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Catalytic Hydrogenolysis of Aryl Ethers: A Key Step in Lignin Valorization to Valuable Chemicals

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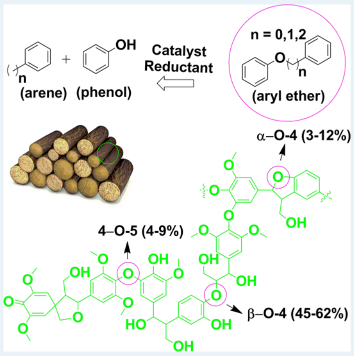
ABSTRACT: Lignin is a robust biomacromolecule (or a polymer) that gives structural integrity to plants and constitutes 25–35% of the woody biomass. Lignin is inedible, barely used, and contains mostly aromatic building blocks. Because of these features, lignin is considered an important renewable feedstock for the production of fine chemicals (or fuels) and the only significant feedstock providing aromatic compounds. The C–O bonds of aryl ethers are the most abundant linkages in the framework of lignin. In this Perspective, the state-of-the-art of selective hydrogenolysis (HGL) of C–O bonds of aryl ethers is discussed. Particularly, progress made recently and ethers relevant to lignin valorization are reviewed.



KEYWORDS: *aryl ether, catalysis, hydrogenolysis, lignin, valorization*

■ INTRODUCTION

The monomers of the polymeric network of lignocellulosic biomass (lignin, hemicellulose, and cellulose) are linked by carbon–oxygen (C–O) bonds. Lignocellulose, which is available in large amounts, is inedible and, thus, considered as the potential feedstock for the sustainable production of fuels and more importantly, chemicals.[1,2] Owing to the rapid depletion of fossil resources and environmental concerns connected to their use, such alternative feedstocks become increasingly important. Purely aliphatic C–O bonds, which amount to cellulose structures, are readily cleaved by a variety of processes,[3−5] whereas the selective scission of C–O bonds of lignin is challenging. Lignin, a three-dimensional polymer, composes 15–30% of the lignocellulosic biomass. It is characterized by the presence of aromatic units linked by C–C and C–O bonds (Figure 1). Lignin is the only relevant renewable feedstock for aromatic compounds.[1] The selective cleavage of its C–O bonds allows access to a pool of aromatic compounds, which can then be further upgraded to fine chemicals.[6−8] Catalytic hydrogenolysis (HGL), especially when employing sustainably generated hydrogen as the reducing agent, is one of the most promising options for lignin conversion. Oxidative depolymerization, an alternative way of cleaving the C–O bond of lignin, increases the already high oxygen content of the material and is therefore less attractive. Several molecular and solid HGL catalysts have been developed, which can cleave C–O bonds of aryl ethers. Mostly, the cleavage of model compounds (see Figure 1, bottom) representing the most abundant linkages in lignin (Figure 1) have been studied.

The diaryl ether linkage 4-O-5 represents 4–9% of the ether moieties of lignin, and the alkyl-aryl ethers *β*-O-4 and *α*-O-4 are about 45–62% and 3–12%, respectively.[7] Due to the importance of lignocellulosic biomass and/or lignin as a feedstock, many review articles have appeared recently covering the many aspects associated with its valorization.[9,10] None of them focuses on the catalytic HGL of aryl ethers, the many catalysts used to mediate such reactions, the selectivity patterns of these catalysts, and mechanistic aspects of the different ways of cleavage of C–O bonds of aryl ethers via HGL. Keeping in view the rapidly increasing interest in the field, there is a need for a Perspective that could provide interested readers with the recent advances in catalytic cleavage of aryl ethers via HGL and challenges associated with it.

Alkyl-aryl ethers can undergo C_{Alkyl}–O or C_{Aryl}–O bond cleavage under HGL conditions (Scheme 1). C_{Alkyl}–O bond cleavage is preferentially observed for the cleavage of *α*-O-4 and *β*-O-4 model compounds (Figure 1) and C_{Aryl}–O bond cleavage is relevant in aryl-methyl ethers and related aryl ethers carrying longer alkyl chains than methyl.

The focus of this Perspective is the HGL of diaryl ethers and the HGL of alkyl-aryl ethers that proceed via C_{Alkyl}–O bond cleavage. Both reactions are highly relevant for the lignin valorization. The related HGL of C_{Aryl}–O bonds of alkyl-aryl ethers is partially discussed too. The recent progress regarding the mechanism of this cleavage reaction may also help to understand (at this stage) C_{Alkyl}–O bond cleavage of alkyl-aryl ethers better.

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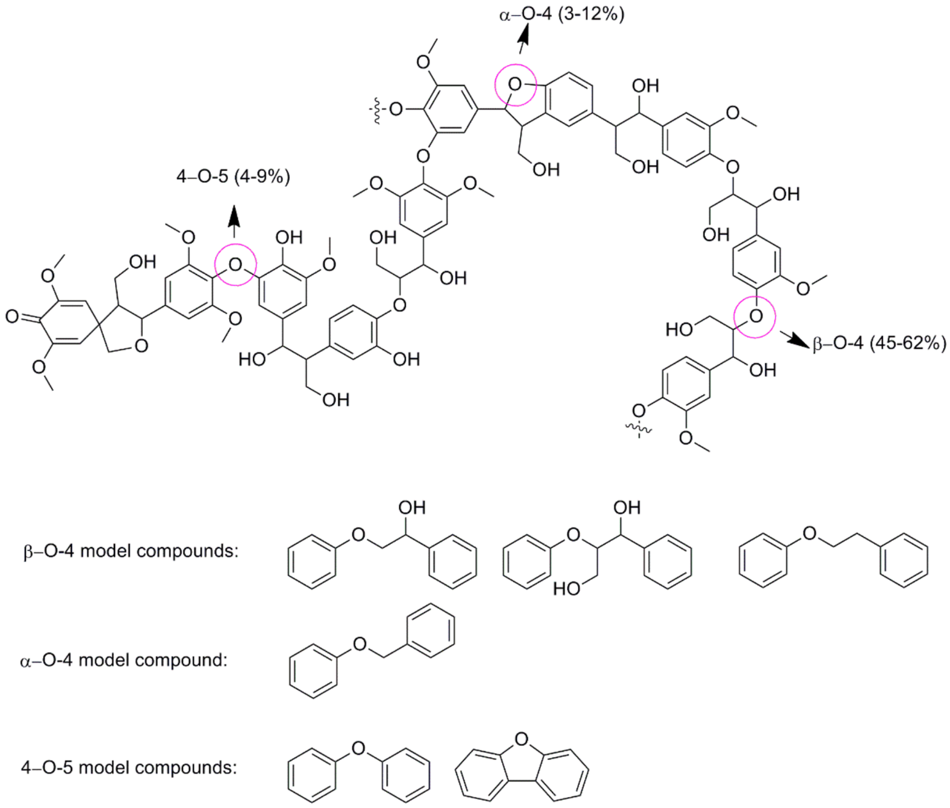
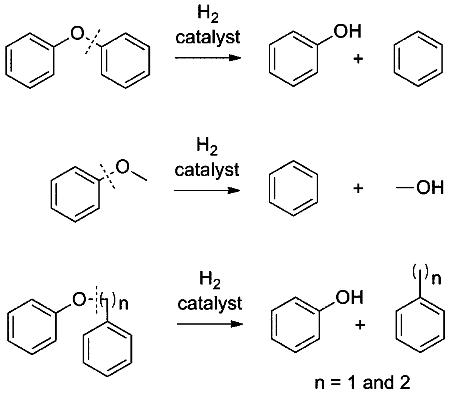


