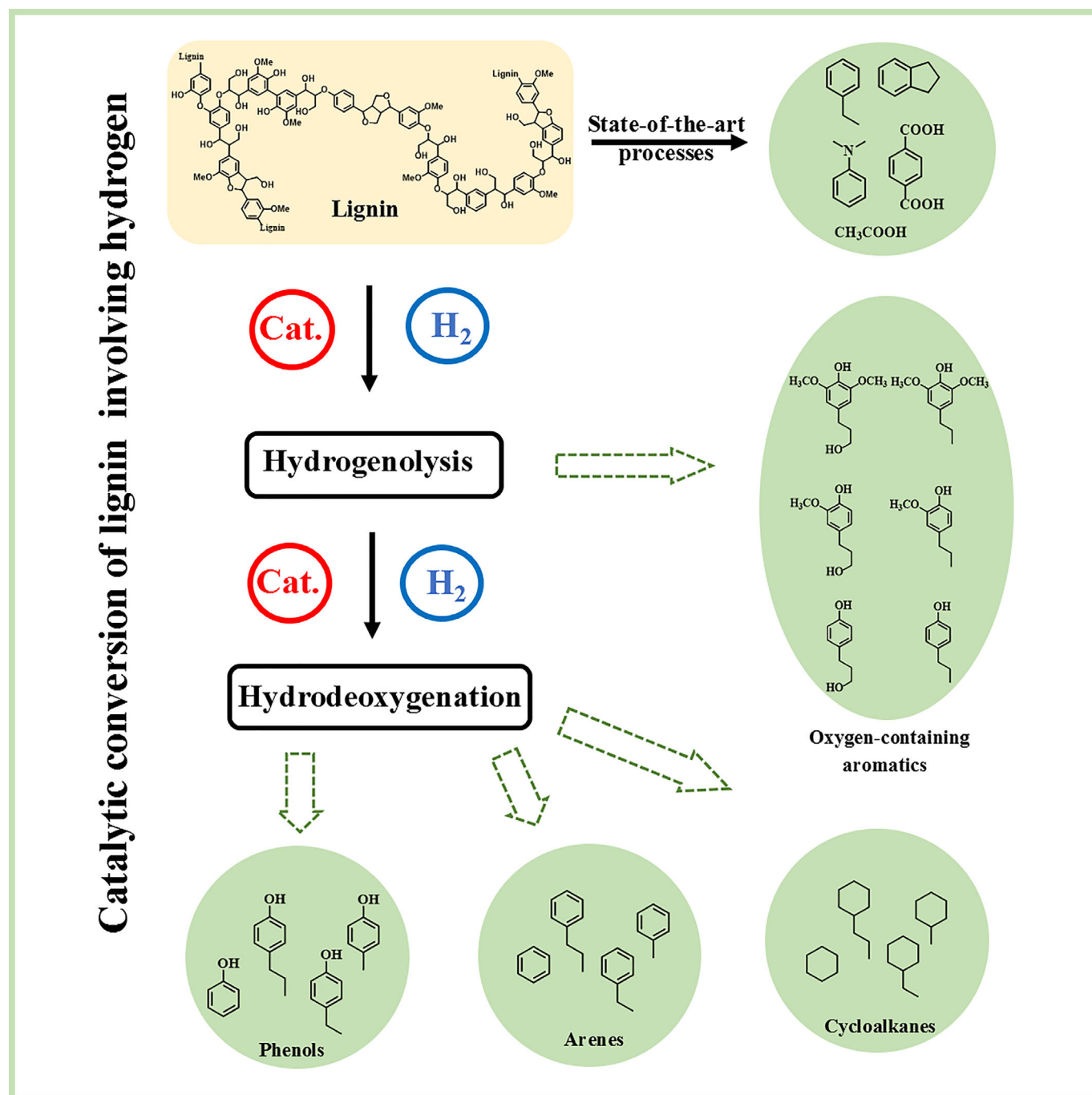
Chemicals from Lignin: A Review of Catalytic Conversion Involving Hydrogen

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Catalytic conversion of lignin involving hydrogen

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Lignin is the most abundant biopolymer with aromatic building blocks and its valorization to sustainable chemicals and fuels has extremely great potential to reduce the excessive dependence on fossil resources, although such conversions remain challenging. The purpose of this Review is to present an insight into the catalytic conversion of lignin involving hydrogen, including reductive depolymerization and the hydrodeoxygenation of lignin-derived monomers to arenes, cycloalkanes and phenols, with a main focus on the catalyst systems and reaction mechanisms. The roles of hydrogenation sites (Ru, Pt, Pd, Rh) and acid sites (Nb, Ti, Mo), as well as their interaction in selective hydrodeoxygenation reactions are emphasized. Furthermore, some inspirational strategies for the production of other value-added chemicals are mentioned. Finally, some personal perspectives are provided to highlight the opportunities within this attractive field.

1. Introduction

The diminishing reserves of nonrenewable fossil resources and aggravation of environmental pollution have steered our society towards focusing on valorization of sustainable resources for the production of renewable chemicals.[1] Biomass is the only organic carbon resource on earth and its utilization is of significant importance.[2] Lignocellulosic biomass, as the main component of biomass, is composed of three polymers including cellulose, hemicellulose and lignin.[3] Among these constituents, lignin is a complex aromatic biopolymer and the most abundant source of aromatics in nature, which endows it with a paramount advantage in producing renewable aromatic products.[4] The conversion of lignin into chemicals, fuels, and carbon-based functional materials is therefore of importance and draws ever-increasing attention.[5]

Lignin consists of various methoxylated phenylpropanoid units.[6] Its natural complexity and recalcitrance make its valorization highly challenging, but this motivates scientists to explore more efficient means for its utilization. In accordance with the guiding principles of green chemistry (i.e., benign by design[7]), researchers have endeavored to develop selective and efficient methods for the conversion of lignin over the decades. In particular, the last five years have seen a significant increase in the number of reports and reviews on lignin valorization, pushing extremely rapid development for lignin conversion.[4a,d, 8]

Starting from lignin, various value-added chemicals and transportation fuels can be obtained through two steps: the depolymerization of lignin, followed by upgrading to the targeted products. Catalytic transformations involving hydrogen sources have received immense attention, owing to relatively mild reaction conditions, relatively simple composition of products, and neutral medium. In addition, for the production of lignin-derived fuels (arenes and cycloalkanes), hydrodeoxygenation is essential for the removal of oxygen. Indeed, catalytic transformations involving hydrogen—either for lignin depolymerization or the following upgrading of lignin-derived monomers—is something of a research hotspot. The development of lignin depolymerization has been documented in several reviews and several depolymerization strategies (base-catalyzed, acid-catalyzed, reductive, oxidative, and thermal) have been recently reviewed and discussed in detail.[4a,d] However, a systematic review on the upgrading of lignin-derived monomers into value-added chemicals is highly desirable to readers, especially for the production of lignin-derived value-added chemicals such as phenol, ethylbenzene, indane, terephthalic acid, and acetic acid, which have been subject to much research in the past three years and are thought to be one of most important research directions for lignin valorization in the coming years.

Herein, with the goal of the production of value-added chemicals from lignin, we critically discuss the catalytic transformations that involve hydrogen from two aspects, namely lignin depolymerization and the upgrading of lignin-derived monomers (Figure 1). The main content of this review is outlined thusly: a) Recent advances in research on reductive depolymerization are discussed. b) Production of arenes, cycloalkanes, and phenols through selective or deep hydrodeoxygenation is critically reviewed from the point of view of the catalytic mechanism. c) Preparation strategies for other value-added chemicals are introduced to exemplify their enormous potential. d) Some personal perspectives on opportunities and challenges for further research are discussed.

2. Lignin Reductive Depolymerization into Aromatic Monomers

Lignin is a complex aromatic biopolymer and the only large-volume renewable source of aromatic chemicals.[4] The extended network of lignin is constructed from methoxylated phenylpropanoid subunits via various C—O and C—C linkages in a random order, in which the C—O linkage accounts for about $^2/_3$ to $^3/_4$ and C—C linkage accounts for $^1/_4$ to $^1/_3$ (Figure 2).[4b, 9] The efficient depolymerization of lignin into aromatic monomers is an attractive first step,[3b,4a,d, 10] but it is also an extremely challenging task, for the following reasons. Firstly, most lignin depolymerization processes are conducted under rigorous reaction conditions, such as high temperature, high pressure, or strong acid/base systems. Secondly, complex phenolic mixtures are always obtained, which presents a tough challenge for

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downstream separation or upgrading to valuable chemicals. Moreover, repolymerization by the formation of new carbon–carbon bonds, as well the formation of char and volatile components, also occurs during the depolymerization process, which greatly reduces the product yields.

Over the past few decades, researchers have endeavored to explore efficient strategies for lignin depolymerization. These improvements are especially embodied in base-catalyzed,[11] acid-catalyzed,[12] oxidative,[13] reductive,[5a,9b,14] pyrolytic,[15] and photocatalytic depolymerization[5b,16] to produce aromatic monomers. Several reviews have concerned depolymerization methods for the conversion of lignin into value-added chemi-

cals.[3b,4a,d,8b] In this section, we mainly focus on one of the most popular depolymerization strategies—reductive depolymerization.

Of all strategies for lignin depolymerization, reductive depolymerization is a very common method to produce lignin monomers. Hydrogen and metal species that can activate hydrogen are essential for reductive depolymerization. With the assistance of hydrogen and metal sites, lignin is not only depolymerized (cleavage of C—O linkages and even C—C linkages) to low-molecular-weight aromatic compounds under relatively mild conditions, but can be further upgraded to targeted compounds through hydrogenation and hydrodeoxygenation (HDO). Building on earlier reports, the primary reductive products include oxygen-containing aromatics, phenols, arenes, cycloalkanes, and so on. It is worth noting that the structure of the lignin itself can also influence the product yield and selectivity.[17]
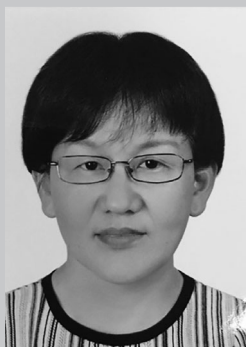
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Lin Dong received his Ph.D. degree in Industrial Catalysis from East China University of Science and Technology (ECUST) in June 2019. At ECUST, under the supervision of Professor Yanqin Wang, he has done research on the design of niobium-based catalysts and their application in the catalytic conversion of lignin to value-added chemicals. He is currently a postdoctoral researcher at ECUST working in the research group of Professor Yanqin Wang.

