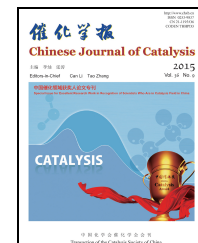


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Review (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

Selective activation of the C–O bonds in lignocellulosic biomass for the efficient production of chemicals

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ABSTRACT

The efficient transformation of abundant and renewable lignocellulosic biomass for the production of chemicals and fuels is of considerable importance for establishing a sustainable society. The selective catalytic conversion of the major components of lignocellulosic biomass, including cellulose, hemicellulose and lignin, into key platform chemicals under mild conditions represents an ideal route for the utilization of this abundant resource. Cellulose is composed of multiple glucose units, which are linked together through β -1,4-glycosidic bonds, and the selective cleavage of these glycosidic bonds would therefore provide access to glucose and glucose derivatives. Hemicellulose is a heteropolysaccharide composed of different sugar units such as glucose, mannose, xylose, arabinose and galactose. The selective cleavage of the glycosidic bonds in hemicelluloses would therefore provide a mixture of different sugars. In contrast to cellulose and hemicellulose, lignin is a complex macropolymer consisting of methoxylated phenylpropane structures. Furthermore, lignin contains a variety of different C–O bond types, including β -O-4, α -O-4 and 4-O-5 bonds, which connect the primary aromatic units in lignin. The selective cleavage of these C–O bonds would therefore lead to the formation of high-value aromatic compounds. In this review article, we have provided a detailed summary of recent advances towards the development of new catalysts and novel strategies for the selective cleavage of the C–O bonds in cellulose, hemicellulose and lignin, as well as closely related model systems, for the production of glucose, glucose derivatives (including alkyl glucosides, hexitols and gluconic acid), xylose, arabinose and aromatic compounds. The key factors determining catalytic performances have been described in detail. The reaction mechanisms have also been discussed to provide the reader with a deeper understanding of the processes involved in the selective activation of C–O bonds.

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1. Introduction

Dwindling fossil fuel supplies, increasing demands for energy and growing environmental concerns have led to a signif-

icant increase in research activities directed towards the efficient utilization of renewable biomass resources. Lignocellulosic biomass is the most abundant and inedible biomass resource, and is considered by many researchers to be a promis-

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ing carbon feedstock for the sustainable production of chemicals and fuels. Several routes have been developed to date for the utilization of lignocellulosic biomass, including the high-temperature gasification of lignocellulosic biomass for the formation of syngas, which can be used for the production of hydrocarbon fuels via the Fischer-Tropsch synthesis [1–3]. The pyrolysis of biomass can be used to produce bio-oils, but further research is required to improve the overall efficiency of this process because the resulting bio-oils are generally low quality, complex mixtures [1–3]. The major limitations of the two processes described above are their high energy consumption and low selectivity [2]. The development of new and improved routes for the selective catalytic conversion of lignocellulosic biomass into target products under mild conditions has therefore attracted considerable interest from researchers working in a variety of different fields [1–17].

Lignocellulosic biomass is composed of cellulose (35%–50%), hemicellulose (25%–30%) and lignin (15%–30%) [5]. Cellulose is a macropolymer of D-glucose, where the individual glucose units are linked together by β -1,4-glycosidic (C–O–C) bonds (Fig. 1). This type of linkage leads to the side-by-side arrangement of the glucose units in a chain-like manner, which results in an strong intramolecular hydrogen bonding interaction between the hydroxyl groups in close proximity to the glycosidic bonds. The molecular chains of cellulose can be efficiently packed through a series of intramolecular hydrogen bonding interactions, making the crystalline structure of cellulose incredibly strong and robust [5]. Alt-

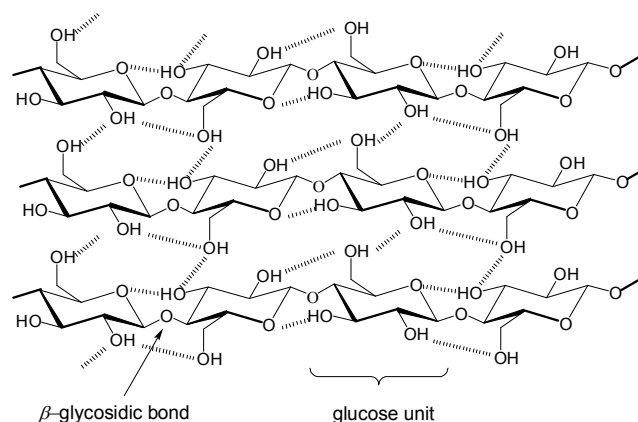


Fig. 1. Structure of cellulose and its extensive hydrogen-bonding networks.

hough the efficient packing of cellulose gives it a strong crystalline structure, it also makes cellulose insoluble in water and most organic solvents at low temperatures. Furthermore, the glycosidic bonds of cellulose can be difficult to access as catalytic sites for the cleavage of the C–O bonds. The catalytic cleavage of the glycosidic bonds in cellulose can therefore be challenging under mild conditions. In contrast to cellulose, hemicellulose is a heteropolysaccharide composed of different sugar units such as glucose, mannose, xylose, arabinose and galactose [17]. Although these basic sugar units are also connected to each other through glycosidic bonds, the overall lack of uniformity in the structure of hemicellulose makes it a highly



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Ye Wang (College of Chemistry and Chemical Engineering, Xiamen University) **received the Catalysis Award for Young Scientists in 2010**, which was presented by The Catalysis Society of China, because of his outstanding fundamental studies on catalysis for selective oxidation of hydrocarbons. Professor Wang received his B. S. and M. Sc. degrees from Nanjing University, and obtained his Ph.D. degree in 1996 from Tokyo Institute of Technology of Japan. He worked as research associate at Tokyo Institute of Technology, Tohoku University and Hiroshima University of Japan during 1996–2000 and was promoted to associate professor at Hiroshima University in 2001. He became a full professor of Xiamen University in the August of 2001. He is currently the director of Institute of Catalysis Science and Technology of Xiamen University. He received Distinguished Young Scholar's Fund of National Natural Science Foundation of China in 2006. Professor Wang's research focuses on fundamental catalysis for efficient utilization of carbon resources, mainly including (1) Oxidative transformations of methane and lower alkanes into value-added chemicals; (2) Fischer-Tropsch synthesis; (3) Conversion of biomass or bio-based platform molecules to chemicals; (4) Photocatalysis for CO₂ conversion and chemical synthesis. He has published more than 160 peer-reviewed papers with an H-index of 41.

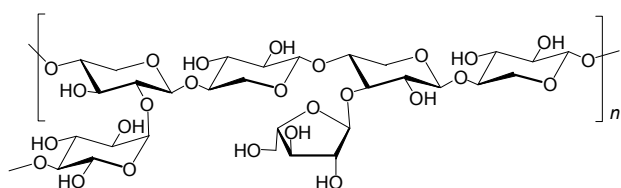


Fig. 2. Representative structure of hemicellulose.

branched polymer (Fig. 2). The crystallinity of hemicellulose is therefore much lower than that of cellulose, making it much more reactive [17].

Lignin is a three-dimensional amorphous polymer that consists of methoxylated phenylpropane structures (Fig. 3) [15, 16]. The three primary monomers in lignin have been identified as *p*-coumaryl, coniferyl and sinapyl alcohols, and the relative abundance of these monomers varies depending on the origin of the lignin. For example, softwood lignin is made up of approximately 90% coniferyl alcohol, whereas hardwood lignin is composed of roughly equal proportions of coniferyl and sinapyl alcohols [16]. The different monomers in lignin are linked through a variety of different C–O (e.g., β -O-4, α -O-4, 4-O-5) and C–C (e.g., 5-5, β -5, β -1, β - β) bonds. Among these linkages, the β -O-4 bond is dominant and represents 45%–62% of the linkages in lignin, with the α -O-4 and 4-O-5 bonds representing 3%–12% and 4%–9% of the remaining bonds, respectively [16]. It is generally envisaged that the selective cleavage of the abundant C–O bonds in lignin, especially the β -O-4 bonds, would result in the formation of aromatic compounds or low-molecular-mass products for downstream processing.