Figure 1. Fragment of hard wood lignin showing the most frequent ether linkages and their abundance in percent. Possible model compounds mimicking these linkages are shown at the bottom.

Scheme 1. Cleavage of C−O Bonds of Aryl Ethers[a]



[a]Top: HGL of diaryl ethers (relevant for lignin valorization). Middle: HGL of alkyl-aryl ethers via C_{Aryl}−O bond cleavage. Bottom: HGL of alkyl-aryl ethers via C_{Alkyl}−O bond cleavage as relevant for lignin valorization.

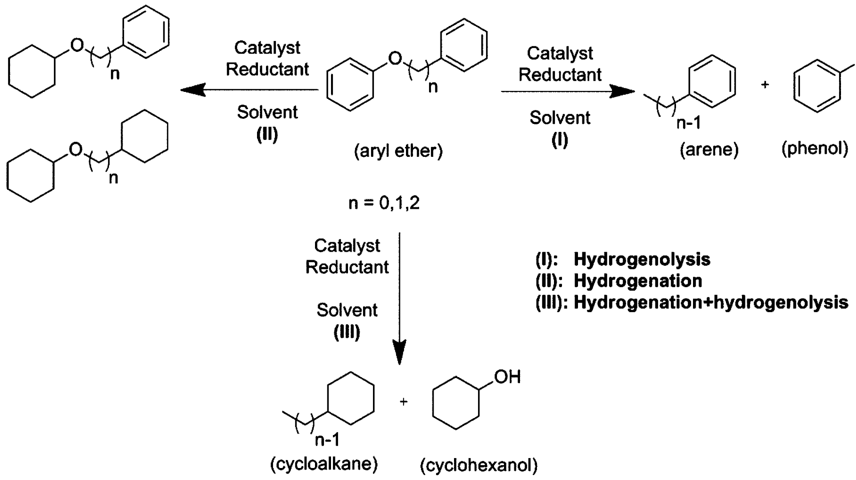
■ HYDROGENOLYSIS OF ARYL ETHERS

1. Homogeneous Catalysts. HGL of C−O bonds of aryl ethers utilizing molecular catalysts has shown an enormous potential and a rapid progress in recent years (2011−2014). This can be attributed to the high selectivity that they offer. Thus, C−O bonds are selectively cleaved providing aromatic compounds (I in Scheme 2) instead of arene hydrogenation (II in Scheme 2). The pool of aromatic compounds hence obtained can be transformed to aromatic chemicals. Furthermore, molecular catalysts are well suited for gaining mechanistic insight into the cleavage reactions. Nonselective HGL leads to the formation of saturated cycloalkanes (III in Scheme 2) whose dehydrogenation is challenging.

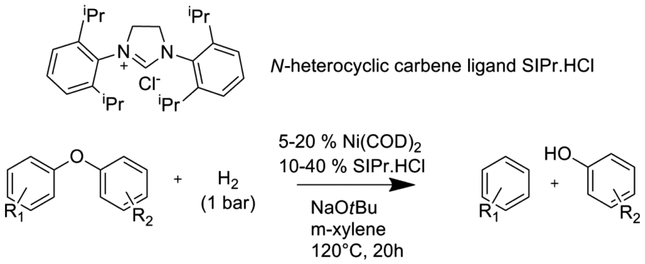
1.1. Nickel Catalysts. Selective HGL of Diaryl and Aryl-Alkyl Ethers. The Hartwig[11] group has recently designed a nickel-based catalyst stabilized by a *N*-heterocyclic carbene (NHC) ligand (Scheme 3). All types of aryl ethers listed in Scheme 1 could be cleaved highly selectively, and the formation of aromatic products was mostly quantitative. The reaction conditions were relatively mild (80−120 °C and 1 bar of hydrogen). Ether bonds in oligomeric phenylene oxide and model compounds mimicking the most abundant *β*-O-4, *α*-O-4, and 4-O-5 linkages were cleaved almost quantitatively too. Most notably, a widely available metal and the inexpensive, mild, and atom-economical reductant hydrogen could provide high selectivity. Furthermore, a broad substrate scope could be addressed. This paper opened new avenues in the valorization of lignin into valuable chemicals via HGL and inspired many researchers working in the same field.

C_{Aryl}−O Bond Cleavage of Alkyl-Aryl Ethers. The roots of Hartwig's work regarding C_{Aryl}−O bond cleavage of alkyl-aryl ethers can be traced back to the pioneering work of Wenkert et al., who reported the cleavage of aromatic C−O bonds with nickel complexes via the cross-coupling of aryl ethers with Grignard's reagent in 1979.[12] Insertion of nickel into a C_{Aryl}−O bond leads to the formation of a nickel alkoxide intermediate whose further reaction with a Grignard's reagent (transmetalation and reductive elimination) results in C−C bond formation. Dankwardt further extended the scope of this reaction. He used $NiCl_2$ stabilized by bulky monodentate phosphine ligands (PCy_3 and $PPhCy_2$, Cy = cyclohexyl, Ph = phenyl) as a precatalyst.[13] Later, Tobisu et al. presented cross-coupling reactions of aryl ethers with organoboron reagents[14]

Scheme 2. Cleavage of C−O Bonds in Aryl Ethers via HGL and Competing Hydrogenation



Scheme 3. HGL of Diaryl Ethers by a Nickel Complex. Reproduced with Permission after Modification from Ref 11. Copyright 2011 AAAS[a]