Yanqin Wang received her BS and MS degrees in Physical Chemistry from Shandong University in 1987 and 1990, respectively. After working as a lecturer at Shandong Normal University (1990–1996), she pursued her study in Peking University and received her Ph.D. degree in 1999. Then, she worked as postdoctoral research fellow at Bar-Ilan University, Israel, Max-Planck Institute of Colloid and Interface Science, Germany, and Max-Planck Institute of Coal Research, Germany. In 2004, she joined East China University of Science and Technology (ECUST) as a full professor. Her current research interests include the design of nano-/mesoporous materials, the synthesis of niobium-based catalysts, and the catalytic conversion of biomass into liquid fuels and fine chemicals.

2.1. Oxygen-containing aromatics from lignin

Due to the preservation of methoxy groups under mild conditions, oxygen-containing aromatics are often produced at low temperatures by a one-step method. These oxygen-containing aromatics include 4-n-propylguaiacol, 4-n-propylsyringol, 4-n-propanolguaiacol, 4-n-propanolsyringol, and other compounds. In 2008, Kou and co-workers[9b] reported that Pd/C catalyst can selectively cleave the aromatic C—O bonds of aryl ethers in the aqueous phase to monomers and dimers, then further transform these monomers and dimers into alkanes by hydrogenation. In fact, palladium-based monometallic or bimetallic catalysts have been widely used for the hydrogenolysis of lignin under mild condition.[18] Interestingly, the product distributions can be tuned by the choice of noble metals. For example, Sels and co-workers[14] reported that changing the catalyst from Pd/C to Ru/C can decrease the OH content of the lignin-derived products, in particular in the phenolic monomers. The different product distributions originate from the low C—O hydrogenolysis activity of Pd/C catalyst, which can retain γ-OH in the side-chain with high selectivity to 4-n-propanolguaiacol and 4-n-propanolsyringol (total up to 91%). In contrast, over Ru/C, the γ-OH in the side-chain was easily removed, leading to 4-n-propylguaiacol and 4-n-propylsyringol (total up to 75%) as the major products (Figure 3) Ruthenium-based catalysts were not only used in the reductive depolymerization lignin[19] but also the upgrading of phenolic monomers and dimers.[20] When applied in reductive lignocellulose fractionation, soluble lignin-derived processable carbohydrate pulps were obtained with almost quantitative retention of the original cellulose and hemicellulose.

Aside from noble metals, some non-noble metals have also been used for the reductive depolymerization of lignin. In particularly, nickel-based catalysts have shown excellent hydrogenolysis activity in lignin depolymerization, with carbon, SiO_2, Al_2O_3, SiC or ZrP as support or Raney Ni as catalyst.[21] Recently, Li and co-workers[22] reported an efficient hydrogenolysis process for organosolv lignin selective decomposition and char elimination over Ni/ZrP.[22] In addition to non-noble catalysts,
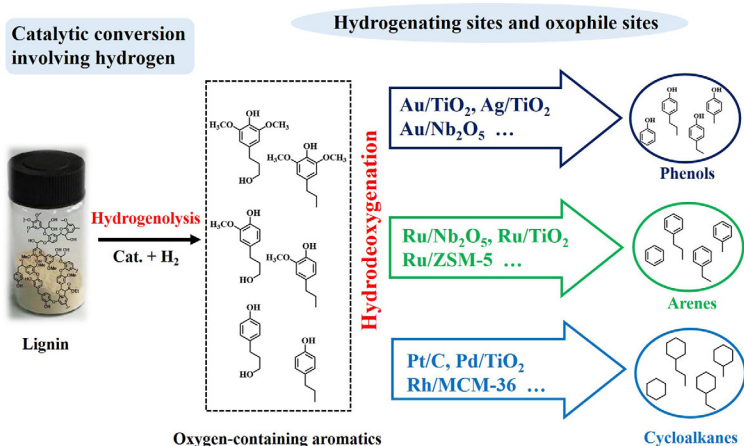
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Figure 1. Reaction network for lignin conversion involving hydrogen.

metal oxide or sulfide catalysts have also attracted increasing attention.[23] Very recently, Zhang and co-workers[23b] developed a ReO$_x$/AC catalytic system that achieves a high yield of aromatic monomers (about 98.0%) from model compounds and up to 80.1% lignin oil with 24.5% yield of monomers from native lignin.

Aside from hydrogen gas, hydrogen can also be derived from hydrogen donors such as formic acid, methanol, ethanol, isopropanol, or lignin itself. In view of the safety and cost of hydrogen gas, the in situ generation of hydrogen with lignin has been extensively studied by using protic solvents as the hydrogen source. For example, Ford and co-workers[24] first demonstrated that the high-efficient hydrogenolysis of lignin can be achieved over copper-based catalyst in supercritical methanol through hydrogen transfer. Subsequently, a Raney Ni catalyst system with isopropanol as hydrogen source was developed.[25] Jae and co-workers further investigated the use of combined Ru/C and MgO/ZrO$_2$ catalysts in supercritical ethanol for depolymerization of lignin through a combination of base-catalyzed solvolysis and metal-catalyzed hydrogenolysis.[26] Very recently, a mild redox-neutral lignin depolymerization system featuring a water-soluble binuclear Rh complex was developed by Wang and co-workers.[27] Interestingly, the hydrogen used here for the cleavage of C—O bonds originated from the alcohol moiety in lignin itself.

Besides one-step reductive depolymerization, two-step strategies have also been developed to achieve high yields of aromatic monomers under mild conditions. One strategy is the oxidation–hydrogenation method, through selective oxidation of C$_\alpha$—OH in lignin to ketones.[28] The selective oxidation of C$_\alpha$—OH to C$_\alpha$=O not only weakens the β-O-4 ether bond but also avoids the hydrogenation method through the selective oxidation of C$_\alpha$—OH in lignin to ketones,[28] as well as the condensation reactions caused by the presence of carbocation.[16a] In 2014, Stahl and co-workers reported a two-step method for the depolymerization of oxidized lignin.[28a] C$_\alpha$—OH was first oxidized to a ketone by using stoichiometric Mn or Cr oxide reagents, followed by formic-acid-induced lignin depolymerization, which resulted in more than 60 wt% yield of low-molecular-mass aromatics. This two-step oxidation–hydrogenation strategy was further developed by Wang and co-workers, who used O$_2$/NaNO$_2$/DDQ/NHPI (DDO = 2,3-dichloro-5,6- dicyano-1,4-benzoquinone; NHPI = N-hydroxyphthalimide) and NiMo sulfide,[28b] CuCl$_2$ and Ru/CeO$_2$,[28c] and Ni/MgAlO-C systems for this transformation.[28d] Additionally, the hydrogen bond in lignin was also broken after preoxidation, greatly facilitating the cleavage of β-O-4 bonds.[29]

Another efficient two-step method was the aldehyde-stabilized hydrogenolysis strategy. In 2016, Luterbacher and co-workers reported that adding formaldehyde during pretreatment of biomass can significantly improve the yield of lignin monomer by avoiding interunit C—C coupling.[5a] In this strategy, formaldehyde hinders the formation of new C—C bonds by forming a stable six-membered 1,3-dioxane structure with 1,3-diols on lignin side-chains, which blocks the formation of benzylic cations, thus preventing repolymerization. Subsequently, the same group further developed other diol protection reagents, such as acetaldehyde and propionaldehyde.[30] The subsequent hydrogenolysis catalyzed by Pd/C generated lignin monomers at near-theoretical yields based on Klason
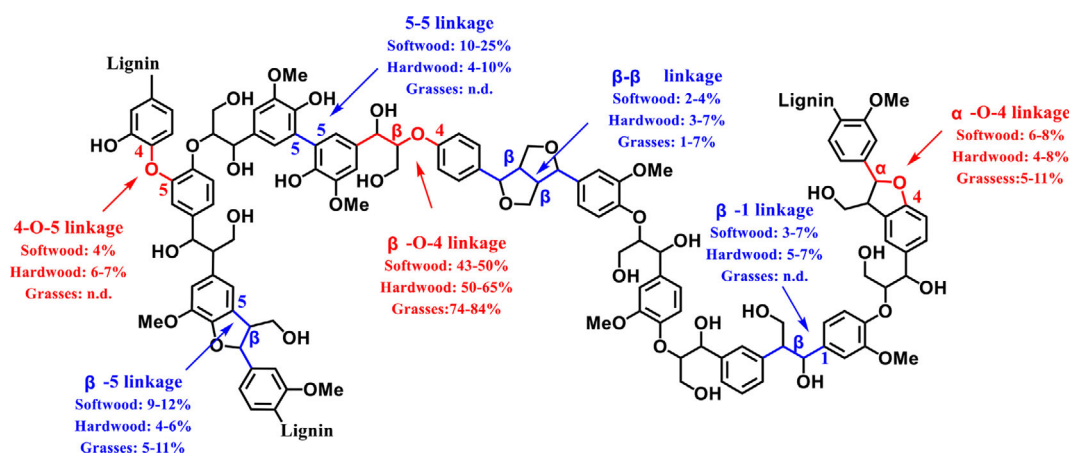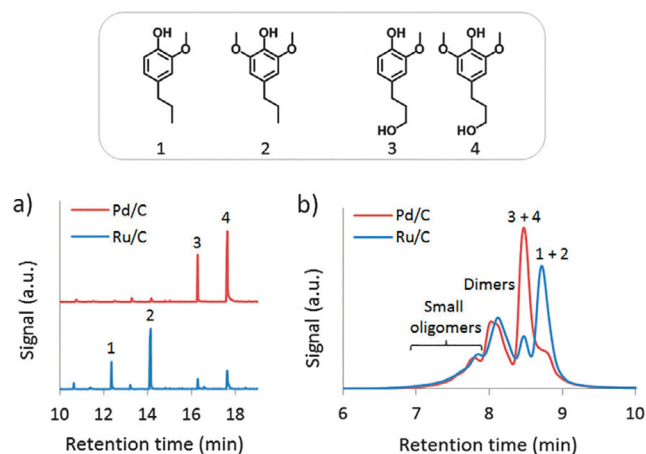

Figure 2. Representative structure of a fragment of lignin and proportions of the various linkages.

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Figure 3. Comparison of the lignin products after Ru/C- and Pd/C-catalyzed processing of birch wood in MeOH. a) Peak identification of the monomers by GC-MS. b) Molecular weight distribution of the "lignin oil" by gel permeation chromatography (GPC). Reprinted from Ref. [14] with permission from the Royal Society of Chemistry.

lignin, and with high selectivity to a single 4-*n*-propanol-syringol product (80%) in the case of the transgenic hybrid poplar.