Several strategies have been established for the isolation of the three different components of lignocellulosic biomass, making it possible to achieve the independent conversion of these materials [16]. For instance, hemicellulose can be readily separated from lignocellulosic biomass through hydrolysis, which provides near quantitative access to C₅ and C₆ sugars [17]. Notably, the dilute acid hydrolysis of biomass in this way affords a solid residue containing cellulose and lignin, which can be recovered by filtration. Kraft and sulfite pulping processes are major processes in the pulp and paper industries, which are used to separate cellulose from lignin. In the former

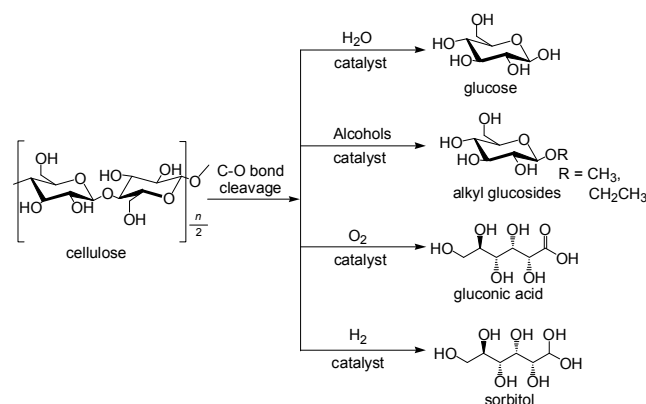


Fig. 4. Selective cleavage of the C–O bonds in cellulose for the production of different platform chemicals.

process, considerable amounts of aqueous NaOH and Na₂S are used to dissolve lignin in a stepwise manner, generating kraft lignin. The later of these two processes involve the use of sulfite with a calcium or magnesium counterion. In addition to these popular pulping processes, the Organosolv process, which employs alcohol/water mixtures as solvent, is another effective method for the isolation of cellulose and lignin from biomass [17].

Given that the compositions and structures of cellulose, hemicellulose and lignin are different, the development of appropriate catalytic systems is critical to the selective conversion of each component into value-added chemicals. Despite the differences in these compounds, the cleavage of their C–O bonds represents a common and critical step in the transformations required to unlock their potential and release their value-added components. The acid catalyzed-hydrolysis of cellulose is an effective strategy for breaking down its glycosidic (C–O–C) bonds to produce glucose as a primary product. When the cleavage of glycosidic bonds is performed in an alcohol solvent or in conjunction with an oxidation or hydrogenation reaction, cellulose can be converted into alkyl glucosides, gluconic acid or hexitols (Fig. 4). These compounds are usually more stable than glucose in water at 373–473 K typically employed for the conversion of cellulose, which could potentially

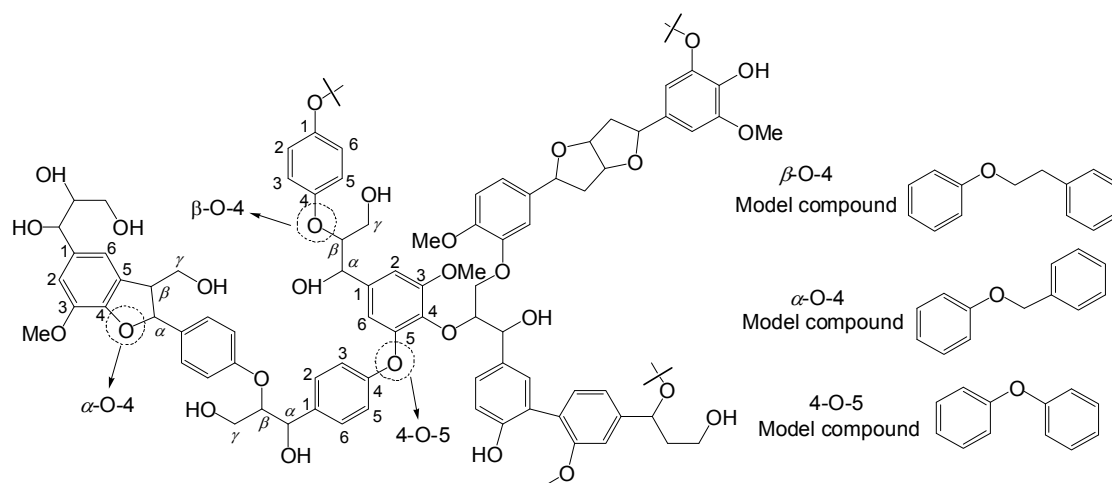


Fig. 3. Lignin fragment showing the different C–O linkages and several model compounds mimicking these linkages.

lead to higher product selectivity. The design of efficient bi-functional catalysts is therefore needed to provide efficient access to organic acids or hexitols from cellulose in this way. The catalytic cleavage of the glycosidic bonds in hemicellulose occurs with greater ease than it does in cellulose because of the higher reactivity of hemicellulose [17]. The dilute acid-catalyzed hydrolysis of hemicellulose can provide access to monosaccharides such as xylose and arabinose. For lignin, hydrolysis and hydrogenolysis reactions are frequently used to break down its C–O bonds to give phenols, together with a range of other aromatic compounds [16]. However, the high reactivity of the phenolic products and intermediates of these reactions can participate in a variety of different side reactions during the transformation of lignin, making the selective cleavage of C–O linkages highly challenging [16]. Moreover, because of the overall complexity of lignin, considerable effort has been focused on the use of model compounds to mimic the C–O linkages in lignin to develop a deeper understanding of its reactions (Fig. 3).

This review is focused on recent advances in the transformations of cellulose, hemicellulose and lignin into value-added chemicals via the selective cleavage of their C–O bonds. The key factors affecting catalytic performance have been presented in detail. Furthermore, the reaction mechanisms for the different transformations of cellulose, hemicellulose, lignin and their model compounds have been discussed in detail to provide an in depth understanding of the steps involved in the activation of the C–O bonds in these compounds.

2. Activation of glycosidic bonds in cellulose

Many catalytic systems have been developed for the conversion of cellulose into C₆ platform compounds such as glucose, alkyl glucosides, hexitols and gluconic acid. Table 1 provides a summary of some typical results reported in recent years for the conversion of cellulose using a variety of different

catalysts and reaction conditions. This section will highlight some of the efficient catalytic systems for the conversion of cellulose through the cleavage of its glycosidic bonds.

2.1. Hydrolysis

Cellulase enzymes are known to catalyze the hydrolysis of cellulose with high selectivity under mild conditions [18]. However, the use of this enzyme to catalyze the hydrolysis of cellulose has been limited by low reaction rates, the high cost of the enzyme and complex handling procedures. Based on these limitations, the development of chemical catalysts for the hydrolysis of cellulose has received considerable attention from numerous researchers. The hydrolysis of cellulose can generally be achieved under aqueous conditions using a Brønsted acid catalyst and two different mechanisms have been proposed for this reaction [5]. As shown in Fig. 5, the first step in the Brønsted acid-catalyzed hydrolysis of cellulose either involves the protonation of the glycosidic oxygen (route A) or the pyranic oxygen (route B). Route A would lead to the formation of a cyclic carbocation by the cleavage of the C–O bond, which would be followed by the release of one pyranoglucose group in the second step. The subsequent reaction of water with the carbocation would regenerate a proton and complete the hydrolysis cycle. In contrast, route B would lead to a ring-opening reaction and the formation of an acyclic carbocation. The glycosidic bond of the acyclic carbocation would then be rapidly cleaved by the addition of a water molecule. Theoretical calculations for the hydrolysis of cellobiose, which is a dimer of glucose and can therefore be considered as the simplest model molecule of cellulose, revealed that the protonation of the glycosidic bond followed by the formation of a cyclic carbocation intermediate (route A) was energetically more favorable than route B. This suggests that cellulose may be hydrolyzed following route A [19]. Experimental evidence has also been obtained to support route

Table 1

Typical catalytic systems reported for the conversion of cellulose into C₆ compounds via selective cleavage of its glycosidic bonds.