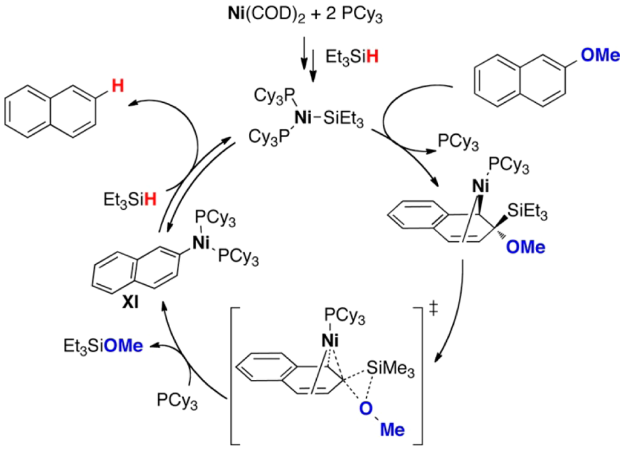
[a] ^{i}Pr = *iso*-propanol, COD = cyclooctadiene and Bu = butyl.).

and amines[15] utilizing Ni^0/PCy_3 catalyst systems. Martin and co-workers recently summarized C−C coupling reactions based on CAryl−O bond cleavage (also of alkyl-aryl ethers).[16]

The Martin group[17] also extended this approach and reported the first reductive cleavage of inert C_{Aryl}−O bonds in alkyl-aryl ethers using tetramethyldisiloxane as reducing agent. Their catalyst system (Ni^0/PCy_3) offered an impressive substrate scope and good to excellent yields. The reaction of deuterium labeled triethylsilane (Et_3Si-D) with an alkyl-aryl ether gave rise to a deutrated arene product while that of an alkyl-aryl ether carrying a deuterium labeled methyl group with Et_3Si−H provided a nondeutrated arene product. These experiments indicate that pathways involving *β*-hydride elimination from arylnickel(II)-alkoxide intermediates seem less relevant. In a more recent publication,[18] this group conducted detailed theoretical and experimental investigations regarding the mechanism of the reductive cleavage of C_{Aryl}−O bonds of alkyl-aryl ethers with hydrosilanes using a $Ni(COD)_2$- and PCy_3-based catalyst. A mechanism was proposed and is shown in Scheme 4. Interesting examples of the reductive cleavage of alkyl-aryl ethers using hydrosilanes and a $Ni(COD)_2/PCy_3$ catalyst system were also reported by Tobisu et al.[19]

The group of Agapie[20] has reported on mechanistic studies of C_{Aryl}−O bond cleavage applying a model system. A specifically designed ligand (1 in Scheme 5) was used. For this ligand, an oxidative addition/*β*-hydride elimination pathway was observed. To investigate the catalytic relevance of the model system, alkyl-aryl ethers were subjected to HGL (C_{Aryl}−O bond cleavage) under similar conditions as used by Hartwig and co-worker [$Ni(COD)_2$ and a NHC ligand]. 2-Methoxynaphthalene, which has a deuterated methyl group, was used as a substrate. In combination with H_2, the deuterated arene was observed as the product. At this stage, Ni-complex-catalyzed C_{Aryl}−O bond cleavage of alkyl-aryl ethers seems to proceed rather differently if H_2 or hydrosilanes are used as reductants. HGL using H_2 seems to proceed via oxidative addition leading to an aryl-Ni(II) alkoxide intermediate followed by ß-hydride elimination and reductive elimination. In addition, Ni-catalyzed aldehyde reduction takes place (Scheme 6).

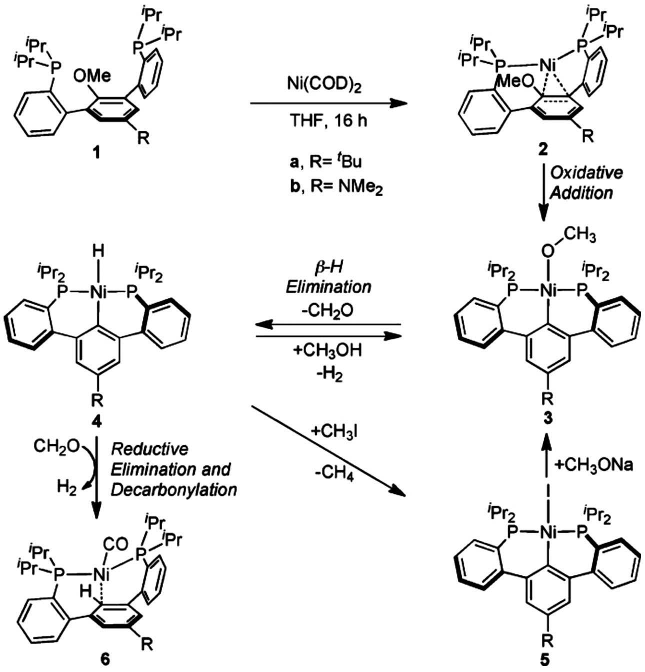
Scheme 4. Proposed Mechanism for Nickel Catalyzed Cleavage of C_{Aryl}−O Bonds of Alkyl-Aryl Ethers in the Presence of Silanes. Reprinted with Permission from Ref 18. Copyright 2013 American Chemical Society



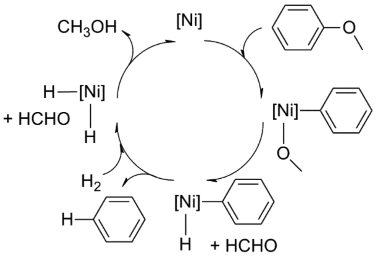
All the aforementioned nickel catalysts for C−O bond cleavage were found to be water sensitive. Samanat and Kabalka[21] achieved the cleavage of diaryl ethers using a nickel catalyst, NaO-*t*-Bu, and lithium tri-*t*-butoxyaluminum hydride as a hydrogen source. The reaction was accomplished in a water-based micellar medium, and the reduction of the aromatics was observed.

1.2. Other Transition Metal Catalysts. HGL of Alkyl-Aryl Ethers via C_{Alkyl}−O Bond Cleavage Using in Situ Generated Hydrogen. Beside nickel, other transition metal complexes were investigated in C_{Alkyl}−O bond cleavage reactions of alkyl-aryl ethers. A ruthenium/4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos)-catalyzed cleavage of 2-aryloxy-1-aryletha-

Scheme 5. Stoichiometric Cleavage of C_{Aryl}−O Bond Mediated by Nickel. Adapted with Permission from Ref 20. Copyright 2013 American Chemical Society

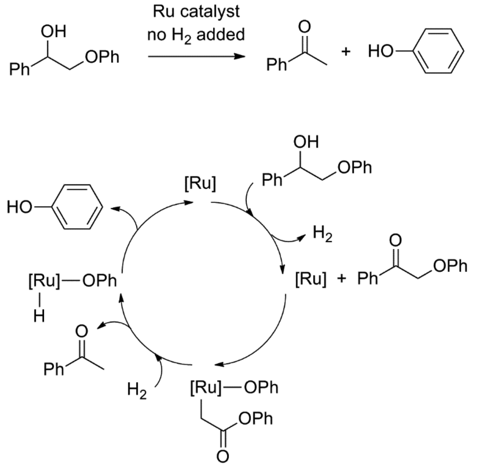


Scheme 6. Possible Mechanism for the Catalytic C_{Aryl}−O Bond Cleavage of Alkyl-Aryl Ethers by Hydrogen[a]



[a]Brackets indicate additional ligands at the catalytically active metal.