2.2. Arenes from lignin

The products obtained from the above reductive approaches are a wide range of oxygen-containing aromatics, and sequential upgrading processes are required to convert them into simple fine chemicals or fuels. Therefore, one-pot valorization of raw lignin to hydrocarbons by combining depolymerization and hydrodeoxygenation represents an interesting challenge.[31] In 2017, Wang and co-workers[31a] reported the first selective production of arenes by direct hydrodeoxygenation of lignin over Ru/Nb$_2$O$_5$ catalyst, which enabled complete removal of the oxygen content (Figure 4A). Further study showed that a layered Nb$_2$O$_5$-supported Ru catalyst with more Nb=O groups (unsaturated NbO$_x$ sites) and higher Ru dispersion had very high activity and arene selectivity.[32] Very recently, a new multifunctional Ru/NbOPO$_4$ catalytic system was used for the catalytic cleavage of both interunit C−C and C−O bonds in one-pot lignin conversions and yielded 124–153% of monocyclic hydrocarbons based on the NBO method (Figure 4B).[33] The superior activity of the Ru/NbOPO$_4$ catalyst originates from a combination of strong adsorption, a synergistic effect between Ru and NbO$_x$ species, and the acid sites on the catalyst, which all work together to selectively cleave the inter-ring C−C linkages and C−O bonds.
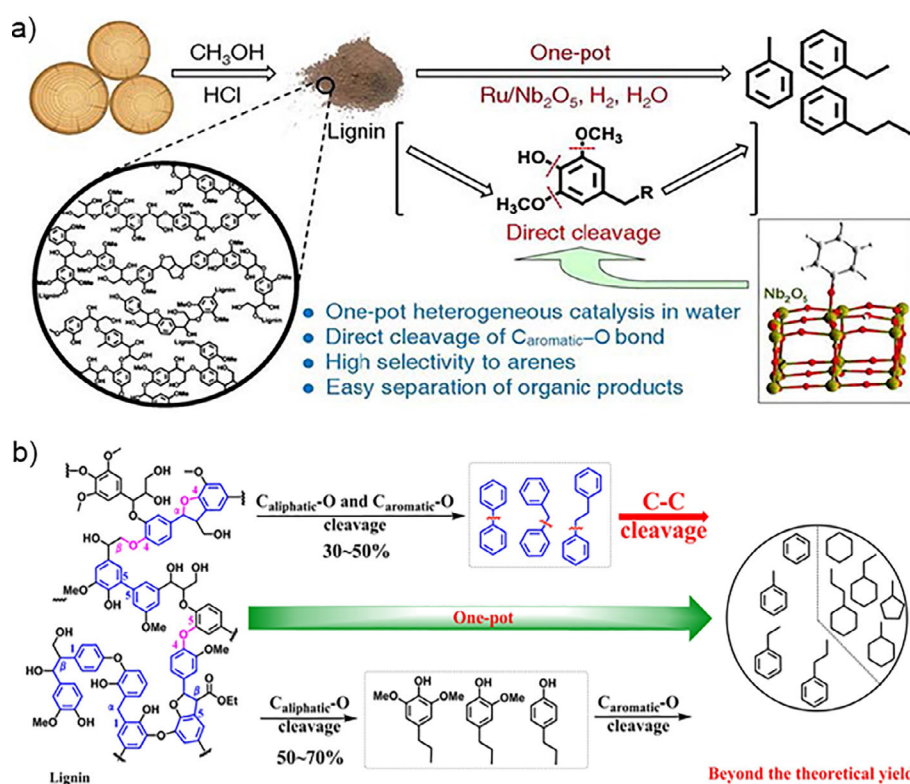
Figure 4. a) The conversion process from lignin to arenes via C−O bonds cleavage over Ru/Nb$_2$O$_5$. b) One-pot depolymerization and hydrodeoxygenation of lignin into monocyclic aromatic hydrocarbons via both C−O and C−C bond cleavage over Ru/NbOPO$_4$. Reprinted from Refs. [31a] and [33] with permission from Springer–Nature and Cell Press, respectively.

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3. Upgrading of Lignin-Derived Monomers

Lignin-derived monomers can be obtained by breaking the interunit C—O and C—C linkages in native lignin and consist of a phenolic body, substituted with one or two *ortho*-methoxy groups and a *para*-hydroxypropyl group. Most of the monomeric compounds obtained by depolymerization methods cannot be directly used as value-added chemicals and need to be further upgraded by various transformations.[3b,d,4a,d] Strategies for monomer upgrading are mainly focused on the hydrodeoxygenation process. The hydrodeoxygenation process, including saturation of the aromatic rings and cleavage of C—O and C—C bonds, holds promise for synthesizing value-added chemicals, such as cycloalkanes, arenes, and phenol. Some studies have targeted the catalytic production of cycloalkanes through deep hydrodeoxygenation of lignin or its constituent monomers.[9b, 31d] The obtained cycloalkanes can be used as transportation fuels. However, deep hydrodeoxygenation eliminates the inherent aromatic properties of lignin or its constituent monomers with the penalty of hydrogen consumption. Therefore, breaking the C—O bond while preserving the aromatic ring for arene preparation has received considerable attention. Moreover, arenes can be added to transportation fuel to increase heating values and prevent the leakage of fuel through promoting the shrinkage of aged elastomer seals. Generally, the obtained arenes consist of three alkylbenzenes, namely toluene, ethylbenzene, and propylbenzene. Among them, ethylbenzene is a key intermediate for the production of styrene, widely used as a precursor of plastics, and its catalytic production through dehydrogenative decarbonylation of *para*-hydroxypropyl groups is worth considering. Aside from production of cycloalkanes and arenes, selectively cleaving the methoxy groups and a *para*-side-chain group in lignin-derived monomers to obtain phenol is another attractive option, since phenol is one of the most important aromatic compounds in the field of fine chemicals.

To gain a fundamental understanding of the catalytic mechanism, researchers have conducted extensive studies by using model phenolic compounds produced by depolymerization of lignin, such as cresol, phenol, guaiacol, and 4-propylguaiacol. Cresol and phenol, incorporating two typical groups of lignin, namely the aromatic ring and phenolic hydroxy group, are used usually to as model compounds to investigate the reaction mechanism in the HDO of lignin to arenes and cycloal-kanes because of their extremely simple structure. Guaiacol and 4-propylguaiacol are generally employed as prototype molecules to represent lignin-derived monomers to study the selective removal of the methoxy groups and a *para*-side-chain group.

3.1. Arenes and cycloalkanes

Starting from lignin and lignin model compounds, the syntheses of arenes and cycloalkanes are generally considered connected and competitive reactions.[5d, 34] A key objective during the process is to maximize the selectivity to arenes or to cycloalkanes. Compared with the cycloalkane production, arene production is more attractive, since it preserves the inherent aromatic properties of lignin with less consumption of the hydrogen source.[5c, 35] Moreover, as mentioned above, arenes show higher densities and volumetric heating values than chain alkanes and are needed to prevent fuel leakage. The design of catalytic systems for production of arenes is more challenging than for that of cycloalkanes. Herein, we mainly focus on arene production from the point of view of the catalyst and reaction mechanism and give a brief mention for the synthesis of cycloalkanes.

Immense attention has been paid to the development of heterogeneous catalysts for the removal of phenolic hydroxy groups, owing to its having the strongest bond energy among all C—O bonds within lignin.[36] The biggest challenge on this topic, which is driven by the evident competition between excessive hydrogenation of the aromatic rings and cleavage of phenolic hydroxy groups, is to develop state-of-the-art catalytic systems that can cleave the phenolic hydroxy groups while preserving the aromatic rings.[28d, 37]

3.1.1. Reaction pathway

Three reaction mechanisms (Scheme 1) for the conversion of phenols into aromatic hydrocarbons have been demonstrated.[38] The first one is the direct hydrogenolysis (DDO) of phenolic hydroxy groups to arenes.[32b, 39] The DDO pathway is most likely to occur at step sites for a Ru-based catalyst. Moreover, a reducible metal oxide support may contribute to deoxygenation by a DDO mechanism at an oxygen defect site. The second pathway involves three tandem steps (HYD) including hydrogenation to cyclohexanol or cyclohexanone, then dehy-
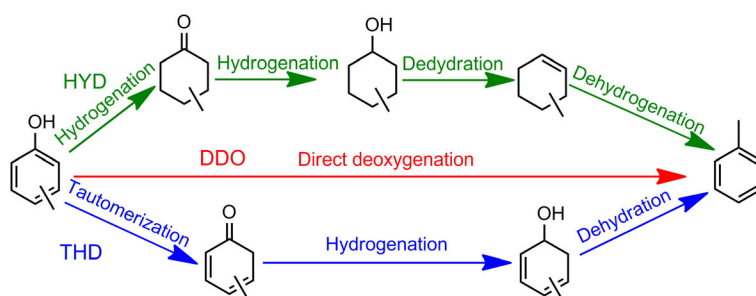
Scheme 1. The reaction pathway for the conversion of cresol into toluene.

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dration to cyclohexene, and finally dehydrogenation to aromatic hydrocarbons.[40] The third way is proposed to proceed via a tautomerization route, followed by C=O bond hydrogenation to cyclohexadienol and finally dehydration to generate arenes (THD).[41] This pathway contains a keto-enol tautomerization, which occurs between the hydroxy group and the adjacent C=C on the aromatic ring. These three parallel pathways are usually affected by various factors, including reaction conditions (temperature and hydrogen pressure), hydrogenation activity of the metal, and role of support and the first two pathways, namely DDO and HYD, are relatively common.[42] These two pathways can occur concurrently at relatively low temperature, whereas a higher temperature favors the DDO route.[43] This is because a relatively low temperature is thermodynamically beneficial for hydrogenation of aromatic ring, causing the loss of the aromaticity.[31b, 40b] The DDO route is more desirable since the cyclohexene immediate of the HYD pathway easily undergoes deep hydrogenation to cyclohexane, resulting in the loss of inherent aromaticity. Moreover, hydrogenation of the aromatic ring is accompanied by the penalty of additional hydrogen consumption. The pressing need is hence to develop state-of-the-art catalytic systems to promote the DDO route but prevent the HYD route in kinetics at relatively low temperature. Ru/Nb-, Ru/Ti-, and Ru/Mo-based catalysts, for example, were developed to meet the pressing need, which is discussed in more detail below. In addition, a lower hydrogen pressure favors the DDO pathway, whereas a lower hydrogen pressure results in a low conversion of the substrate.[43a,b]

Although the removal of phenolic hydroxy groups has been intensively explored over the past decade, the global interest in this topic started from the pioneering works of Delmon and co-workers.[44] Early studies on the removal of phenolic hydroxy groups used the catalyst systems for hydrodesulfurization for reference. Sulfided metal catalysts, especially sulfided Mo-based catalysts, are active in producing aromatics,[38a, 44, 45] but face challenges owing to the loss of sulfur and generation of coke. Although the continuous introduction of sulfur sources can overcome the challenge, it is inevitable to cause sulfur contamination in the environment. To address these problems, Mo- and W-based catalysts were reported for the hydrogenolysis of phenols, but required relatively harsh reaction conditions.[23c, 43c, 46] Subsequent studies mainly focused on the development of supported non-sulfide metal catalysts, with hydrogenation and oxophilic sites. Generally, noble metals such as

Ru, Pt, Pd, and Rh can serve as hydrogenation sites and have been widely used in the total cleavage of C—O bonds in lignin, because of relatively strong hydrogenation activity. Hence, these metals form the subject of the following section on the total cleavage of C—O bonds. Other metals (e.g., Au, Ni, Ag) that contributed to the removal of the methoxy groups will be discussed in the section on phenol production.