Cellulose type	Catalyst	Reaction conditions	Product	Yield (%)	Ref.
Microcrystalline	H ₅ BW ₁₂ O ₄₀	333 K, 48 h	glucose	77	[30]
Ball-milled	SiO ₂ -C-SO ₃ H	423 K, 24 h	glucose	50	[31]
Ball-milled	CMK-3-SO ₃ H	423 K, 24 h	glucose	75	[34]
Microcrystalline	C-SO ₃ H	373 K, 3 h	oligosaccharides	64	[38]
Microcrystalline	CP-SO ₃ H	393 K, 10 h	glucose	93	[39]
Microcrystalline	H ₄ SiW ₁₂ O ₄₀	473 K, 2 h, in methanol	methyl glucosides	57	[54]
Microcrystalline	Amberlyst-15	373 K, 24 h, in BMIMCl and octanol	octyl glucosides	82	[57]
Microcrystalline	PVP- H ₄ SiW ₁₂ O ₄₀	433 K, 4 h, in butanol	butyl glucosides	78	[58]
Ball-milled	Au/Cs ₃ PW ₁₂ O ₄₀ -H ₃ PW ₁₂ O ₄₀	418 K, 0.5 h, P(O ₂) = 1 MPa	gluconic acid	85	[63]
Ball-milled	Ru/C-H ₄ SiW ₁₂ O ₄₀	463 K, 1 h, P(H ₂) = 9.5 MPa	hexitols	85	[72]
Ball-milled	Ru/C-Cs _{3.5} SiW ₁₂ O ₄₀	443 K, 48 h, P(H ₂) = 5 MPa	hexitols and sorbitan	90	[73]
Microcrystalline	Ru/C-H ₂ SO ₄	423 K, 1 h, P(H ₂) = 5 MPa	hexitols	94	[76]
H ₃ PO ₄ -treated	Ru/CNT	458 K, 24 h, P(H ₂) = 5 MPa	hexitols	73	[79]
Ball-milled	Ni/CNF	463 K, 24 h, P(H ₂) = 6 MPa	hexitols	57	[84]
Ball-milled	Ni/oxidized CNF	463 K, 24 h, P(H ₂) = 6 MPa	hexitols	71	[85]
Microcrystalline	Ir-Ni/MC	518 K, 0.5 h, P(H ₂) = 6 MPa	hexitols	58	[86]
Ball-milled	Pt/BP2000	463 K, 24 h, P(H ₂) = 5 MPa	hexitols	58	[89]
Microcrystalline	Ni ₂ P	498 K, 1.5 h, P(H ₂) = 6 MPa	hexitols	53	[90]

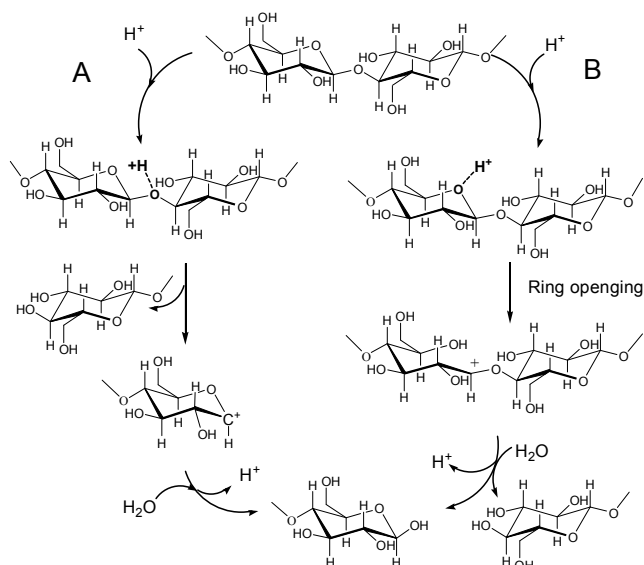


Fig. 5. Possible mechanism for the Brønsted acid-catalyzed hydrolysis of cellulose.

A for the hydrolysis of glycosidic bond [20,21].

Many studies have been devoted to the hydrolysis of cellulose in the presence of a homogeneous mineral acid (especially H_2SO_4 and HCl) or carboxylic acid. Concentrated mineral acids are generally capable of penetrating and breaking down the huge hydrogen bonding networks of cellulose, causing it to swell, and therefore making the glycosidic bonds more accessible to protons. Concentrated H_3PO_4 and H_2SO_4 have been reported to hydrolyze cellulose under mild conditions [21]. Although diluted acid can also be used to catalyze the hydrolysis of cellulose to glucose, high temperatures are typically required to ensure high catalytic performances [22,23]. These energy-demanding conditions can lead to the formation of undesired by-products through the degradation of the cellulose and the resulting products. The organic acid (e.g., oxalic and maleic acid)-catalyzed depolymerization of cellulose can also proceed efficiently in water under mild reaction conditions (373–398 K) in the presence of NaCl (30 wt%) [24]. It has been proposed in this particular case that the salt solution functions in a similar manner to an ionic liquid, and disrupts the hydrogen-bonding networks of the cellulose fibers.

Compared with typical mineral acids, polyoxometalates possess stronger Brønsted acidity [25–28] and are therefore considered to be promising candidates for the hydrolysis of glycosidic bonds. Shimizu et al. [29] compared the catalytic activities of two heteropolyacids (i.e., $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$) with those of three mineral acids (i.e., HClO_4 , H_2SO_4 and H_3PO_4) for the hydrolysis of cellobiose and cellulose under aqueous conditions. The results revealed that these Brønsted acids gave glucose as the main product from cellobiose. Furthermore, the glucose yield achieved by the five different catalysts increased in the order $\text{H}_3\text{PO}_4 < \text{H}_2\text{SO}_4 < \text{HClO}_4 < \text{H}_3\text{PW}_{12}\text{O}_{40} \approx \text{H}_4\text{SiW}_{12}\text{O}_{40}$. The conversion of cellulose also produced reducing sugars in addition to glucose under these reaction conditions. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ afforded total reducing

sugar (TRS) and glucose yields of 18% and 15%, respectively, whereas H_2SO_4 provided a TRS yield of only 10% with almost no glucose. As well as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, the highly negatively charged heteropolyacids (e.g., $\text{H}_5\text{BW}_{12}\text{O}_{40}$, $\text{H}_5\text{AlW}_{12}\text{O}_{40}$, $\text{H}_5\text{GaW}_{12}\text{O}_{40}$ and $\text{H}_6\text{CoW}_{12}\text{O}_{40}$), which are more acidic than $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and mineral acids, have been reported to be more efficient for the cleavage of the glycosidic bonds in cellulose [30]. For example, a glucose yield of 77% was achieved for the conversion of cellulose using an aqueous solution of $\text{H}_5\text{BW}_{12}\text{O}_{40}$ (0.7 mol/L) at 333 K. Notably, H_2SO_4 and HCl only provided glucose yields of 5% and 10%, respectively, under the same conditions. Improved glucose yields of 38% and 61% were obtained for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, respectively. These results therefore demonstrate that stronger Brønsted acidity favors the cleavage of the glycosidic bonds in cellulose. Furthermore, heteropolyanions contain a large number of external oxygen atoms and may therefore behave as strong hydrogen-bond acceptors. Indeed, when an aqueous solution of $\text{Na}_5\text{BW}_{12}\text{O}_{40}$ (0.7 mol/L) or $\text{H}_5\text{BW}_{12}\text{O}_{40}$ (0.7 mol/L) was used to treat cellulose at room temperature, its crystallinity decreased [30]. In contrast, no changes were observed in the crystallinity of cellulose when it was treated with H_2SO_4 or HCl . The decreased crystallinity of cellulose could therefore be another important contributory factor in terms of defining the enhanced catalytic performances of highly negatively charged heteropolyacids (e.g., $\text{H}_5\text{BW}_{12}\text{O}_{40}$).