Scheme 7. HGL of ß-O-4 Models Catalyzed by Ru Catalysts (Ph = Phenyl)[a]



[a]Brackets indicate additional ligands at the catalytically active metal.

nols (β-O-4 models) in a nitrogen atmosphere was introduced by Ellman/Bergman and co-workers.[22] Ligand screening revealed that xantphos-based Ru complexes are exceptionally reactive and selective. The mechanism was proposed to proceed by initial dehydrogenation to give the ketone followed by HGL using the hydrogen that was generated in the dehydrogenation step (Scheme 7).

James and co-workers used a similar catalyst system.[23] The presence of a γ−OH functionality in the β-O-4 model substrates inhibited HGL due to catalyst deactivation. HGL was also observed in the presence of 1 bar of hydrogen. DFT calculations by Paton/Beckham and co-workers revealed an unusual five-membered transition-state structure for the oxidative insertion and the reductive elimination of the ketone (and not the phenol, as shown in Scheme 7).[24] Furthermore, Klankermayer/Leitner and co-workers introduced a Ru-based catalyst stabilized by a tridentate phosphane ligand [bis(diphenylphosphinoethyl)-phenylphosphane] for the active and selective cleavage of 2-aryloxy-1-arylethanols (Scheme 7).[25] Weickmann and Plietker combined the dearyloxylation of various lignin-type model compounds under hydrogen-autotransfer conditions with the alkylation of ketones by alcohols.[26] A commercially available Ru complex catalyzes both reactions, sequentially. Huo et al. reported the effective C−O bond cleavage of ß-O-4 model compounds by $RuHCl(CO)(PPh_3)_3$/KOH (Ph = phenyl) in the presence of a strong base (KOH). Their catalyst screening also indicates significant activity by the base itself (60% conversion in 12 h with 50 mol % KOH).[27]

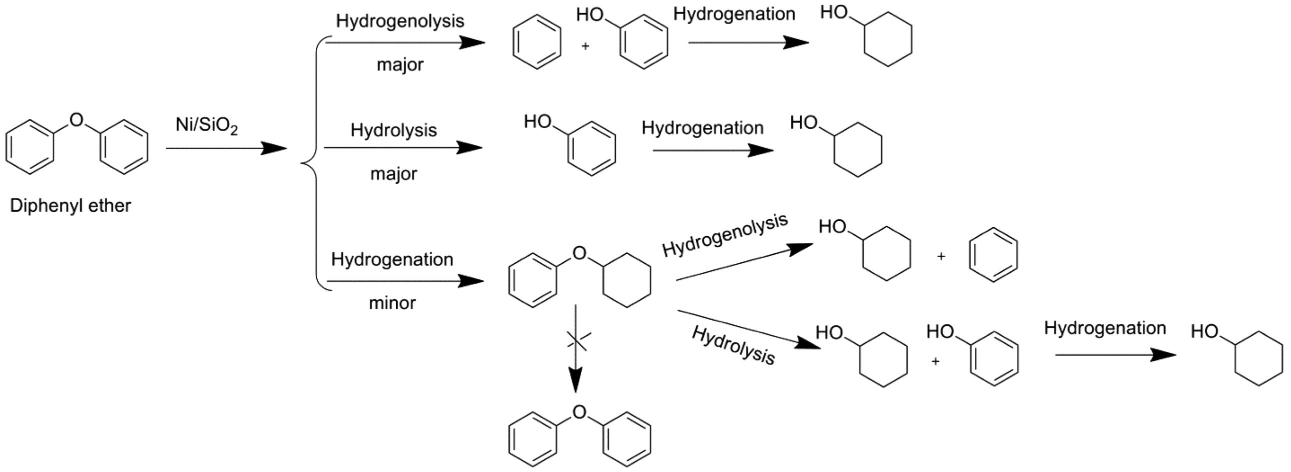
Catalytic Alkyl-Aryl Ethers Cleavage via C−H Activation. Goldman and co-workers described the catalytic C−O bond cleavage of alkyl-aryl ethers forming an olefin and a phenol by an Ir complex. This reaction was proposed to proceed via a sequence of C−H bond addition, aryloxide migration, olefin elimination, and reductive elimination of the phenol.[28]

HGL Using $LiAlH_4$. An iron-based catalyst system has been reported by Wang and co-workers for the reductive cleavage of diaryl and alkyl-aryl ethers (C_{Aryl}−O bonds).[29] Iron acetylacetonate was used as the catalyst precursor and $LiAlH_4$ (2.5 equiv) as the reducing agent. Other iron catalysts showed lower activities. Furthermore, a stoichiometric amount (2.5 equiv) of base was added. Diphenyl ether (for instance) was cleaved quantitatively with the selective formation of aromatic products at 140 °C in toluene. The HGL of β-O-4 models were also observed using H_2 as a reducing agent (1 bar). The role of the base alone was not discussed. In the light of the base-mediated cleavage of β-O-4 model compounds,[27] it is difficult to judge what is the role of the Fe/Co catalyst in these reactions. Diaryl ethers could not be cleaved in the presence of dihydrogen instead of $LiAlH_4$. This author group obtained similar results using a cobalt-based catalyst system.[30]

1.3. Transition-Metal-Free Catalyst Systems. Selective HGL of diaryl ethers with silanes (excess) in the absence of any transition metal catalyst was attempted by Grubbs and co-workers.[31] The optimized conditions include three equivalents of KO-*t*-Bu. Orthosilylation was observed at lower temperatures. It can be avoided at 165 °C. Interestingly, C_{Alkyl}−O bond cleavage of aryl-methyl ethers was observed. The authors assume that alkyl organosilicates are the key reactive species involved. The selective reduction of α-O-4 and β-O-4 model compounds by silanes to phenol derivatives was also achieved by Cantat and co-worker, who used $B(C_6F_5)_3$ as a catalyst.[32]

2. Heterogeneous Catalysts. *2.1. Monometallic Catalysts. 2.1.1. HGL Using H_2.* In their paper published in 1935,[33] van Duzee and Adkins reported the HGL of various aryl ethers