### 3.1.2. Role of metals

3.1.2.1. Ru-based catalysts

Good hydrogenation performance is highly desired to maximize arene selectivity.[47] A generally agreed proposition is that Ru has satisfactory hydrogenation activity, leading to high arene selectivity and medium conversion of lignin or its derivatives.[3a] Hence, many Ru-based catalysts have been developed for this reaction, including Ru-WO$_x$/SiAl, Ru/Nb$_2$O$_5$, Ru/TiO$_2$, Ru/HZSM-5, Ru/MCM-41, Ru/C, and bimetallic RuNi catalyst (Table 1).[48] Among these Ru-based catalysts, Ru/Nb-based catalysts not only show high selectivity to aromatic hydrocarbons, but also enable the direct conversion of native lignin into arenes, which will be discussed in detail in the following section. Interestingly, three completely different pathways for the hydrodeoxygenation of phenol over Ru/Nb$_2$O$_5$, Pd/Nb$_2$O$_5$ and Pt/Nb$_2$O$_5$ were proven by experimental and vibration spectroscopy analysis.[31a,d] When Ru/Nb$_2$O$_5$ was used as catalyst, the direct cleavage of C—O bonds was overwhelming, owing to a combination of strong adsorption, selective activation of the phenolic hydroxy groups, and a synergistic effect between the Ru and NbO$_x$ species, leading to a distinct selectivity to arenes.[31a] In contrast, with Pd/Nb$_2$O$_5$, the aromatic ring saturation shows higher selectivity than the direct hydrogenolysis of C—O bonds because of stronger bonding of the aromatic ring with the catalyst surface and the higher hydrogenation ability of Pd than that of Ru. Over Pt/Nb$_2$O$_5$, a combination of a direct dehydroxylation and a tandem route with fast kinetics results in a higher arene selectivity than that over Pd/Nb$_2$O$_5$ at the beginning of the reaction.[31d] Even so, the arene selectivity over Pt/Nb$_2$O$_5$ is still lower than that over Ru/Nb$_2$O$_5$, owing to its stronger hydrogenation activity.

By controlling the hydrogenolysis ability of Ru, the hydrodeoxygenation product distributions of lignin and its derivatives can be completely different. Ru particle sizes, modification of Ru and Ru-based bimetallic catalyst for improving the

Table 1. Overview of the hydrodeoxygenation of lignin and lignin model compounds over various Ru-based catalysts.

Feedstock	Conv. [%]	Catalyst	Reaction conditions	Major product	Sel./yield [%]	Ref.
organosolv lignin	100	Ru/Nb$_2$O$_5$	0.1/15 g mL^{-1} in H$_2$O, 250 °C, 0.7 MPa H$_2$, 20 h	arenes	59.5 (wt)	[31a]
enzymatic lignin	100	Ru/Nb$_2$O$_5$-L1	0.1/10 g mL^{-1} in H$_2$O, 250 °C, 0.7 MPa H$_2$, 10 h.	arenes	85 (S)	[32a]
phenol	30	Ru/TiO$_2$	5 g, ~10 wt% in H$_2$O, 300 °C, 45.8 bar H$_2$, 1 h	benzene	95 (S)	[38b]
p-tert-butylphenol	100	Ru-WO$_x$/SiAl	1/12 mmol mL^{-1} in H$_2$O, 270 °C, 2 MPa H$_2$, 2 h	*tert*-butylbenzene	81 (S)	[39]
phenol	100	Ru/Nb$_2$O$_5$-C	0.05/15/5 g mL^{-1} mL^{-1} in decalin/H$_2$O, 250 °C, 2 bar H$_2$, 4 h	benzene	80 (S)	[40b]
phenol	≈72	Ru/MCM-41	5/20 g mL^{-1} in H$_2$O, 280 °C, 0.265 mol formic acid, 1 h	cyclohexane/benzene	≈44/≈15 (Y)	[48a]
Guaiacol	100	Ru/HZSM-5	0.2/100 g mL^{-1} in H$_2$O, 240 °C, 2 bar H$_2$ and 6 bar N$_2$, 1 h	benzene	≈95 (Y)	[42a]
guaiacol	100	Ru/SiO$_2$-Al$_2$O$_3$	7.5 wt% in decane, 250 °C; 4 MPa; 1 h	cyclohexane	60 (Y)	[49]
guaiacol	100	Ru/TiO$_2$-ZrO$_2$	3 wt% in dodecane 260 °C; 2 MPa; 6 h	benzene/cyclohexane	≈45/≈33	[50]

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arenes selectivity and the lignin conversion have been taken into consideration.[31c, 48c, 51] Smaller Ru particles (1.2 and 1.8 nm) loaded onto NbOPO$_4$ support had high activity and favored the production of aromatic compounds, owing to their lower barriers for the cleavage of both C$_{aromatic}$—O and C$_{aliphatic}$—O bonds, which was further confirmed by DFT calculations.[31c] A similar Ru size effect was also observed for the conversion of anisole into benzene when TiO$_2$ was used as as support.[48c] Interestingly, weakening the hydrogenolysis ability of Ru through the strong interaction brought about by decoration with CH$_2$Cl$_2$ favors another parallel route, namely the intramolecular cyclization reaction, rather than the direct hydrogenolysis of hydroxypropyl groups, affording a high yield of indane and its derivatives.[51a] By introducing Ni into Ru, the selectivity and activity for the C—O bond cleavage of guaiacol were markedly enhanced and the adjustment of the H radical transfer length between Ru and Ni nanoparticles is responsible for the selective hydrogenolysis steps (Figure 5).[51b] In short, the above strategies are of significance for controlling the hydrogenation ability of Ru and the product distribution from lignin.
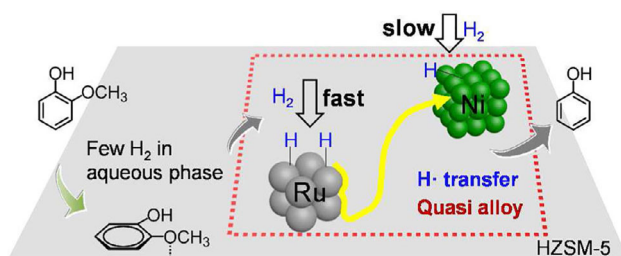
Figure 5. Proposed mechanisms for C—O hydrogenolysis of guaiacol over Ni/HZSM-5 and RuNi/HZSM-5. Reprinted from Ref. [51b] with permission from the American Chemical Society.

3.1.2.2. Pt-, Pd-, and Rh-based catalysts

Pt, Pd, and Rh, as common hydrogenation/hydrogenolysis catalysts, have been intensively investigated for the hydrodeoxygenation of lignin and lignin model compounds over the past decade.[52] In contrast to Ru-based catalysts, hydrodeoxygenation catalysts involving Pt, Pd, and Rh are generally favorable for the saturation of aromatic rings instead of the removal of phenolic hydroxy groups, giving a high yield of cycloalkanes because of their strong hydrogenation activity.[9b, 31a,d, 53] M/Nb$_2$O$_5$ (M = Ru, Pt, or Pd) catalysts, as discussed above for the hydrodeoxygenation of lignin and lignin model compounds, are known to show hydrodeoxygenation mechanisms, which result in different product distributions.[31a,d] However, the hydrodeoxygenation activity of Pt, Pd, and Rh strongly depends on the supports. The interaction of the metal M (Pt and Pd) and the Lewis acidic support was proven to be the key for the hydrodeoxygenation of biomass-derived compounds.[54] For instance, Pd enables hydrogen spillover to partially reduce Ti^{4+}, causing a highly hydrodeoxygenation reaction-sensitive TiO$_x$ species.[54e] In addition, the phase, pore structure, and acid site numbers of the support accordingly affect the hydrodeoxygenation activity in lignin model compounds conversion.[53e, 55]

For example, when using Rh as the active metal, it is found that Rh/MCM-36 has the highest Rh dispersion among Rh catalysts supported on zeolites, including MCM-22(C), MCM-22(SC), and MCM-36, mainly contributing to a high hydrodeoxygenation activity. In addition, quantity of acid sites and mass transfer of reactants and products at the mesopores are also responsible for the overall activity.[56] When Pd and Pt were employed as the hydrogenation site, the dispersion of Pd and Pt nanoparticles influenced by support (ZSM-5 and TiO$_2$) also dramatically affects the product selectivity.[54f, 55a] However, owing to the relatively high expense and rarity of Rh, the application of Rh-based catalysts is relatively limited compared with that of Pd or Pt.