Although liquid acid-based homogeneous processes are efficient, these systems can be limited by problems associated with product/catalyst separation, reactor corrosion, catalyst recycling and waste-effluent treatment. Consequently, considerable research efforts have been devoted to the development of solid acid catalysts for the hydrolysis of cellulose. The resulting solid acid catalysts generally consist of carbon materials bearing SO_3H or some other oxygen-containing groups that possess some Brønsted acidity [31–34]. Layered transition metals oxides such as HNbMoO_6 have also been employed for the hydrolysis of saccharides, but the glucose yields of these reactions are generally low (e.g., 8.5% for the hydrolysis of cellobiose at 403 K for 12 h) [35]. A zirconium hydrogen phosphate catalyst (most likely in the form of $\text{Zr}(\text{HPO}_4)_2$) was recently developed with an acidity similar to that of zeolite H-Y. This particular catalyst gave glucose yields of 30% and 5.8% at 473 K for the conversions of ball-milled and crystalline celluloses, respectively [36].

Here, we have provided a few examples to highlight the catalytic behaviors of carbon materials bearing sulfonic groups, which have been studied extensively as catalysts for the hydrolysis of cellulose. Onda et al. [37] demonstrated that the treatment of activated carbon (AC) surfaces with concentrated H_2SO_4 led to the formation SO_3H groups on AC surfaces, and that the SO_3H -bearing AC surfaces offered a glucose yield of 50% for the conversion of ball-milled cellulose. In this particular case, the hydrolysis of the C–O–C bonds in cellulose was attributed to the strongly acidic SO_3H groups. Hara and co-workers prepared an amorphous carbon material containing $-\text{SO}_3\text{H}$, $-\text{OH}$ and $-\text{COOH}$ groups by the carbonization of cellulose under N_2 flow followed by sulfonation in fuming

sulfuric acid [38]. The resulting amorphous carbon material bearing an abundance of functional groups catalyzed the hydrolysis of cellulose at 373 K, providing oligomers (β -1,4-glucan) and glucose with yields of 64% and 4%, respectively, following a reaction of 3 h. It is noteworthy that H-mordenite, Nafion and Amberlyst-15 were almost inactive under the same reaction conditions. Adsorption experiments with cellobiose, which also contained β -1,4 glycosidic bond, showed that the phenolic groups on the SO_3H -bearing carbon materials enhanced the adsorption of the β -1,4 glycosidic bonds onto the surface of the catalyst via the formation of a strong hydrogen-bonding interaction. An interaction of this type could not occur on Amberlyst-15 or Nafion, which only possessed SO_3H groups. This result therefore suggests that the formation of hydrogen-bonding interactions between cellulose and the surface of the catalyst enhances the accessibility of the glycosidic bonds to the acidic sites and consequently enhances the hydrolysis reaction.

A similar strategy to this has also been employed to design an acidic resin for the hydrolysis of cellulose [39]. In this particular case a chloromethyl polystyrene (CP) resin was carefully modified by sulfanilic acid treatment. Under certain conditions, the $-\text{Cl}$ groups in the resin were partially substituted with $-\text{SO}_3\text{H}$ groups to give a CP- SO_3H catalyst. In this case, the authors demonstrated that the $-\text{Cl}$ groups facilitated the adsorption of cellulose through the formation of hydrogen bonding interactions, whereas the $-\text{SO}_3\text{H}$ groups served as active sites for the cleavage of the glycosidic bonds. The synergistic effects of the $-\text{Cl}$ and $-\text{SO}_3\text{H}$ groups consequently made CP- SO_3H an excellent catalyst for the hydrolysis of crystalline cellulose, with the glucose yield reaching as high as 93%. In contrast, almost no cellulose was hydrolyzed in the presence of H_2SO_4 under the same reaction conditions.

Zhang and co-workers recently reported that graphene oxide (GO), which is a two-dimensional carbon material decorated with abundant functional groups, behaved as an efficient catalyst for the hydrolysis of cellulose to glucose [40]. The authors went on to claim that the glycosidic bonds in cellulose could be adsorbed on to the surface of the GO through hydrogen bonding interactions, with the simultaneous formation of ester bonds between the hydroxyl groups of cellulose and the carboxyl groups on GO. The CH groups of glucan and the graphene sheets could also form further CH- π interactions [41]. Furthermore, GO is a soft material that can be readily bent when it is suspended in an aqueous solution [40]. The flexible properties of GO could therefore facilitate the synergistic functions of the neighboring phenolic and carboxylic groups, making GO a superior catalyst for the hydrolysis of cellulose.

Besides enhanced hydrogen bonding interactions between the substrate and the catalyst, mechanochemical technology could also be used to enhance the activation of glycosidic bonds. Fukuoka and co-workers studied the hydrolysis of cellulose under aqueous conditions using an alkali-activated carbon material as a catalyst [42]. A carbon catalyst known as K26 was obtained by the treatment of carbon powder with

KOH at 973 K, followed by an acid washing process. This treatment procedure could help to generate weakly acidic sites (e.g., carboxyl and hydroxyl groups) on the carbon material. The K26 catalyst bearing weakly acidic sites afforded glucose and oligomer yields of 2.9% and 10%, respectively, for the hydrolysis of ball-milled cellulose at 453 K. Most notably, the glucose and oligomer yields of this process increased to 20% and 70%, respectively, when the K26 catalysts was mixed with cellulose using a ball-milling technique. The use of a ball-milling technique in this particular case therefore played a significant role in promoting the hydrolysis of cellulose using a solid catalyst. At the same time, the functional groups on the K26 surface undoubtedly had a significant impact on the catalytic performance [42]. A remarkable decrease was observed in the activity of the K26 catalyst when it was subjected to a heat treatment process, which is well known to be capable of removing functional groups such as carboxyl and hydroxyl groups. Aromatic molecules bearing carboxylic and/or phenolic groups have been studied as model catalysts for the hydrolysis of cellobiose at 443 K in water. The use of *o*-hydroxybenzoic acid ($\text{p}K_{\text{a}} = 3.0$) bearing vicinal carboxylic and phenolic groups provided the highest activity ($\text{TOF} = 28 \text{ h}^{-1}$) (Fig. 6). In contrast, *m*- and *p*-hydroxybenzoic acids ($\text{p}K_{\text{a}} = 4.1$ and 4.6) were less active ($\text{TOF} = 5.7$ and 2.4 h^{-1}). Moreover, phenol ($\text{p}K_{\text{a}} = 10.0$) and benzoic acid ($\text{p}K_{\text{a}} = 4.2$) were inactive. These results therefore suggest that, in addition to the acidity (i.e., $\text{p}K_{\text{a}}$ value), the structure of the catalyst also plays a crucial role in determining its catalytic performance. The neighboring carboxylic and phenolic groups in *o*-hydroxybenzoic acid may work synergistically to provide the highest possible activity for the hydrolysis of cellobiose. It is also likely that the phenolic groups could form ethers or hydrogen bonding interactions with the hydroxyl groups in cellobiose or cellulose, which would further enhance the cleavage of glycosidic bonds by the adjacent carboxyl groups.