Scheme 8. Proposed Reaction Pathway for the Cleavage of Diphenyl Ether over Ni/SiO$_2$ in the Aqueous Phase. Adapted after Permission from Ref 43. Copyright 2014 Elsevier



using Raney-nickel as a catalyst under hydrogen pressure >150 bar and temperatures up to 200 °C. They tried to address the following questions: (a) In what temperature range will the cleavage of the ether occur? (b) Which of the carbon to oxygen linkages will be preferentially cleaved? (c) In what temperature range will the hydrogenation of aromatics become relevant? Prior to their work, C−O bond cleavage of ethers was observed to occur over nickel, palladium, and platinum catalysts. The state-of-the-art of that time is well documented in ref 33. HGL of benzyl-aryl ethers (α-O-4 models) catalyzed by Raney-nickel was found to occur at relatively low temperature (100−150 °C). Good selectivity regarding the formation of phenols (up to 87%) was observed. Diaryl ethers were found to be more stable toward HGL. At temperatures at which HGL took place (175−200 °C), hydrogenation of both aromatic substituents were observed. For instance, diphenyl ether HGL resulted in 53% cyclohexene, 74% cyclohexanol, and 14% (cyclohexyloxy)benzene at 175 °C.

In the mid-1950s, Tweedie et al. reported the HGL of aryl-vinyl ethers via C_{Vinyl}−O bond cleavage.[34,35] They used LiAlH$_4$ as a reducing agent and a variety of metal salts as catalysts. Ni salts as NiSO$_4$ or NiCl$_2$ gave the best conversions. Interestingly, under the mild condition used (THF, 65 °C), hydrogenation is suppressed. Furthermore, LiAlH$_4$ alone gave 12% conversion. Chandlar and Sasse[36] investigated the HGL of various substituted diphenyl ethers using Raney-nickel as a catalyst. Benzenes and cyclohexanols were formed at atmospheric pressure.

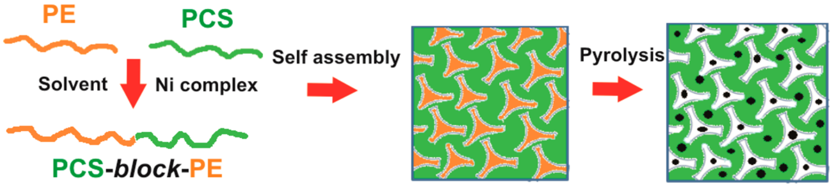
Utoh et al.[37] investigated the HGL of diphenyl and benzyl-phenyl ether (hydrogen pressure of 50 bar and temperature of 380 °C for 1 h). Metal oxide (Cu, Cr, Fe, Mo, Sn, and Ni) or chloride (Zn) catalysts, which were known to be active in coal liquefaction, were applied. All the catalysts except ZnCl$_2$ were active in HGL of both educts. The cleavage of diphenyl ethers was difficult in comparison to that of α-O-4 models and arene hydrogenation was observed for the most active catalysts.

Recently, Wang and Rinaldi[38] studied the effect of solvents on HGL of diphenyl ether with Raney-Ni (50 bar of H$_2$ pressure at 90 °C). Furthermore, the HGL of poplar-wood-based organosolv lignin at higher H$_2$ pressure and temperature was reported. We would also like to draw the reader's attention to the summary of the state-of-the-art in lignin valorization in the introduction of that paper. The Lewis basicity of the solvent was found to be an important factor in determining the activity and the selectivity. Raney-nickel and nonbasic solvents resulted in high activities in HGL and hydrogenation. Basic solvents decrease the activity but increase the HGL selectivity, and less arene hydrogenation was observed.

Song et al. achieved the depolymerization of birch wood lignin in the presence of different alcohols and supported Ni catalysts.[39] They observed the fragmentation of lignin into oligomers in the first step followed by their alcoholysis. Previously, the same authors had also reported the HGL of lignosulfonate over heterogeneous Ni catalysts.[40]

Lercher/Zhao and co-worker[41] reported on the C−O bond cleavage of α-O-4, β-O-4, and 4-O-5 model compounds by a silica-supported Ni catalyst (particle size between 4 and 8 nm) in aqueous media under relatively mild conditions (120 °C, 6 bar of H$_2$). For the β-O-4 model phenethoxybenzene, the product distribution as a function of time was studied. Cyclohexanol and ethylbenzene (about 50% each) were the only products observed at the very beginning of the reaction. About 52% of cyclohexanol and 48% of ethylbenzene were observed at a conversion of about 60%. The C_{Alkyl}−O bond is selectively cleaved followed by fast phenol hydrogenation. Separate experiments revealed that the hydrogenation of phenol in water at 120 °C with such Ni/SiO$_2$ catalysts is about 2 orders of magnitude faster than that of ethylbenzene. For (benzyloxy)benzene, HGL is significantly faster [initial TOF of 1017 versus 13 mol/h*mol(Surface-Ni) for phenethoxybenzene]. Consequently, the selective formation of phenol and toluene was observed (cyclohexanol formation below 10%). For the 4-O-5 model diphenyl ether, product distribution as a function of time revealed a complex reaction pathway, as shown in Scheme 8. In a following publication, Lercher/Zhao and co-workers[42] reported details of the benzyl-phenyl ether cleavage in water and undecane. Catalyst-free runs were compared with reactions mediated by HZSM-5, Ni/HZSM-5, and Ni/SiO$_2$ catalysts. In the absence of the Ni catalysts, hydrolysis, forming phenol and benzyl alcohol as intermediates, followed by alkylation was observed. Furthermore, the aqueous phase cleavage of C−O bonds in various diaryl ethers over a Ni/SiO$_2$ catalyst was investigated.[43] The rates as a function of the H$_2$ pressure from 0 to 100 bar indicate that the rate-determining step is the C−O bond cleavage on the Ni surface. H atoms, organic educts, and intermediates compete for adsorption leading to a maximum in the rate at lower H$_2$ pressure.

Scheme 9. Synthesis of Nanoporous Ni/SiC Catalysts from the Self Assembly of Nickel-Modified PCS-*b*-PE Polymer (PCS = polycarbosilazane, PE = polyethylene). Adapted from Ref 51. Copyright 2014 Wiley-VCH Verlag GmbH & Co



The HZSM-5-based Ni, Pd, and Ru catalyst have also shown impressive activities in upgrading pyrolysis oil[44] and hydrodeoxygenation reactions of lignin-derived phenolic monomers.[45,46]

Other acidic supports, for instance carbon aerogel bearing a sulfonic acid group, were investigated by Park et al.[47] The decomposition of 4-phenoxyphenol (4-O-5 model) by Pd NPs supported by these acidic supports were studied. High acidity correlates with high conversions of 4-phenoxyphenol (up to 72%). The formation of cyclohexanol indicates significant arene hydrogenation.