3.1.2.3. Non-noble metal-based catalysts

Non-noble metals, such as Ni, Fe, Cu, and Co, have been found to be efficient for the catalytic decomposition of lignin and lignin model compounds. Among these non-noble metals, Ni-based catalysts have drawn considerable attention because of their excellent performance in hydrogenation chemistry, but usually favors the saturation of aromatic ring. For example, a series of Ni-based catalysts, including Ni/AC,[57] Ni/ZrO$_2$,[58] Ni/SiO$_2$,[21d] and Ni/α-Al$_2$O$_3$,[59] have been developed for the hydrogenolysis of lignin and exhibit high catalytic activity. Owing to its strong hydrogenation activity, the major hydrodeoxygenation products are cycloalkanes, rather than arenes. To obtain high selectivity to arenes over Ni-based catalysts, weakening the hydrogenation activity of Ni by modification with other metals has proven a promising method. Bimetallic Re-Ni/ZrO$_2$ catalysts were found to improve the selectivity to arenes greatly in the conversion of 4-propylphenol or m-cresol.[60] The addition of Re to the Ni-based catalyst forms surface Ni—Re alloy and electron deficiency in the Ni d-band, thus weakening the adsorption of phenyl rings on the surface. When Fe is used to modify Ni-based catalysts, a similar product distribution was obtained.[61] Over bimetallic Ni-Fe/SiO$_2$ catalyst, the hydrogenation of a keto tautomer intermediate can be greatly enhanced, resulting in a cyclodiene alcohol that is readily dehydrated to give the aromatic hydrocarbon. Moreover, Ni$_2$P/SiO$_2$ catalyst also showed excellent hydrodeoxygenation ability in the conversion of lignin model compounds.[62] The active site of Ni$_2$P catalysts is composed of threefold hollow Ni and P sites, which lead to adsorption of H or OH groups. Although Ni-based catalysts are considered promising for the HDO of lignin, stabilization remains a big challenge and the poor stability limits their industrial application. Ni particles may suffer from leaching, sintering, and/or being oxidized, causing deactivation. Regarding Ni-based catalysts, future study should focus on improving the stability. Compared with Ni-based catalysts, Fe-, Cu-, and Co-based catalysts are beneficial for the production of arenes through DDO pathway. Fe, Cu, and Co are usually used as a second component to form bimetallic catalysts, but also play key roles in the HDO, especially for the tuning of geometric and electronic structures of the active metal. For example, introducing Fe into Pd-based catalysts significantly enhances their catalytic performance for the HDO of phenol to arenes

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because of the preferential adsorption and activation of phenol on Fe species, avoiding hydrogenation of the aromatic ring on Pd species.[40a, 41a] Although non-noble metal-based catalysts have shown some success in the conversion of lignin model compounds, unlike noble metals catalyst, the success of non-noble metals-based catalysts in directly converting native lignin into arenes and cycloalkanes is still at the proof-of-concept stage and future studies should be devoted to developing the direct transformation of native lignin over non-noble metals.

3.1.3. Role of supports

Aside from the metal hydrogenation sites, acidic supports with strong oxygen affinity are also critical for the removal of phenolic hydroxy groups.[63] In this respect, high-valence and strong Lewis-acidity metals, such as Ti, Mo, Nb, Re, and W, are desirable candidates for the oxophilic sites.[64] In particular, Ti-, Mo-, and Nb-based catalysts have achieved considerable attention for the hydrodeoxygenation of lignin and lignin model compounds and this section mainly presents an overview of Ti-, Mo-, and Nb-based catalysts for the removal of phenolic hydroxy groups, demonstrating their catalytic properties and mechanisms.

3.1.3.1. Ti-based catalysts

The influence of the support properties on hydrodeoxygenation product distribution is of significance. For instance, various Ru-loaded mesoporous supports including TiO_2, Al_2O_3, SBA-15 and P25 presented different hydrodeoxygenation pathways.[48c] Ru/Al_2O_3 and Ru/SBA-15 were found to promote the hydrodeoxygenation reaction via the HYD pathway, whereas Ru/TiO_2 and Ru/P25 showed a preference for the DDO pathway (Figure 6). Compared with Ru/Al_2O_3 and Ru/SBA-15, the deficient Ti^{3+} sites or oxygen vacancies play a key role in the DDO pathway;[48c] that is, unsaturated TiO_x species have strong activation ability for C−O bonds, which is also confirmed for Nb-based catalyst systems.[32a,b, 65] The Ti-based catalyst also showed higher activity than Ru/Al_2O_3, Ru/C, and Ru/SiO_2 in the hydrodeoxygenation of phenol, owing to defect sites created by hydrogen spillover.[48b] Based on the efficient performance

of Ti-based catalysts, some mixed supports containing TiO_x species were designed to push the development in this field.[50] Aside from the outstanding performance for phenolic hydroxy groups, Ti-based catalysts were also developed for the hydrodeoxygenation of guaiacol to phenol, which will be discussed in detail below.

3.1.3.2. Mo-based catalysts

Conventional Mo-based catalysts, such as MoS_2, $NiMoS_2$, and $CoMoS_2$, have shown great potential and attracted significant attention.[38a,44a, 66] MoO_3 is regarded as a cost-effective catalyst and even in the absence of any noble metals showed exceptional selectivity to unsaturated hydrocarbons among various catalysts (MoO_3, V_2O_5, Fe_2O_3, CuO, and WO_3).[35a, 67] Oxygen vacancies on unsaturated MoO_x (mainly Mo^V) species are generally considered as the origin of high hydrodeoxygenation activity over Mo-based catalysts.[67, 68] The energy profiles for oxygen vacancy site generation on a simulated molybdenum oxide surface are shown as Figure 7 and the partially reduced MoO_3 species reduces the C−O bond energy through strong adsorption.[67] With MoO_3 species dispersed over SiO_2, Al_2O_3, TiO_2, ZrO_2, and CeO_2, all Mo-based catalysts selectively break C−O bond while preserving the aromatic ring. The catalytic activities of the different Mo-based catalysts depend strongly on the reducibility of surface MoO_x and the electronegativity of the support.[35b] The above studies demonstrate Mo-based catalysts indeed are promising for hydrodeoxygenation of lignin and lignin model compounds. However, Mo-based catalysts are easily deactivated by coke formation, reduction of active MoO_x species, and water poisoning in the hydrodeoxygenation reaction.[35b,67,68b, 69] Hence, further research should focus on improving the stability of Mo-based catalysts and developing targeted methods to overcome the challenge of deactivation.

3.1.3.3. Nb-based catalysts

With Ru serving as the hydrogenating sites, Nb-based catalysts have shown exceptional activity and selectivity for arene production from lignin and its model compounds and the catalytic sites have been systematically investigated.[31a,40b, 70] A porous Ru/Nb_2O_5 catalyzed the conversion of organosolv lignin into
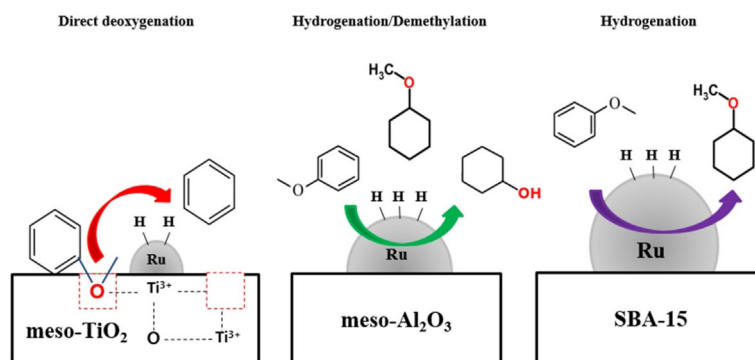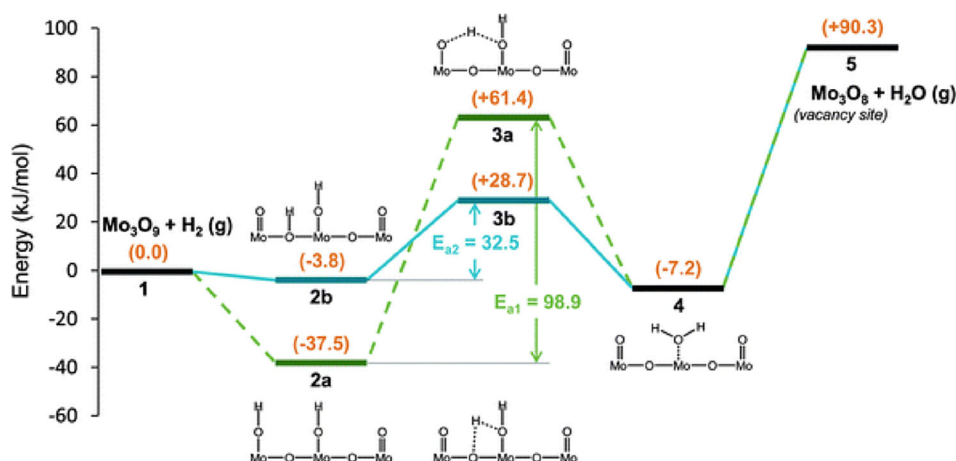

Figure 6. Hydrodeoxygenation mechanisms for anisole depending on Ru particle size. Reprinted from Ref. [48c] with permission from Elsevier.

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Figure 7. Energy profiles for oxygen vacancy site generation on a simulated molybdenum oxide surface. Reprinted from Ref. [67] with permission from the Royal Society of Chemistry.

arenes with high selectivity and the Nb_2O_5 support enables selective activation of the phenolic hydroxy groups, resulting in significant reduction of the disassociation energy for phenolic hydroxy groups.[31a] This unique oxygen affinity was also evident in other C—O bond cleavage reactions, especially in the cleavage of the tetrahydrofuran ring and C=O bond activation to give the enolate intermediate, leading to the excellent hydrodeoxygenation and aldol condensation performance of the Nb-based catalyst.[71] The activation behaviors of 4-methylphenol, tetrahydrofuran, and acetone over Nb-based catalysts were clearly shown by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS; Figure 8).[31a,32a,54a,71a] The adsorption and binding of phenol molecules on the Nb_2O_5 (001), ZrO_2 (010), Al_2O_3 (110), and TiO_2 (101) surfaces further confirm that, among these oxides, Nb_2O_5 has strong adsorption of phenol and low disassociation energy of $C_{aromatic}$—OH bonds (Figure 9).[31a] Subsequent investigations, including those of metal size effects, electronic effects, and Nb_2O_5 surface properties, revolved around the activation of the phenolic hydroxy groups over Nb-based catalysts.[31c,32a,72] As previously mentioned, the size of the Ru nanoparticles strongly affects the lignin hydrogenolysis activities and product distributions.[31c,32a] For a more elaborate discussion on the electronic effect involv-

ing Nb-based catalysts, the reader is referred to the later chapter on phenol production (Section 3.2). The exploration of the relationships between Nb_2O_5 surface properties and its catalytic performance in hydrodeoxygenation of lignin and its derivatives reveals that the coordination states of Nb (NbO_x sites) affect the catalytic activity, while Ru nanoparticles size is responsible for the product selectivity.[32a,b] More unsaturated NbO_x species show stronger adsorption and activation ability for C—O bonds, thus promoting the hydrodeoxygenation of lignin-derived compounds and furanic oxygenates.[32a,b,65] Based on the unique activation ability for the phenolic hydroxy groups, a simple Ru-loaded niobium oxide dispersed in silica was prepared to convert lignin model compounds and native lignin into aromatic hydrocarbons by hydrogen transfer reactions with 2-PrOH as a hydrogen donor.[31b]