A variety of carbon material-supported Ru catalysts have been employed for the hydrolysis of cellulose [43,44]. Among the various catalysts with different carbon supports, including mesoporous carbon (CMK), carbon black (XC-72) and AC, the Ru/CMK-3 catalyst showed the highest glucose yield. CMK-3

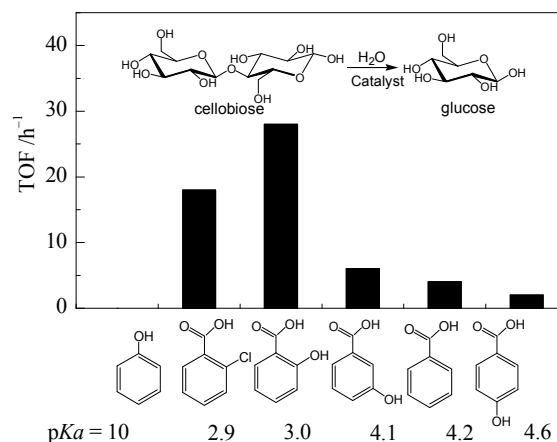


Fig. 6. Hydrolysis of cellobiose by model molecular catalysts at 443 K [42].

itself also catalyzed the hydrolysis of cellulose in water at 503 K, providing glucose and oligosaccharide yields of 21% and 22%, respectively. The loading of 2% Ru onto CMK-3 enhanced the glucose yield to 28%. A further increase in the loading of Ru to 10% led to a further increase in the glucose yield to 34%, although the oligosaccharide yield suffered a significant decrease to 5%. These results therefore indicate that CMK-3 can catalyze the hydrolysis of cellulose into oligosaccharides and glucose, and that the presence of Ru simply facilitates the subsequent conversion of the oligosaccharides to glucose. Further studies have suggested that $\text{RuO}_2\cdot\text{H}_2\text{O}$ is the genuine active Ru species, which may provide both Lewis and Brønsted acidic sites capable of performing the hydrolysis reaction [44].

The pre-oxidation treatment of microcrystalline cellulose with air was very recently shown to be helpful for the activation of its glycosidic bonds [45]. Microcrystalline cellulose was initially treated with air at 483 K for 48 h, and the subsequent hydrolysis of the pretreated cellulose under aqueous conditions at 443 K for 8 h in absence of any catalyst gave a glucose yield of 25%. The hydroxymethyl groups of the glucose units were found to have been oxidized to carboxyl groups during the pre-oxidation treatment. These acid groups could therefore function as catalytically active sites for the hydrolysis of cellulose. Although this strategy for the hydrolysis of cellulose appears to be attractive, the efficiency of this auto-catalytic system remains low. The combination of this strategy with an active acid catalyst for the transformation of cellulose could therefore represent a promising future direction for the efficient activation of glycosidic bonds and the hydrolysis of cellulose.

2.2. Alcoholysis

A wide variety of different reaction solvents besides water have been used to facilitate the activation of glycosidic bonds for the conversion of cellulose. Ionic liquids (ILs) can be used to dissolve cellulose, depending on their structure, and have therefore received considerable attention in terms of their application for the transformation of cellulose [46–50]. For example, Li and Zhao [47] reported that the IL 1-butyl-3-methylimidazolium chloride ($[\text{C4mim}]\text{Cl}$) could be used as a solvent for the hydrolysis of cellulose, which proceeded efficiently in the presence of mineral acids under mild conditions (373 K and atmospheric pressure). Furthermore, the rate of the cellulose hydrolysis reaction was much higher in $[\text{C4mim}]\text{Cl}$ than it was under aqueous conditions. This increase in the rate was attributed to the fact that cellulose can be completely dissolved in $[\text{C4mim}]\text{Cl}$ to give a homogeneous solution, making it easier for the β -glycosidic bonds to be accessed by the acid catalyst. ILs have also been employed for the pretreatment of cellulose, where they were used to break down its robust crystalline structure [50]. The resulting pretreated cellulose could then be hydrolyzed by a mineral acid with a higher degree of efficiency. However, the high solubility of sugars in ILs makes it difficult to extract and recover the sugars generated during the hydrolysis of cellulose.

Alcohol is another attractive reaction medium for the

depolymerization of cellulose in the presence of a mineral acid. The alcoholysis of cellulose was reported in two early studies, but the products were not identified [51,52]. In the absence of a catalyst, supercritical methanol (623 K and 43 MPa) was shown to activate the glycosidic bonds in cellulose, with methyl glucosides being formed as the main products [53]. The results of our previous study showed that the alcoholysis of cellulose in methanol could proceed under much milder conditions (≤ 473 K) in the presence of an acid catalyst with α - and β -methyl glucosides being produced as the major products [54,55]. Among the various mineral acids with the same H^+ concentration, H_2SO_4 provided the highest yield for the conversion of cellulose to methyl glucosides. For example, a methyl glucoside yield of 48% was obtained following the conversion of microcrystalline cellulose in methanol at 473 K for 0.5 h. The use of solid acids such as Nafion, Amberlyst-15 and sulfonated carbon materials also afforded relatively high yields of methyl glucosides under similar conditions. However, the leaching of the SO_3H groups from these catalysts meant that they could not be recycled. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, which are both strongly Brønsted acidic heteropolyacids, also gave high glucoside yields of 43% and 48%, respectively. Notably, the heteropolyacid catalysts could be readily recovered in these cases by a simple diethyl ether extraction.

The alcoholysis of cellulose in methanol and hydrolysis of cellulose in water were compared under the same reaction conditions with the exception of the solvent [54]. A cellulose conversion of 20% and glucose yield of 7.1% were attained for the hydrolysis of cellulose in water at 468 K in the presence of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. The use of methanol as a solvent instead of water afforded a monomer (methyl glucosides) yield approaching 57% together with a cellulose conversion of 85% for the same polyoxometalate catalyst. This result clearly demonstrates that the use of an alcohol as the reaction medium facilitates the acid-catalyzed transformation of cellulose to monosaccharides. The formation of stronger interactions between cellulose and methanol compared with water is probably a key factor in determining the better performance of methanol for the conversion of cellulose. The use of methanol as a solvent therefore appears to provide enhanced access to the glycosidic bonds of cellulose. Furthermore, a comparison of the results for the conversion of methyl glucosides in methanol with those for the conversion of glucose in water shows that the methyl glucosides are more stable towards degradation than glucose under the same conditions, with the exception of the solvent. The higher stability of the methyl glucosides would also contribute to their higher yields during the conversion of cellulose in methanol.

Several other long chain alcohols, including ethanol, butanol, hexanol, octanol, decanol and dodecanol, have also been evaluated as solvents for the acid-catalyzed transformation of cellulose [55–57]. For example, Villandier and Corma used an IL solvent to convert cellulose into butyl-, hexyl-, octyl-, decyl- and dodecyl-glycosides in the presence of the acidic resin catalyst Amberlyst-15 and the corresponding alcohols. The highest octyl-glycoside yield reported in this particular study was 82% when the reaction was conducted at 363 K for 1.5 h

[57]. It is noteworthy that the long-chain alkyl glucosides produced in this way can be used as biodegradable surfactants with low toxicity. Catalysts based on the combination of an IL with a polyoxometalate (i.e., polyvinylpyrrolidone-stabilized heteropolyacid (PVP-HPA)) have reported to be efficient catalysts for the alcoholysis of cellulose in butanol [58]. The use of PVP- $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 5\text{H}_2\text{O}$ as a catalysts in this regard provided >87% conversion of cellulose and 90% selectivity for butyl glucosides at 428 K. Notably, this catalyst could be readily recovered by a simple centrifugation step and reused in subsequent runs. However, the acidic sites of the catalyst gradually leached into the reaction medium during the reaction, leading to the eventual deactivation of the catalyst after it had been recycled several times.