The Hartwig group, in the extension of their previous work, developed highly selective heterogeneous nickel catalyst for the HGL of diaryl, benzyl-aryl, and benzyl-alkyl ethers to form arenes and alcohols as the exclusive products.[48] No support was used to stabilize the heterogeneous catalysts, and *m*-xylene was used as a solvent. The catalysts were generated from the nickel precursor [Ni(COD)$_2$] or a nickel dialkyl in the presence of a base (NaO-*t*-Bu) whose absence displayed lower reactivity and selectivity for HGL over hydrogenation. Catalyst loadings from 20 mol % to 0.25 mol % were explored.

Song et al.[49] compared a heterogeneous nickel catalyst with precious metal catalysts. Ni, Ru, and Pd NP supported over carbon were tested for their activity in the HGL of *β*-O-4 model compounds. The selectivity of the C−O bond cleavage of the Ni/C catalyst was 85%, and higher than that of Ru/C (40%) and Pd/C (69%) catalyst systems.

Chaterjee et al.[50] have used supercritical carbon dioxide as reaction medium for the HGL of diphenyl ether by carbon supported Rh, Pt, and Pd catalysts. Rh/C showed a better performance than Pt/C and Pd/C catalysts in the HGL of diphenyl ether. The CO$_2$ pressure and the presence of water influence the performance of the catalysts strongly. Furthermore, unsymmetrically substituted diaryl ether and alkyl-aryl ether compounds were investigated.

Recently, our group reported[51] the selective HGL of aryl ethers using novel porous Ni/SiC catalysts in water. The catalysts were fabricated by the self-assembly of nickel modified polycarbosilane-*block*-polyethylene (PCS-*b*-PE) polymer followed by pyrolysis (Scheme 9). The porosity was fine-tuned by changing the length of the organic block (PE) and Ni/SiC materials with micro-, meso-, and micromeso (hierarchical) pores were generated. The hierarchically porous Ni/SiC catalyst was found superior in activity to the other two catalysts with only micro or meso pores. Benzyl-phenyl ether was hydrogenolysed quantitatively with high phenol selectivity in the absence of base at 110 °C (10 bar of H$_2$). *β*-O-4, *α*-O-4, and 4-O-5 model compounds were cleaved quantitatively in the presence of KO-*t*-Bu providing exclusively aromatic products (90−120 °C at 6 bar of H$_2$). The catalysts showed no loss of activity up to five catalytic runs. This was the first example of a reusable catalyst with hydrothermal stability able to cleave examples of all lignin model classes quantitatively with exclusive formation of aromatic products.

A layered double hydroxide supported nickel catalyst was employed for the cleavage of 2-phenoxy-1-phenyl ethanol (*β*-O-4 model) at 270 °C by Beckham/Biddy and co-workers.[52] The influence of the temperature, the basicity of the support, and the Ni loading on the cleavage of the C−O bond was explored. Because of the basic nature of support, no base was required and the catalysts showed good reusability.

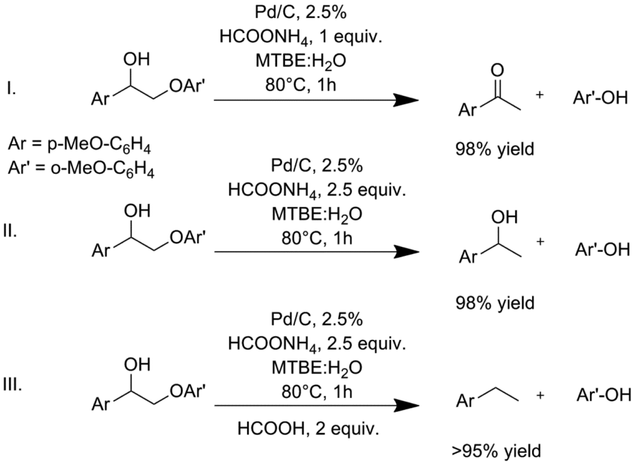
Very recently, Esposito et al. reported the HGL of *α*-O-4, *β*-O-4, and 4-O-5 model compounds in ethanol at 100−150 °C (12 bar of hydrogen) using a novel Ni/TiN catalyst.[53] High selectivity to aromatic compounds was observed for *α*-O-4 and *β*-O-4 models. Diphenyl ether (4-O-5 model), however, was also hydrogenated to cyclohexanol (49%). Strong Ni−TiN interactions were proposed to render high activity and good selectivity of the catalyst.

2.1.2. HGL via Hydrogen Transfer. On the basis of observations made by Miller at al.[54], namely, a base-mediated hydrogenolysis, Ford and co-worker described the hydrogen transfer from methanol to the lignin model dihydrobenzofuran (DHBF).[55] A Cu-doped porous metal (Mg, Al) oxide catalyst was used. Related Ni- and Mn-doped catalysts showed less activity and Fe- or Co-doped catalysts marginal or no activity, respectively. The reaction was carried out at temperature of 300 °C, which is above the supercritical temperature of methanol. No activity was observed below 240 °C. During the reactions, the formation of a gas mixture containing H$_2$ as the main component was observed. Methanol reformation, known to be catalyzed by Cu/metal oxide catalyst systems was proposed to form H$_2$. The reaction is not very selective. Ether hydrogenolysis and hydrogenation of the aromatic ring were observed. At the concentration maximum of the non-hydrogenated hydrogenolysis product (ethylphenol), about 55% of DHBF is converted and about 40% of the arene hydrogenation product was observed already. Shortly after, the same group described that hydrogen transfer from methanol at 300 °C catalyzed by a Cu-doped metal oxide catalyst (UCSB process) can also disassembly organosolv lignin.[56] A complex product mixture consisting out of monomeric substituted cyclohexyl derivatives with a greatly reduced oxygen content was obtained. Again, arene hydrogenation is dominating under conditions in which methanol reforming takes place. ^{1}H NMR spectroscopy was used to analyze the products. The UCSB process was then used to allow quantitative catalytic conversion of wood to liquid and gaseous products in a single-stage reactor with low char formation.[57] A mixture of aliphatic alcohols and methylated products thereof was the major liquid product. Such alcohols are, in principle, suitable as liquid fuel (additives).

Beside methanol, formic acid can be used as hydrogen source, as demonstrated by Jones and co-workers for the depolymerization of organosolv switchgrass.[58] A Pt/C catalyst was used, and the reactions were conducted at 350 °C, a temperature at which formic acid starts to decompose uncatalyzed. The combination of formic acid and the catalyst gave rise to higher fractions of lower molecular weight compounds in the liquid products. Twenty-one wt % of the biomass is converted into molecular aliphatic species after 4 h of reaction time. The O/C ratio was reduced by 50%, and the H/C molar ratio increased by 10%.