Although Mo-based catalysts can catalyze the hydrodeoxygenation reaction to afford arenes without hydrogenating metal sites because of their unique crystal structures and oxidation states, harsh reaction conditions and the aforementioned deactivation behaviors limit their application. Ru/Ti-based and Ru/Nb-based catalysts can overcome the above problems mentioned for Mo-based catalyst systems. The ultimate aim in this field is to directly convert native lignin into
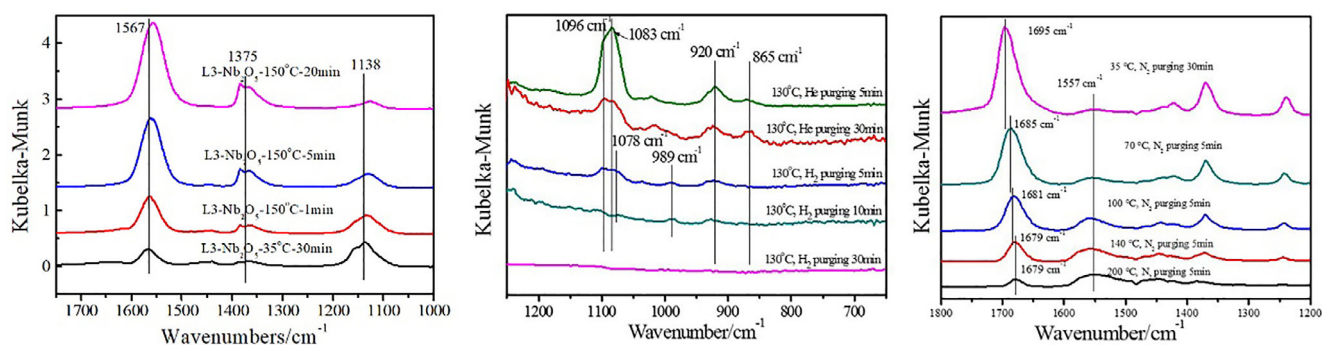
Figure 8. DRIFTS analysis to monitor the changes in 4-methylphenol (left), tetrahydrofuran (middle), and acetone (right) adsorption and conversion. Reprinted from refs. [32a] and [71] with permission from Elsevier.

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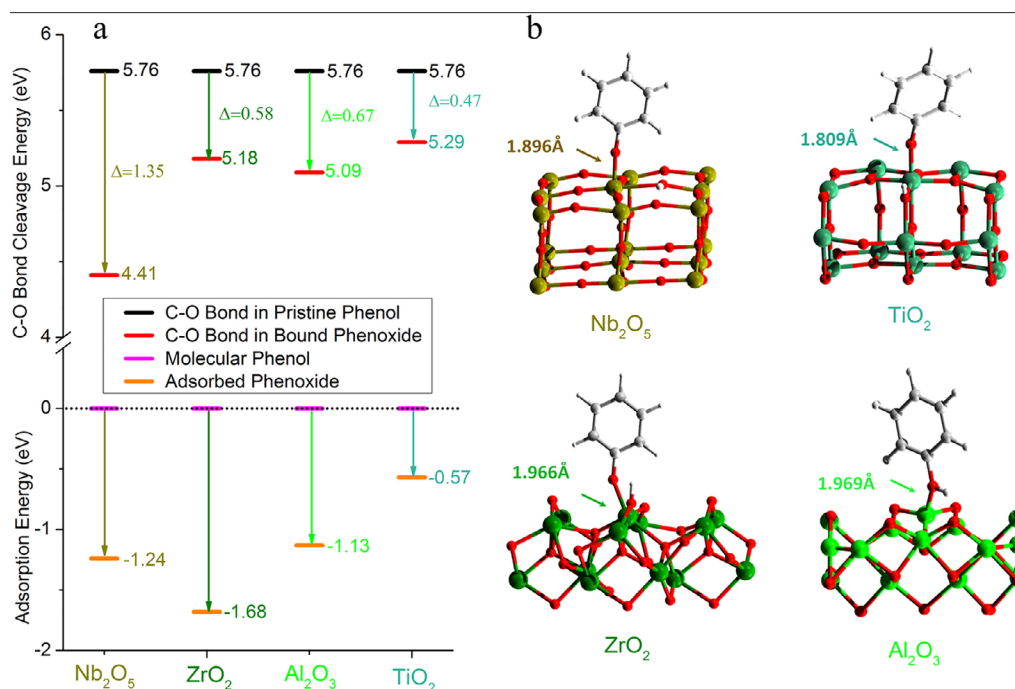
Figure 9. Calculated energies and views of the optimized structural models for phenol binding on catalyst surfaces. a) Calculated energies for phenol adsorption (combination of deprotonation of $C_{aromatic}$—OH to form phenoxide bound to the vacant surface metal sites and formation of surface OH groups and disassociation of the C—O bonds upon adsorption over Nb_2O_5, ZrO_2, Al_2O_3 and TiO_2). b) Views of the corresponding DFT-optimized structural models for the phenoxide bound on Nb_2O_5 (001), ZrO_2 (010), Al_2O_3 (110), and TiO_2 (101) surfaces. Reprinted from Ref. [31a] with permission from Springer–Nature.

arenes, rather than just lignin model compounds. In this respect, Nb-based catalysts have more obvious advantages than Ti-based catalysts and other supported Ru catalysts, such as Ru/ZrO_2, Ru/Al_2O_3, Ru/H-ZSM-5, and Ru/C.[31a, 32a,b] Both organosolv lignin and enzymatic lignin, as two typical native lignins, were directly converted into arenes with high selectivity over Nb-based catalysts.[31a, 32b] The reaction pathway of lignin model compounds over Nb-based catalysts is totally different from that over other supported Ru catalysts, but was not reported to date. Unpublished results from our group on the time course of phenol hydrodeoxygenation over $Ru/NbOPO_4$, Ru/TiO_2, Ru/C, and Ru/Al_2O_3 with the same Ru particle size, clearly reveal the difference (Figure 10). Over $Ru/NbOPO_4$, the reaction undergoes rapid DDO to give benzene in 2 h and the generated benzene is hardly converted into cyclohexane by hydrogenation with increased reaction time, whereas over Ru/C, phenol is first hydrogenated into cyclohexanol, then undergoes hydrogenolysis to cyclohexane. In addition, direct hydrogenolysis to benzene and saturation of the aromatic ring to cyclohexanol can occur concurrently over Ru/TiO_2 or Ru/Al_2O_3 catalysts at the beginning of the reaction. By further prolonging the reaction time, Ru/TiO_2 favors dehydration of cyclohexanol to cyclohexene, then dehydrogenates to give benzene, whereas Ru/Al_2O_3 is beneficial for the hydrogenolysis of cyclohexanol to cyclohexane. In short, $Ru/NbOPO_4$ shows the strongest activity of direct hydrogenolysis among various supported Ru catalysts, affording exceptional selectivity to arenes, in accordance with previous reports.[31a, 32a,b]

3.1.4. Synergistic effects between metal and support

In addition to the direct influences of metal and support, synergistic effects between them are also crucial for the direct cleavage of the $C(sp^2)$—O bonds.[3b, 31a, 39] The co-impregnation method was found to be beneficial for the intimate contact between hydrogenating Ru sites and Lewis acidic W sites, accordingly promoting the removal of O atoms chelated with Lewis acidic W sites with the help of the adjacent hydrogenation sites.[39] A mechanically blended Ru—Nb catalyst proved less active for the direct cleavage of $C(sp^2)$—O bonds than Ru/Nb_2O_5 prepared by incipient wetness impregnation method, which further supports the key role of a synergistic effect between hydrogenating Ru sites and acid sites with strong oxygen affinity.[31a] Understanding the interaction of metal and acid sites with strong oxygen affinity is of importance for the development of highly efficient hydrodeoxygenation catalysts.[73] The interaction of metal and support was named as the "intimacy criterion", whereby, beyond a maximum distance between metal and support, the catalytic performance will significantly decrease.[74] In this respect, employing surface-sensitive characterization methods to understand the real surface structure and change during catalytic process becomes the best way. The aforementioned studies also intensified interest in the development and preparation of Ru-loaded Nb-based catalysts, and Ru/Nb_2O_5-SiO_2 and Ru/Nb_2O_5-C were recently prepared for the hydrodeoxygenation of lignin and lignin model compounds.[31b, 40b] In addition, the importance of the interfaces between hydrogenating sites and Lewis
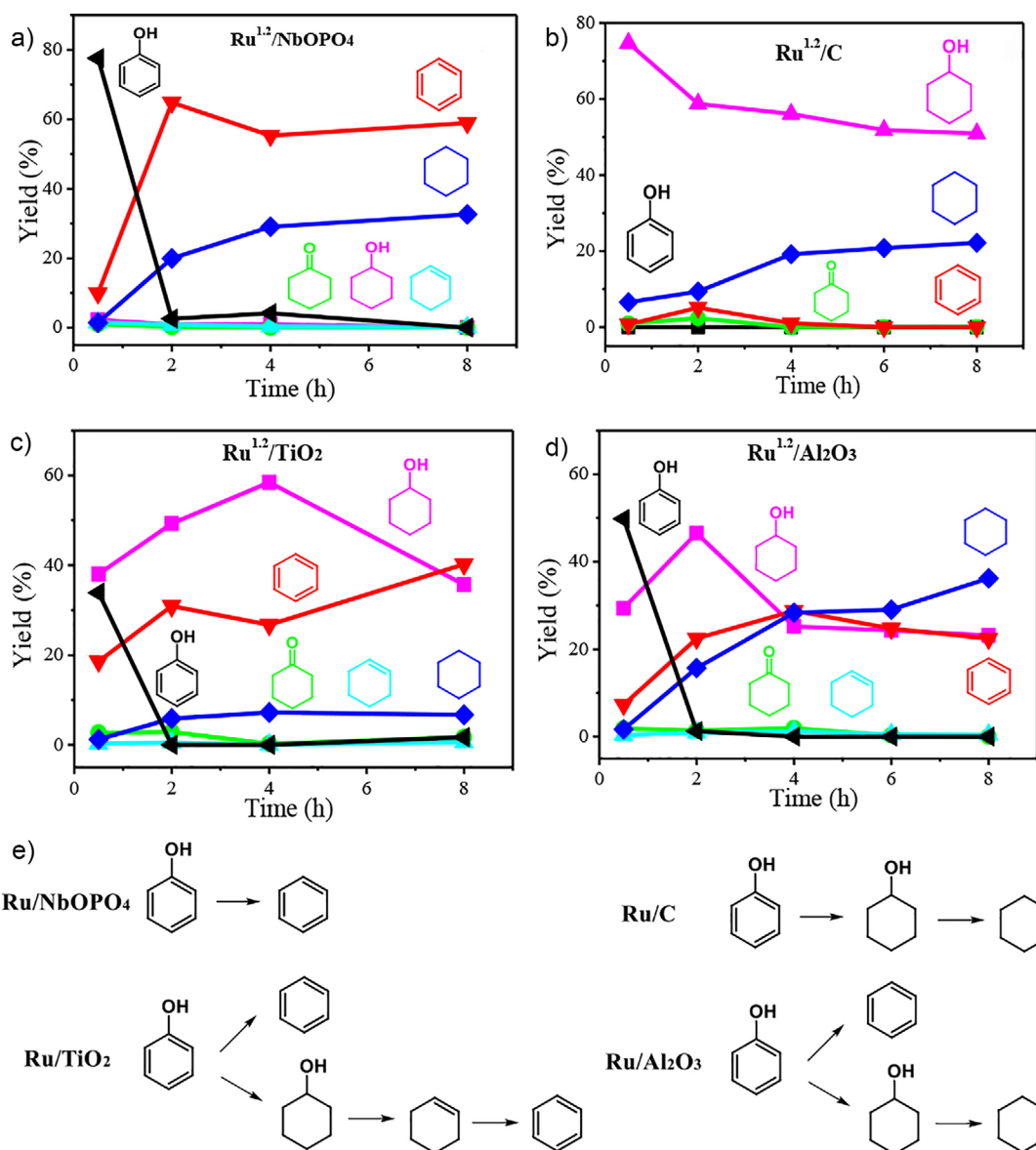
Figure 10. a–d) The time courses of the phenol hydrodeoxygenation catalyzed by $Ru^{1.2}/NbOPO_4$ (a), $Ru^{1.2}/TiO_2$ (b), $Ru^{1.2}/C$ (c), and $Ru^{1.2}/Al_2O_3$ (d) (1.2 represents the average particle size of Ru nanoparticles (1.2 nm)). Reaction conditions: catalyst (0.05 g), substrate (0.1 g), deionized water (14 mL), 230 °C, initial H_2 pressure 0.5 MPa. e) Reaction scheme of phenol hydrogenolysis over various supported catalysts.