2.3. Bifunctional catalysis

The selective cleavage of the glycosidic bonds in cellulose in the presence of an acid catalyst under aqueous conditions should provide facile access to glucose. However, glucose is very reactive under the hydrothermal conditions employed for the hydrolysis of cellulose because it contains a reactive aldehyde. Glucose can therefore undergo a wide variety of consecutive reactions, including isomerization, dehydration, rehydration, retro-aldol and polymerization reactions under hydrothermal conditions. The oligomers formed through the partial hydrolysis of cellulose can also undergo side reactions with glucose to give a broad range of complicated products. Consequently, the selectivity to glucose cannot be increased to a high enough level at high cellulose conversions. One promising strategy for solving this problem would involve the direct conversion of cellulose to more stable products such as organic acids or polyols. It is therefore envisaged that bifunctional or multifunctional catalysts capable of combining hydrolysis with another function, such as oxidation or hydrogenation, will play a key role in the development of such transformations.

2.3.1. Hydrolysis-oxidation

A bifunctional catalyst with hydrolysis and oxidation abilities could catalyze the conversion of cellulose to gluconic acid, which is an important organic acid with numerous applications in the food and pharmaceutical industries. Gluconic acid can be formed by the selective oxidation of glucose under an O_2 atmosphere, and several Au-based catalysts have been reported to perform efficiently for this transformation [59]. However, only a limited number of studies have been reported to date pertaining to the development of efficient catalysts for the direct conversion of cellulose to gluconic acid [60–64]. By loading Au nanoparticles onto a functionalized carbon nanotube (Au/CNT), we recently succeeded in the conversion of cellobiose, which is a dimer of glucose connected by β -glycosidic bonds, to gluconic acid under an atmosphere of O_2 [60]. Concentrated HNO_3 was used to functionalize CNTs via the formation of acidic groups (e.g., -COOH) on their surfaces, and these functional groups were subsequently shown to play a critical role in the formation of

gluconic acid. The use of a higher concentration of HNO_3 resulted in a larger density of acidic functional groups on the surfaces of the CNT and the resulting Au/CNT catalyst bearing a higher concentration of acidic functional groups gave a higher level of cellobiose conversion. The acidity of the catalyst could also have a significant impact on the rate at which the acidic product (gluconic acid) is desorbed from the surface of the catalyst, which could avoid its consecutive oxidation and improve the selectivity of the reaction. The Au/CNT catalyst was also applied to the conversion of cellulose under an O_2 atmosphere, but the activity was found to be quite low, most likely because of the weak acidity of the oxygen-containing functional groups on the CNTs [60]. A sulfonated activated carbon-supported Pt catalyst has also been reported to be active for the oxidative conversion of biomass, and this bifunctional catalyst could be used for the conversions of cellobiose and starch to gluconic acid [61].

Keggin-type polyoxometalates, especially the H-form Cs salts of heteropolyacids such as $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, which possess strong Brønsted acidity and mesopores, can work as acidic heterogeneous catalysts or catalyst supports. Au nanoparticles loaded on to $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ have been demonstrated to be efficient bifunctional catalysts for the conversion of cellobiose and cellulose to gluconic acid [62,63]. Among the various supports reported in the literature, including metal oxides (e.g., Al_2O_3 , SiO_2 , TiO_2), zeolites (HY, H-ZSM-5), functionalized CNTs and polyoxometalates, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, which has a proper Cs content, has been shown to provide the best catalytic performance towards the formation of gluconic acid. The Cs content of the catalyst had a significant impact on its performance, with small Cs contents giving the best results. The yield of gluconic acid reached 60% at a cellulose conversion of 70% when $\text{Au/Cs}_{1.2}\text{H}_{1.8}\text{PW}_{12}\text{O}_{40}$ was used as a catalyst for the conversion of ball-milled cellulose in water under an O_2 pressure of 1.0 MPa at 418 K for 11 h [63]. The density of the Brønsted acid increased gradually with decreasing Cs content. This result therefore demonstrated that the Brønsted acidity was a key factor for the formation of gluconic acid. Further studies involving the conversion of gluconic acid using $\text{Au/Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ as a catalyst indicated that stability of the gluconic acid product was dependent on the Cs content of the catalysts, with low Cs contents providing higher stability. Based on these results, we proposed that the Brønsted acidity of the catalyst played two roles during the formation of gluconic acid, including (1) to facilitate the hydrolysis of the glycosidic bonds; and (2) to promote the desorption of gluconic acid from the catalyst and prevent its consecutive oxidation. However, it is noteworthy that the deactivation of these catalysts is unavoidable because of the leaching of the H^+ -rich hydrophilic moieties from the surface of the $\text{Au/Cs}_{1.2}\text{H}_{1.7}\text{PW}_{12}\text{O}_{40}$ catalyst following repeated use. An alternative approach would be to harness a combination of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Au/Cs}_3\text{PW}_{12}\text{O}_{40}$ for the conversion of cellulose. Combinations of this type have been reported in the literature to provide gluconic acid yields of 85% and 39% for the conversions of ball-milled and microcrystalline cellulose, respectively, in water under 1.0 MPa of O_2 pressure at 418 K for 11 h [63]. Notably, the

Au/Cs₃PW₁₂O₄₀ catalyst could be recovered by centrifugation after each run, whilst the H₃PW₁₂O₄₀ catalyst dissolved in the reaction mixture could be recovered by diethyl ether extraction and recrystallization.

Zeolite HY-supported Au nanoparticles (Au/HY) can also be used as catalysts for the direct conversion of microcrystalline cellulose to gluconic acid under an O₂ atmosphere in water [64]. In this case, the surface of the cellulose had to be modified with amino acids prior to the oxidative conversion process. A variety of different amino acids, including alanine, proline and phenyl alanine, can be adsorbed on the surface of cellulose. The adsorption of amino acids in this way can lead to changes in the polarity and roughness properties of the cellulose, which can have a significant impact on its reactivity. Among the amino acids investigated, phenyl alanine led to the greatest increases in the polarity and roughness properties of the cellulose surface. The subsequent conversion of the phenyl alanine-modified cellulose provided gluconic acid and glucose with total yields that were 17–18 times greater than those obtained for the conversion of unmodified microcrystalline cellulose in the presence of a Au/HY catalyst under an O₂ atmosphere.

2.3.2. Hydrolysis-hydrogenation

The hydrolysis-hydrogenation of cellulose can provide polyols as major products, which are more stable than glucose under the hydrothermal conditions used in these reactions. Hexitols such as sorbitol and mannitol are important polyols, which are regularly used in the food and chemical industries. Sorbitol can serve as a platform chemical for the synthesis of various value-added chemicals such as isosorbide, 1,4-sorbitan, glycerol, glycols, lactic acid and L-sorbose. Sorbitol has also been considered as a resource for the production of H₂ and liquid alkanes. Mannitol is another useful hexitol, which has found numerous applications as a food additive, as well as being used for the production of resins and surfactants [65].

Since the pioneering works of Kou [66], Fukuoka [67] and Liu [68] for the direct conversion of cellobiose or cellulose into hexitols, many efficient catalytic systems have been developed involving the combination of a dilute liquid acid such as H₂SO₄ or HCl with a noble metal catalyst [69–74]. For example, the combination of 2.5% H₂SO₄ and 5 wt% Ru/C afforded a polyol yield of 60% following the conversion of cellulose at 433 K under 5 MPa H₂, with hexitols accounting for 69% of the products [70]. When the Ru/C catalyst was coupled with HCl, the conversion of cellulose at 468 K for 0.5 h provided sorbitol and sorbitans with yields of 37% and 22%, respectively [71]. Sorbitans were formed as the cyclodehydration products from sorbitol. The use of a higher temperature (488 K) and longer reaction time (4 h) favored the formation of isosorbide, which was formed by the further cyclodehydration of sorbitans with a high yield (49%) [71].