The transfer HGL of *β*-O-4 model (Scheme 10) using ammonium formate and metal-supported carbon catalysts (M/C) in water under air were reported by the Samec group.[59] A base and a cosolvent (ethanol) were required for this reaction to take place, and Pd/C showed the best performance among others (Rh/C, Re/C, Ir/C, Ni/C).

Scheme 10. Model Compound Mimicking *β*-O-4 Linkage of Lignin Selectively Converted to (I) Ketone, (II) Alcohol, and (III) Alkanes by Changing the Conditions (MTBE = metyl-*t*-butylether). Adapted after Permission from Ref 59. Copyright 2014 Wiley-VCH Verlag GmbH & Co



Recently, Song et al. reported on the valorization of birch wood lignin at 200 °C using a Ni/C catalyst prepared by an incipient-wetness method. The best conversions (about 50%) were observed in methanol, ethanol, and ethylene glycol.[60]

Following the work of the Ford group,[55−57] Hensen and co-workers reported the valorization of soda lignin in supercritical ethanol using a Cu Al/Mg oxide catalyst. Low ring hydrogenation activity was observed, and nearly half of the monomer fraction is oxygen free. NMR studies indicate the alkylation and esterification of the lignin depolymerization fragments by ethanol. In comparison to methanol, ethanol was found to be more effective in producing monomers and in avoiding char formation.[61]

Li and co-worker used a Mo-carbide catalyst in ethanol at 280 °C. Kraft lignin was converted into low molecular weight compounds with a yield of 1.64 g per g of lignin for the 25 most abundant liquid products.[62]

Very recently, Anastas and co-worker reported on the catalytic depolymerization of solvent-extracted lignin from candlenut nutshells. In the presence of supercritical methanol, an almost quantitative conversion of lignin to bio-oil (composed of monomers and low-mass oligomers with high aromatic content) was obtained in 6 h at 310 °C.[63] A Cu- and La-doped metal oxide catalyst system was used.[64] The same lignin source was successfully depolymerized in methanol with added pressure of hydrogen.[65] A Cu-doped porous metal oxide catalyst was used to convert low-molecular weight lignin into mixtures of aromatic products in high yields. In the temperature range of 140−180 °C, 60−93% conversion was observed (8−20 h of reaction time). Predominantly, monomers (catechol derivatives) and some oligomers were formed. We also like to draw the reader's attention to an interesting table listed in this manuscript comparing reaction conditions from selected biomass conversion studies.

2.2. Bimetallic Catalyst Systems. Apart from monometallic solid catalysts supported over various carriers, there are many reports about the use of bimetallic solid catalysts for the breaking of C−O bonds of aryl ethers. Here, bimetallic means that the catalytically active site is of bimetallic nature. A catalyst system is not listed in the bimetallic section if the support contains the second metal.

The group of Marks had utilized lanthanoid or Hf triflates and Pd NPs deposited on Al_2O_3 in an ionic liquid for the HGL of cyclic and linear ethers, among them alkyl-aryl ethers.[66] Selective HGL was observed. In this tandem pathway, the metal triflates catalyze the endothermic dehydroalkoxylation.[67,68]

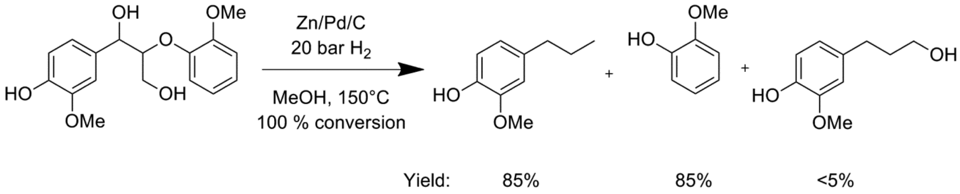
A commercial $CoMo/Al_2O_3$ catalyst was used by Jongerius et al. They applied this catalyst to a library of lignin model compounds at 50 bar of hydrogen and 300 °C in dodecane, using a batch autoclave system.[69] In the case of *β*-O-4 models, complete conversion and recovery of about 1/3 of the aromatics were observed after 4 h of reaction time. This process was then combined with a liquid phase reforming reaction[70] over Pt supported by Al_2O_3 at 225 °C to convert organosolv, kraft, and sugar cane bagasse.[71]

A stable and reusable bimetallic FeMoP catalyst for the cleavage of alkyl-aryl ethers has been reported by Hicks and co-workers.[72] A selectivity up to 50% of ethylbenzene and 5% phenol for ß-O-4 model HGL was observed.

Another bimetallic catalyst (Zn/Pd/C) catalyst for the cleavage and hydrodeoxygenation of C−O bonds was recently reported by Abu-Omar and co-workers.[73] The cleavage of *β*-O-4 lignin models by this catalyst system is shown in Scheme 11. The catalyst offered better selectivity to aromatic products as compared to Pd/C catalyst under the optimized reaction conditions (150 °C, 21 bar of hydrogen pressure).

Various bimetallic core−shell M-Ni (M = Ru, Rh, Pd, Pt, Ir, Ag, Au, Cu, Fe, Co, Re, Sn) catalysts were tested for the HGL of a *β*-O-4 model (2-phenoxy-1-phenyl ethanol) at 130 °C, 10 bar of

Scheme 11. Cleavage of a *β*-O-4 Model Compound Using Bimetallic Zn/Pd/C Catalyst (Ref 54). Adapted with Permission from Ref 73. Copyright 2013 The Royal Society of Chemistry



hydrogen pressure by Zhang et al.[74] 87% yield of C−O cleavage products was achieved in just 1 h with NiAu, the catalyst which showed the best performance. Lignin HGL with this catalyst led to 14 wt % aromatic monomers.

In a very recent publication,[75] the authors extended their investigation to bimetallic NiRu, NiRh, and NiPd catalysts. A NiRu catalyst with the metal composition $Ni_{85}Ru_{15}$ showed the best performance in *β*-O-4 type C−O bond HGL at low temperature (100 °C) and low H_2 pressure (1 bar). The authors attribute this superior activity to the small size of the bimetallic nanoparticles (2 nm).

3. Electrocatalysis. The cleavage of aryl ethers can occur under electrocatalysis conditions. Bartak and co-worker have reported a series of studies on electrochemical carbon−oxygen bond-cleavage in alkyl-aryl (*p*-cyanoanisole)[76] and diaryl ethers (diphenyl ether,[77,78] phenoxynaphthalene[79]) under inert conditions. Their studies provide an insight about the reaction pathways and the relative stability of different C−O bonds.