sites was also proposed and H_2 undergoes heterolytic cleavage to form an active site at the interface sites when water is employed as a cocatalyst, facilitating the direct C–O bond cleavage of phenol.[38b]

3.2. Phenol

The synthesis of phenol from lignin or lignin model compounds has been intensively investigated in the past three years and is becoming a hot area of lignin valorization.[2d, 4a] Guaiacol or 4-propylguaiacol is generally employed as a prototype molecule to represent lignin-derived monomers to study the selective cleavage of C–O bonds because both of them incorporate methoxy groups, the phenolic hydroxy groups, and aromatic rings. The preparation of phenol from lignin-derived

monomers by selectively removing the methoxy groups and a *para*-side-chain group is of great importance. Several state-of-the-art catalysts, such as $CoMoS/ZrO_2$, metal-loaded TiO_2 (Au, Ag, Ni), Au/Nb_2O_5, carbon-supported molybdenum, NiMoS/Al_2O_3 and Ru/CeO_2, have been developed for the hydrodeoxygenation of guaiacol or 4-propylguaiacol to phenol or propylphenol (Table 2).[75]

3.2.1. Reaction pathway

Phenol is known to be formed from guaiacol through three major pathways (Scheme 2).[76,78,82] One is by first converting into a catechol intermediate through demethylation, followed by dehydroxylation to give phenol. The second is direct demethoxylation to form phenol. In the third, anisole is first formed

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Table 2. Overview of the synthesis of phenols from lignin model compounds.

Feedstock	Conv. [%]	Catalyst	Reaction conditions	Major product	Sel./yield [%]	Ref.
guaiacol	100	CoMoS/ZrO$_2$	partial pressure of guaiacol of 2.7 kPa, 300 °C, 4 MPa H$_2$	phenol	60 (S)	[75a]
guaiacol	98	MoO$_2$/AC	0.035 g mL^{-1} in tetralin, 300 °C, 3 MPa H$_2$, 3 h	phenol	72 (S)	[66a]
guaiacol	≈90	Au/TiO$_2$	60 NmL m^{-1} in, 300 °C, 6 h, 4 MPa H$_2$, 2.7 KPa guaiacol	phenol	≈70 (S)	[76]
guaiacol	100	Au/TiO$_2$	0.16 mol L^{-1} in toluene, 300 °C, 6.5 MPa H$_2$, 700 rpm, 3 h.	phenol	49.6 (Y)	[75d]
guaiacol	≈75	Ag/TiO$_2$	1.5/18.5 g g^{-1} in heptane, 300 °C, 3 MPa H$_2$, 700 rpm, 3 h	phenol	≈45 (Y)	[77]
guaiacol	100	Ni&TiO$_2$	0.048 g mL^{-1} in decane, 300 °C, 4 MPa H$_2$, 500 rpm, 6 h	phenol	≈85 (Y)	[78]
2-methoxy-4-propyl-phenol	100	Au/Nb$_2$O$_5$	5 % g mL^{-1} in water, 300 °C, 8 h, 6.5 MPa H$_2$	propylphenol	84.2 (Y)	[31e]
vanillin	100	ZnO/Co@N-CNTs	250/30 mg mL^{-1} in water, 300 °C, 6 h, 5 MPa H$_2$	p-cresol	82.2 (S)	[79]
4-propylguaiacol	≈65	Au/TiO$_2$ +HZMS-5	10 % g mL^{-1} in benzene, 350 °C, 2 h, MPa H$_2$	phenol	≈60 (Y)	[80]
2-methoxy-4-propyl-phenol	≈100	Pt/C+HZMS-5	Feedstock injection rate 240 μL h^{-1}, water injection rate 240 μL h^{-1}, H$_2$ flow rate 10 mL min^{-1}, 375 °C	phenol	60 (Y)	[81]

DMO: Demethoxylation
DME: Demethylation
DHO: Dehydroxylation
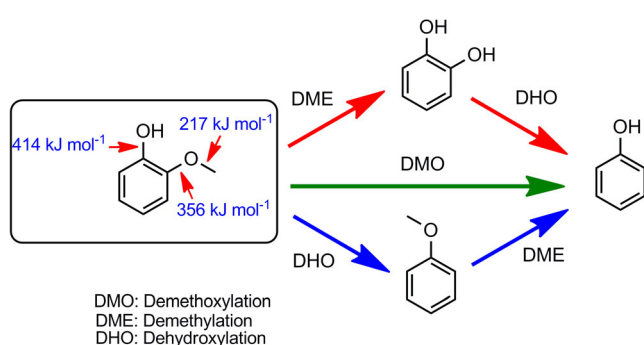
Scheme 2. Reaction pathways for the conversion of guaiacol into phenol. Reprinted from Ref. [36a] with permission from Elsevier.

through dehydroxylation, which is followed by demethylation to afford phenol. Based on the bond energies of three groups in guaiacol, the first two pathways were accordingly proposed and proven by most researchers.[31e, 36d,e, 61, 77] In other words, the intense interest of researchers has mainly focused on the mechanism.

3.2.2. Roles of metals

When targeting phenol production, the biggest challenge, driven by the evident competition among the desired removal of the methoxy groups, excessive hydrogenolysis of the phenolic hydroxy groups, and the undesired hydrogenation of the aromatic rings, is to develop state-of-the-art catalytic systems that can cleave the methoxy groups while preserving the phenolic hydroxy groups and the aromatic rings. To overcome the challenge, supported metal sulfide catalysts (CoMoS/ZrO$_2$ and sulfided CoMo/Al$_2$O$_3$) were employed to catalyze the hydrodeoxygenation of guaiacol, but loss of sulfur limits their application.[75a, 83] Although continuous addition of sulfur can regenerate the catalysts, it caused new problems for the downstream processes.

As an attractive alternative, supported metal catalysts, mainly those with low catalytic hydrogenation/hydrogenolysis activity were developed to produce phenol from guaiacol and the relationship between catalytic performance and catalyst structure was investigated.[31e, 75d, 76–78, 80] Generally, from the point of view of the active metal, intrinsic hydrogenation activity, size effect, electronic effect and resulting hydrogen spillover were endeavored to explore the most efficient metal to maximize guaiacol conversion and phenol selectivity.

Supported gold catalysts in this system have attracted considerable attention because of their high selectivity to aromatic compounds and low hydrogenation/hydrogenolysis activity. A high selectivity to phenolics (87.1 %) was obtained over Au/TiO$_2$, owing to its poor hydrogenation performance, enabling the retaining of phenolic hydroxy groups with strong bond energy and aromatic ring.[36a, 75d] After introducing Rh into the Au catalyst by nanoalloying, the total hydrodeoxygenation of guaiacol to cyclohexane dominates over removal of the methoxy groups to afford phenol, giving a high selectivity to cyclohexane.[76] The particle size of Au only affects the reaction activity, but not the product selectivity.[75d] However, size effects of metal nanoparticles, such as ruthenium, with stronger hydrogenation activity than gold can not only affect the catalytic activity, but also determine the distribution of the hydrodeoxygenation products.[31c, 32b, 51a] The difference of size effect between Ru and Au may be due to the distinction of their hydrogenation activity. Aside from the size effect of Au, its electronic effect also plays a crucial role in the efficient production of phenolics from 4-propylguaiacol and the electron-rich Au clusters on Au/Nb$_2$O$_5$ can promote hydrogen dissociation, resulting in high hydrodeoxygenation performance.[31e] Very recently, Ag/TiO$_2$ was found to promote H$_2$ dissociation and hydrogen spillover onto the TiO$_2$ surface. The spillover hydrogen can reduce the TiO$_2$ surface to create oxygen vacancy as the active site of hydrodeoxygenation, giving an efficient performance for the selective conversion of guaiacol into phenol.[48b, 77] Similar hydrogen spillover from Pt onto WO$_x$/TiO$_2$ also plays a key role in the hydrogenolysis of cyclic ethers.[54d]

3.2.3. Roles of Supports

Further to the hydrogenation activity, size and electronic effects, and resulting hydrogen spillover from metals, supports (generally metal oxides) also play crucial roles in phenol production.[31e,78] For example, the active sites formed through the strong interaction between Ni and the surface of anatase TiO_2 favor selective transformation of guaiacol into phenolic compounds.[78] However, this specific interaction was not found between Ni and other supports such as ZrO_2, Al_2O_3, rutile TiO_2, and CeO_2.[78] In addition, Nb_2O_5 is also a promising support for the selective conversion of lignin oil into phenolics because of its unique oxygen affinity to cleave the C−O bond and excellent acid properties to promote hydrolysis.[31e] In short, maximizing guaiacol conversion and phenol selectivity can be achieved through the design of the above efficient catalysts, based on the deep understanding on how the bifunctional interfaces (metal mixed with acid sites with strong oxygen affinity) catalyze guaiacol conversion.