Heteropolyacids (e.g., H₄SiW₁₂O₄₀ and H₃PW₁₂O₄₀), which have been shown to exhibit excellent activity towards the hydrolysis of cellulose, have also been used in conjunction with supported noble metal catalysts for the conversion of cellulose to hexitols [72,73]. For example, Sels and co-workers [72]

obtained hexitol yields of up to 87% for the conversion of cellulose in water after 1 h at 463 K under 5.0 MPa of H₂ pressure using a combination of H₄SiW₁₂O₄₀ and Ru/C as the catalyst. Furthermore, an increase in the H₂ pressure from 5.0 to 9.5 MPa at 463 K led to an increase in the yield of the hexitols, with the cellulose being quantitatively converted to hexitols (85%) and sorbitan (15%). Palkovits et al. [74] compared the performance of the Ru/C catalyst in combination with various acids for the conversion of cellulose in water under an atmosphere of H₂. The results of this study revealed that the H₄SiW₁₂O₄₀-Ru/C and H₃PW₁₂O₄₀-Ru/C systems gave better performances for the formation of hexitol than the mineral acid (i.e., HCl, H₂SO₄ or H₃PO₄)-Ru/C systems. The H₄SiW₁₂O₄₀-Ru/C catalyst was also applied to the transformation of real biomass at 433 K. Sugar alcohols (mainly sorbitol and sorbitans) were obtained in a yield of ~65% when spruce was heated in water in the presence of H₄SiW₁₂O₄₀-Ru/C at 433 K under 5 MPa of H₂ pressure [74]. Sels and co-workers reported that the combination of Cs_{2.5}H_{0.5}PW₁₂O₄₀ or Cs_{3.5}H_{0.5}SiW₁₂O₄₀ with Ru/C effectively catalyzed the conversion of cellulose to hexitols under an atmosphere of H₂ [73]. Compared with the corresponding heteropolyacids (i.e., H₃PW₁₂O₄₀ or H₄SiW₁₂O₄₀), the use of Cs_{2.5}H_{0.5}PW₁₂O₄₀ or Cs_{3.5}H_{0.5}SiW₁₂O₄₀ in conjunction with Ru/C provided a much better performance for the conversions of cellulose. The use of Cs_{3.5}H_{0.5}SiW₁₂O₄₀-Ru/C for the conversion of cellulose in water under an atmosphere of H₂ at 443 K for 48 h led to a total hexitol yield of 90%. Notably, the Cs salts of the heteropolyacids could be recovered from the products by recrystallization at room temperature without the use of an organic solvent [73].

As mentioned above, bifunctional catalytic systems based on liquid acids are particularly efficient for the conversion of cellulose to hexitols. However, the separation and recycling of the liquid acid from the reaction mixture remain challenging. For this reason, the use of solid acids to replace liquid acids has attracted considerable attention. Significant research efforts have therefore been devoted to the development of bifunctional catalysts based on combining solid acids and noble metals such as Pt or Ru for the conversion of cellulose to hexitols under H₂ [75–78]. For example, we previously reported that the loading of Ru nanoparticles on to CNTs that had been functionalized by a pretreatment process with concentrated HNO₃ could catalyze the efficient conversion of cellulose at 458 K [79]. The subsequent conversion of H₃PO₄-pretreated cellulose over 1.0 wt% of the resulting Ru/CNT catalyst gave a hexitol yield of 73% under 5 MPa of H₂ pressure. Detailed kinetic studies for the conversions of cellobiose and cellotriose revealed that the hydrogenation of the carbonyl groups in these oligomers occurred during the first step. The subsequent hydrolysis of the glycosidic bonds led to the formation of sorbitol [80,81]. The results of the kinetic studies also revealed that the energy barrier for the hydrogenation reaction was lower than that of the hydrolysis reaction. These results therefore demonstrated that the implementation of a strategy capable of enhancing the hydrolysis step would be crucial to the efficient formation of

hexitol. Therefore, the development of a robust solid acid with strong acidity would be particularly helpful for the direct conversion of cellulose into hexitols.

Chen et al. [82] incorporated phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, denoted as PTA), which is a strong Brønsted acid, into the mesopores of the metal-organic-framework material MIL-100(Cr) for the fabrication of a hybrid solid acid. The resulting PTA/MIL-100(Cr)-supported Ru nanoparticles were subsequently shown to perform as an efficient bifunctional catalyst for the conversion of cellobiose and cellulose to sorbitol in neutral water under an atmosphere of H_2 . Sorbitol yields of 95% and 58% were achieved for the conversions of cellobiose and ball-milled cellulose, respectively. The ratio of the density of acidic sites to the number of Ru surface atoms (n_A/n_{Ru}) on the Ru-PTA/MIL-100(Cr) was found to be crucial for regulation the rates of the hydrogenation and hydrolysis reactions. Catalysts with a n_A/n_{Ru} ratio in the range of 8.84–12.9 provided quantitative yields of hexitols from cellobiose and ball-milled cellulose. It has been reported that Ru nanoparticles loaded on sulfonic acid-functionalized silica ($\text{SiO}_2\text{-SO}_3\text{H}$) can perform as a bifunctional catalyst for the direct conversion of cellulose at 423 K in water under an atmosphere of H_2 [83]. A sorbitol yield of 61% was obtained for the conversion of cellulose after reaction of 10 h over the Ru/ $\text{SiO}_2\text{-SO}_3\text{H}$ catalyst. In comparison, the use of a physical mixture of the solid acid ($\text{SiO}_2\text{-SO}_3\text{H}$) and Ru/ SiO_2 as a catalyst under the same conditions gave a much lower sorbitol yield of 43%, which indicated the occurrence of a synergistic effect between the acidic sites and the proximate Ru sites. The occurrence of interactions of this type in bifunctional catalysts has been confirmed by XPS, and it has been proposed that these interactions play an important role in the hydrogenation of glucose to sorbitol. Sorbitol could be desorbed from the Ru sites of these catalytic systems with greater ease because of the coordination/poisoning effect of the sulfonic acid group on the Ru nanoparticles. This would therefore avoid further degradative reactions and enhance the selectivity of the reaction [83].

It is noteworthy that the loading of metal nanoparticles on to certain solid materials without any intrinsic acidity can also be used as a strategy for the direct transformation of cellulose into hexitols under aqueous conditions [84–88]. Fukuoka et al. [89–91] investigated the catalytic performances of Pt, Ru and Ni nanoparticles loaded on to a variety of different carbon materials for the conversion of cellulose under aqueous conditions. The use of a Pt/BP2000 (Black Pearls 2000) catalyst resulted in a hexitol yield of 65% together with the complete conversion of cellulose at 463 K under 5 MPa of H_2 pressure. It was proposed that the conversion of cellulose in this particular case involved the initial conversion of cellulose to water-soluble oligosaccharides, which subsequently underwent a rapid hydrolysis reaction to give glucose, followed by the hydrogenation of glucose to give sorbitol. The H_3O^+ generated in hot water as a consequence of the low ionic product of water at high temperatures ($\text{p}K_w = 11.3$ at 463 K) could perform as the active species for the hydrolysis of cellulose to glucose via oligosaccharides. Furthermore, the

protons potentially generated by the dissociation of H_2 on Pt could also contribute to the cleavage of glycosidic bonds [89]. Kinetic studies on the Ru/AC(N) (Active Carbon Norit XS ultra)-catalyzed conversion of cellulose revealed that Ru not only enhanced the rate of the hydrolysis of cellulose to glucose and the subsequent hydrogenation of glucose to hexitols, but also enhanced the degradation of C_6 sugar alcohols to smaller polyols ($\text{C}_2\text{-C}_6$) and gaseous products. It was proposed in this case that the decomposition of sorbitol proceeded via the cleavage of the terminal C–C bond through a dehydrogenation-decarbonylation sequence, which limited the total yield of hexitols to less than 40%. Given that the hydrolysis of cellulose is the rate-determining step, it could be possible to enhance the yield of the hexitols by increasing the ratio of the rate of hydrolysis to the rate of decomposition. It has been reported that the ball-milling of cellulose with a Ru catalyst can selectively accelerate the hydrolysis step to give an improved hexitol yield of 68%. The selective conversion of cellulose to hexitols in water under an atmosphere of H_2 can also be achieved using a carbon black (KB, Ketjenblack)-supported Ni catalyst [91]. The use of Ni/KB catalyst for the conversion of cellulose gave a hexitol yield of 64% with a cellulose conversion of 90%. In contrast, Ni catalysts loaded on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, TiO_2 and ZrO_2 supports provided much lower yields of the hexitols (28%–43%) and higher yields of numerous degradation products, including propylene glycol and ethylene glycol. It has been suggested that the basicity of the metal oxides could play a significant role in enhancing the hydrogenolysis of sugar alcohols. Given that the carbon support used in the example provided above did not possess any basicity, it was possible to avoid some of the unwanted side reactions, including the C–C bond cleavage reactions, which led to the observed high yield of the hexitols [91].