Cathodic reduction of (C_{aryl}−O) of 4-O-5 lignin model (diphenyl ether) was investigated by Kariv-Miller and co-worker.[80] They used tetrabutylammonium salts as electrolytes and mercury cathode in aqueous and mixed organic−aqueous solutions. A mixture of both hydrogenation and cleavage products were observed.

The Menard group[81] had used Raney-nickel electrodes for electrocatalytic HGL (ECH) of benzyl-phenyl ether in aqueous ethanol. The catalyst offered broad substrate scope, and the efficiency of HGL of the C−O bonds were optimized to 100% by choosing the proper substrate concentration, current density and temperature. In a later publication,[82] the same group designed electrodes consisting of particles of a transition metal entrapped and dispersed in a reticulated vitreous carbon matrix and studied them in ECH of 4-phenoxyphenol. Catalysts based on Raney-nickel showed very good activities. Furthermore, ECH of *β*-O-4 models was studied by the Menard group using Raney-nickel and Pd electrodes.[83] Very recently, the Huang group reported that sodium borohydride ($NaBH_4$) promoted electrochemical reductive cleavage of aryl ethers.[84] High yields of phenol and arenes were obtained at room temperature by their water and air stable process.

■ CONCLUSION AND OUTLOOK

The HGL of aryl ethers has been described by many catalysts (homogeneous and solid catalysts), under extremely diverse conditions (gas phase and liquid phase), and by different mechanistic pathways. Furthermore, a variety of reducing agents, including the in situ generation of H_2, has been reported. The different conditions, mechanisms, and reducing agents reported complicate the comparison between the catalysts.

Catalysts. With the many catalysts at hand, the best overview is given by ordering them according to the catalytically active metal. Nickel—identified nearly a century ago—seems to be very promising. First, it is an inexpensive and abundant metal. Second, there are no clear indications that expensive noble metals are significantly more active. Third, nickel catalysts gave the best selectivity for the most challenging substrates (diaryl ethers) in combination with the reducing agent of choice (i.e., dihydrogen). Because lignin is the only sustainable resource of aromatic compounds, this selectivity issue is critical. Table 1 shows the homogeneous and heterogeneous catalysts that were able to cleave diphenyl ether quantitatively and selectively to aromatic products, including reaction conditions.

Table 1. Listing of the Best Catalyst in HGL of Diphenyl Ether Using H_2 as the Reducing Agent[a]

entry	catalyst	cat. loading [mol % Ni]	H_2 pressure [bar]	time [h]	ref
1	Ni−NHC complex	20	1	16	11
2	heterogeneous Ni cat. generated from [$Ni(COD)_2$]	20	1	96	48
3	heterogeneous Ni cat. generated from [N_2NiR_2]	2	1	96	48
4	Ni NP (mean diameter 2.7 nm) supported by porous SiC[b,c]	7	6	20	51

[a] Conditions are given for full conversion and quantitative selectivity towards benzene and phenol (NHC, see Scheme 3, N_2 = tetramethylethane-1,2-diamine, R = trimethylsilylmethyl). General conditions used for all catalysts: temperature =120 °C, 2.5 equiv of base (NaO*t*Bu or KO*t*Bu). [b] Catalyst is stable toward moisture (solvent was water). [c] Catalyst was recycled 4 times with no activity loss.

Table 1 indicates that it is possible to cleave quantitatively and highly selectively with at least a few catalysts. Furthermore, reusability and stability in water have been shown for one of them (Entry 4, Table1). The condition under which the catalyst listed in Table 1 gives full conversion in the HGL of diphenyl ether and quantitative formation of aromatic products requires an excess of base. Such conditions are most likely not applicable in large-scale lignin valorization.

Catalyst comparison is difficult with the other two lignin models (*α*-O-4 and ß-O-4). Here, many catalysts are described for the selective HGL. The many different conditions permit a proper comparison. The introduction of benchmark conditions might be helpful to allow a better comparison in the future. We suggest 10 bar and 100 °C, which is not too mild for heterogeneous catalysts and homogeneous metal catalysts can still survive under such conditions. Furthermore, the models of the lignin C−O bonds differ drastically. For instance, the rate of acid-catalyzed *β*-O-4 cleavage in models exhibiting a phenolic hydroxyl group is 2 orders of magnitude faster than in nonphenolic models.[85]

In terms of lignin valorization, Cu-doped metal oxide catalysts are very promising. They undergo HGL efficiently via hydrogen transfer from alcohols.

Mechanisms and Reducing Agents. Lignin valorization via HGL involves the cleavage of diphenyl ethers (4-O-5 linkages) and the C_{Alkyl}−O bond cleavage of alkyl-aryl ethers (*α*-O-4 and ß-O-4 linkages). Detailed mechanistic investigations of both cleavage reactions are rare, especially in the presence of H_2. On the other hand, the C_{Aryl}−O bond cleavage of alkyl-aryl ethers has been investigated mechanistically to some extent.[17,18,20] Different mechanistic pathways have been published for Ni catalysts in combination with H_2 or silanes as reducing agent. Insertion of Ni(0) species into the C_{Aryl}−O bond (an aryl-Ni(II) alkoxide is formed) followed by ß-H elimination and reductive elimination in combination of hydrogenation has been proposed for H_2-based HGL (Scheme 6). The role of arene coordination in C−O bond cleavage reactions of alkyl-aryl ethers was recently described in combination with iridium.[86] The Ru complex catalyzed HGL of 2-aryloxy-1-arylethanols (*β*-O-4 models) under a nitrogen atmosphere is proposed to proceed by initial dehydrogenation to give the ketone, which then undergoes HGL using the hydrogen that was generated in the dehydrogenation step (Scheme 7).[22−25]

Heterogeneous catalysis in liquid phase is difficult to analyze with regard to relevant surface species in comparison to the gas phase reaction mediated by the solid catalyst. This general limitation makes it difficult to identify key intermediates and their binding at catalytically active sites. Furthermore, it is not clear what relevance reversibly formed and solvent stabilized metal nanoclusters may have in HGL of aryl ethers in solution. Regarding kinetic investigation of HGL of Ni catalysts in water and nonpolar solvents, we like to draw the reader's attention to the inspiring work of Lercher/Zhao and co-workers[42,43] and the section in which we summarize parts of this work.

Relevance of Model Studies for Lignin Valorization. Most of the efforts have been devoted to the use of lignin models as substrates for the investigation of the cleavage of C−O bonds of lignin polymers, which are worthwhile for understanding the nature of the reaction and the performance of the catalysts. More attention should be given to lignin itself and catalysts to be developed which could cleave lignin actively and selectively into useful platform chemicals.[87]

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Notes

The authors declare no competing financial interest.

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