3.2.4. Effects of the reaction medium

In addition to catalysts, reaction media also play an important role in phenol production.[84] For example, when toluene is used as solvent, some undesirable transmethylation products were formed, leading to low phenol selectivity,[75d] whereas in water the transmethylation reaction was markedly prevented, owing to the quenching effect on positive charges.[31e] Interestingly, when low-value benzene was used as the reaction medium and a mixture of Au/TiO_2 and HZSM-5 as catalysts, the alkyl groups can be transferred to benzene instead of phenol, giving value-added alkylbenzenes, which is ascribed to intimate contact between Au/TiO_2 and HZSM-5.[80]

3.2.5. Cleavage of the alkyl group

After removing methoxy groups, the selective cleavage of the alkyl group in lignin-derived alkylphenols becomes the final hurdle to obtain phenol. Acidic ZSM-5 zeolites were identified as suitable catalysts for the removal of the alkyl group.[80,81,85] Among a series of acidic materials, such as γ-Al_2O_3, ferrierite, ZSM-22, ZSM-5, zeolite beta, and USY, ZSM-5 showed clearly superior dealkylation performance, which originates from an effect of shape selectivity, resulting in significant suppression of disproportionation/transalkylation.[85a,b] In addition, the presence of water is beneficial for ZSM-5 stability as the competitive adsorption of water and phenol enables to sweep phenol from the catalyst.[85a,c] Recently, Yan and co-workers reported the single-step conversion of lignin monomers into phenol through combining the two catalysts, namely Pt/C and H-ZSM-5 together to simultaneously break the C−O bond of the methoxy groups and the C−C bond of the alkyl group, but the deactivation of the dealkylation catalyst limits its application.[81] The development of efficient and stable multifunctional catalysts to integrate demethoxylation and dealkylation in a single step is therefore required to avoid multistep processes and complex separations.

In contrast to the above demethoxylation–dealkylation route, Wang and co-workers[28c] communicated a strategy to produce phenol from lignin through oxidative C_α–C_β bond cleavage to acids and subsequent decarboxylation (Scheme 3). This strategy is also capable of converting raw biomass sources, such as poplar, birch, pine, peanut, bamboo, willow, and straw, into phenol.
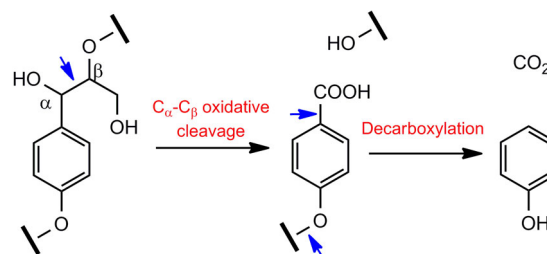
Scheme 3. Production of phenol from lignin by an oxidation–hydrogenation route. Reprinted from Ref. [28c] with permission from the American Chemical Society.

3.3. Other chemicals from lignin

Although the production of arenes, cycloalkanes, and phenol from lignin is the main direction for upgrading lignin-derived monomers, the synthesis of other value-added chemicals, such as ethylbenzene, indane, terephthalic acid, diethyl maleate, acetic acid, and methyl-substituted amines, has received gradually increasing attention in the last two years and becomes a new research hotspot.[17b,31a,51a,86] When targeting ethylbenzene and indane, attention should be paid to modification of the aforementioned Ru-based catalysts.[31a,51a] For the production of terephthalic acid, the development of a stepwise system is promising.[86f] Through selective utilization of the methoxy groups in lignin, acetic acid and methyl-substituted amines can be obtained.[86g,h] Routes to these chemicals will be discussed in detail in this section.

Ethylbenzene is an intermediate in the process of styrene production and its catalytic production from lignin can be realized in two steps, including Re−Y/HZSM-5-catalyzed hydrodeoxygenation of lignin to aromatic monomers (mainly benzene) and the subsequent alkylation of aromatic monomers with ethanol to afford ethylbenzene.[86e] However, the removal and reintroduction of alkyl groups may be a less-than-optimal pathway. Direct utilization of the inherent alkyl groups is more desirable for the production of ethylbenzene from lignin. In this respect, integrating dehydrogenative decarbonylation of the terminal hydroxypropyl groups and hydrodeoxygenation may prove a better route to ethylbenzene production. As discussed in the above section on arene production, the design of modified Ti-, Nb-, and Mo-based catalysts should be considered for the catalytic synthesis of ethylbenzene. For example, by introducing FeO_x species into Ru/Nb_2O_5, ethylbenzene can be selectively obtained from birch lignin oil by dehydrogenative decarbonylation and sequential hydrodeoxygenation.[87] It was found that FeO_x not only triggered the dehydrogenative decarbonylation through weakening the catalyst's activity for

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direct hydrogenolysis of terminal hydroxypropyl groups, but also created more oxygen vacancies (NbO_x species), thus favoring the removal of phenolic hydroxy groups.[87]

Indane and its derivatives can serve as important drug molecules and high-quality transportation fuels and their selective preparation from lignin is of increasing interest.[51a,86a–d] Weakening the hydrogenolysis activity of metal Ru through the modification of CH_2Cl_2 slows down the hydrogenolysis reaction of lignin-derived monomers and accelerates the intramolecular Friedel–Crafts cyclization, affording a high selectivity of indane and its derivatives.[51a] Similarly, designing other strategies to weaken the hydrogenolysis activity of Ru may be promising to this end. In addition, indane and its derivatives have also been obtained through the transformation of cinnamaldehyde, but the detailed cyclization mechanism has not been disclosed to date.[86a]

Terephthalic acid is an important monomer of polyethylene terephthalate (PET) plastic and developing renewable strategies to produce terephthalic acid from biomass has attracted significant attention. Tandem Diels–Alder reaction and dehydration of biomass-derived 2,5-dimethylfuran with ethylene to synthesize p-xylene, a precursor for terephthalic acid, has been intensively reported over the past decade.[88] Besides this, a stepwise system involving demethoxylation, carbonylation, and oxidation was designed to synthesize terephthalic acid from lignin-derived monomers.[86f] The precipitation of solid terephthalic acid from the final reaction solution avoids the subsequent purification, giving a tangible strategy for further application. Inspired by this idea, developing stepwise systems to prepare other value-added chemicals from lignin must be taken into consideration.

The production of the above aromatic chemicals focused on the aromatic rings. The utilization of methoxy groups, another abundant functional group in lignin, appears to be starting to develop. For example, water and CO as co-reactants react with the methoxy groups of lignin to produce acetic acid.[86g] Aniline compounds have also shown great potential to capture the methoxy group of lignin to synthesize methyl-substituted amines.[86h] After reaction, the solid residual lignin, which is rich in hydroxy groups, may have specific applications in the fields of catalyst and materials,[86g,h] and the development of its subsequent utilization is therefore required to promote energy conservation.

Besides the above chemicals, lignin and its derivative monomers can also be used to produce polymers, such as phenolic resins, epoxy resins, polyesters, and polyurethanes, and compounds with pharmacological activity through selective functionalization and defunctionalization.[89] For a more elaborate discussion on the polymers and compounds with pharmacological activity from lignin, the reader is referred to a dedicated review on this topic.[4d]

4. Summary and Outlook

Efficient conversion of renewable lignin into valuable chemicals and fuels according to the guiding principles of green chemistry is of great significance to solve the energy crisis and miti-

gate global warming. Lignin depolymerization and the upgrading of lignin-derived monomers form two of the foremost directions of this research. In these two respects, the reactions involving hydrogen are considered core content, presenting not only a long-term challenge, but also a huge opportunity. In this Review, recent developments on the reductive conversion of lignin into chemicals and fuels are discussed, with an emphasis on the reductive depolymerization and upgrading of lignin-derived monomers to three important products (arenes, cycloalkanes and phenol). In addition, several promising strategies for the preparation of fine chemicals are simply introduced to inspire readers.

Based on the recent results in catalytic transformations involving hydrogen discussed herein, we would like to highlight the following issues for future consideration. a) Developing catalytic hydrogen transfer reactions with biomass-derived alcohols and acids as hydrogen sources instead of hydrogen gas is highly desired to reduce transportation and storage costs. In addition, lignin is rich in hydroxy groups and could be used as a hydrogen donor. The design of a unique hydrogen transfer system using lignin as a hydrogen source will pave a way to realizing "self-production". b) Modifying native lignin through chemical pretreatments (e.g., pre-oxidation and formaldehyde stabilization) to weaken the hydrogen bond energy in lignin and avoid repolymerization is favorable for the following transformation. c) As mentioned above, water is widely used as a green solvent in the production of arenes, cycloalkanes, and phenol. However, only a few solid catalysts retain high activity and stability in aqueous conditions. The exploitation of water-tolerant catalysts is hence of crucial importance for lignin valorization. d) The problem of contact between lignin feedstocks and the solid catalyst limited the reaction rate, owing to the heterogeneous and robust structure of lignin. Developing versatile ionic liquids and organic solvents to dissolve lignin is thus highly desired. As another alternative, the preparation of catalysts that have more active sites and suitable pore structure to promote mass transfer is believed to be beneficial to address the solid–solid contact problem. e) The adjustment and modification of catalysts can contribute to varying the product distribution, especially for pathway-sensitive systems, such as those for indane and ethylbenzene synthesis. Developing similar systems by adjusting and modifying active sites will open new perspectives for lignin utilization. f) In most processes, lignin hydrogenolysis proceeds via cleavage of the C—O bond to afford low-molecular-weight monomers, but the interunit C—C bonds with higher dissociation energy are not cleaved. Because of the presence of stable interunit C—C bonds within native lignin or those formed during lignin extraction, the yields of lignin monomers are seriously limited. Designing high-efficiency catalytic systems that can conduct cleavage of both interunit C—C and C—O linkages is believed to mitigate the limitations on lignin monomer production.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aromatics · biomass · heterogeneous catalysis · hydrodeoxygenation · lignin

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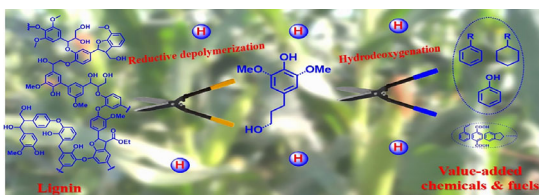
REVIEWS

Y. Jing, L. Dong,* Y. Guo, X. Liu, Y. Wang*

■■ – ■■

Chemicals from Lignin: A Review of Catalytic Conversion Involving Hydrogen

Getting better with H: This Review presents an insight into the catalytic conversion of lignin involving hydrogen, including reductive depolymerization and hydrodeoxygenation of lignin-derived monomers, with a focus on cata-lyst systems and reaction mechanisms. The roles of hydrogenation sites and acid sites, strategies for the production of other value-added chemicals, and future opportunities within this attrac-tive field are discussed.

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