Zhang and co-workers [92] reported an activated carbon-supported Ni_2P catalyst with no intrinsic Brønsted acidity for the conversion of cellulose at 498 K under an atmosphere of H_2 with a hexitol yield of 53%. However, further studies suggested that the excess phosphorus species present in the catalyst could potentially function as acidic sites, and that the synergistic effect of the excess phosphorus species and the metallic Ni_2P particle was responsible for the conversion of the cellulose. Furthermore, the catalyst was deactivated after being recycled and reused several times because of the leaching of phosphorus species. In a subsequent study, the same group fabricated a bimetallic Ni-Ir catalyst, which was loaded onto mesoporous carbon [86]. This particular catalyst was found to be active and stable for the hydrolysis and hydrogenation reactions of cellulose, and gave a hexitol yield of 57.5% following a reaction time of 0.5 h at 518 K. Notably, there was no discernible decrease in the performance of this catalyst after five consecutive runs.

We previously identified Ru/ $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ as a unique bifunctional catalyst without any intrinsic Brønsted acidity for the conversion of cellobiose and cellulose in water under an atmosphere of H_2 [93,94]. A comparison of the catalytic performances of Ru catalysts loaded on to $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ with

those loaded on to several other conventional solid acids, including Al_2O_3 , H-ZSM-5 and H-MCM-22, for the conversion of cellobiose under mild conditions (413 K) revealed that only $\text{Ru}/\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ could catalyze the formation of considerable amounts of sorbitol. In contrast, the other catalysts mainly provided 3- β -glucopyranosyl-D-glucitol from the hydrogenation of one of the C–O bonds in the glucose ring of cellobiose [93]. In other words, $\text{Ru}/\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ can be used as a catalyst for the efficient cleavage of glycosidic bonds. This catalyst was also used to catalyze the conversion of ball-milled cellulose and inulin, which is a polymer of fructose linked by glycosidic bonds, to hexitols at 443 K. Further studies on this catalyst revealed that the conversion of cellobiose was low in the absence of gaseous H_2 , and that only a small amount of glucose was formed. The introduction of H_2 led to a significant increase in the conversion of cellobiose and the yield of sorbitol. These observations therefore suggested that Brønsted acidic sites could be generated on the $\text{Ru}/\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ catalyst from H_2 . Indeed, the results of pyridine-adsorption FT-IR measurements provided evidence for *in situ* formation of Brønsted acidic sites on the surface of the $\text{Ru}/\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ catalyst in the presence of H_2 . Furthermore, the results of Raman and ESR spectroscopic analyses showed that a small fraction of the W species in $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ was reduced to W^{5+} in the presence of H_2 and that the replacement of H_2 with N_2 re-oxidized W^{5+} to give W^{6+} . A possible mechanism for the generation of the Brønsted acidic sites in this catalytic system is shown in Fig. 7 [94]. Harnessing the power of *in situ*-generated protons therefore represents a useful strategy for the design of bifunctional catalysts with robust acidic sites for the transformation of biomass under hydrothermal conditions.

3. Activation of the C–O bonds in hemicellulose

The dilute mineral acid-catalyzed hydrolysis of hemicellulose is frequently used for the separation of hemicellulose from cellulose and lignin. During the course of this reaction, hemicellulose can be completely converted to a variety of different products via the cleavage of its glycosidic bonds. Beside the formation of monosaccharides, the cleavage of hemicellulose can also lead to the formation of degradation

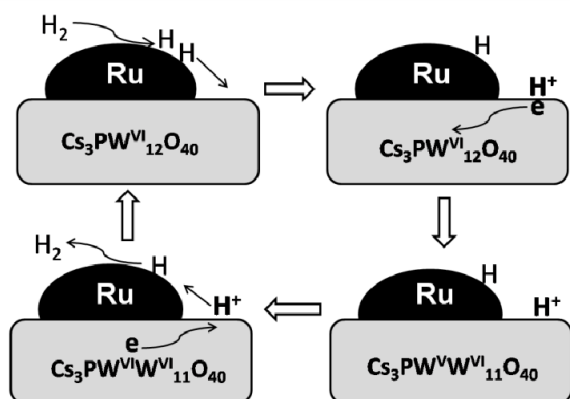


Fig. 7. Proposed mechanism for *in situ* generation of protons on $\text{Ru}/\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ [94].

products, such as furfural and its derivatives through dehydration reactions, leading to a complex mixture of products. Hemicellulases are particularly efficient for the hydrolysis of hemicellulose to monosaccharides without over-degradation. However, the high cost of these enzymes has severely limited their use for scale-up applications. The development of cheap and efficient catalysts or catalytic systems is therefore critical to the development of efficient process for the selective production of sugars from hemicellulose.

Lu et al. [95] compared the catalytic performances of maleic acid and sulfuric acid for the hydrolysis of hemicellulose in corn stover at 443–463 K. At a low hemicellulose concentration (40 g/L), both of these acids provided xylose yields greater than 98% at 443 K. However, as the hemicellulose concentration was increased to 150–200 g/L, the yield of xylose decreased significantly to around 60% when the reaction was performed in the presence of sulfuric acid, with the yield of the degradation products exceeding 30%. In contrast, the use of such high concentrations of hemicellulose in the presence of maleic acid still afforded high xylose yields of up to 95%. Similar studies on the degradation of xylose revealed that sulfuric acid could promote the conversion of the xylose product to furfural under hydrothermal conditions. The sulfuric acid-catalyzed conversion of xylose to furfural was 3 to 10 times faster than the corresponding maleic acid-catalyzed reaction under the optimized conditions [95]. The combination of sulfuric acid with maleic acid or trifluoroacetic acid (TFA) was shown to be highly efficient for the hydrolysis of *Miscanthus* [96]. In particular, the combination of sulfuric acid with TFA (50/50, mol/mol) resulted in a synergistic effect for the depolymerization of hemicellulose, which led to a significant increase in the xylose yield. These results therefore demonstrated that the presence of TFA could prevent the degradation of xylose.

Using oxalic acid as a catalyst, Dominguez and co-workers investigated the direct hydrolysis of beech wood in a biphasic solvent system [97]. At mild reaction temperatures (353–413 K), oxalic acid successfully catalyzed the selective depolymerization of amorphous hemicellulose, whereas the crystalline cellulose remained intact. A xylose yield of 18% was obtained after a reaction time of 6 h at 413 K in a water/2-methyltetrahydrofuran (2-MeTHF) solution. Based on the hemicellulose composition of the beech wood used in this experiment (15%–25%), it was suggested that the depolymerization had reached completion under these conditions. It is noteworthy that the oxalic acid catalyst could be recovered and reused by crystallization from the aqueous solution. In the organic phase consisting of bio-based 2-MeTHF, lignin was directly separated from the beech wood and the soluble carbohydrates by *in situ* extraction. The solid residue was determined to be unchanged cellulose. This catalytic system provided an effective method for the disentanglement of the compact lignocellulose structure, which allowed for the liberation and separation of the major components in a single step.

Beside homogeneous liquid acids, solid acids, such as

sulfonated resins [98,99], carbon materials [100] and zeolites [101], have also been used for the hydrolysis of hemicellulose under mild conditions. Kusema et al. [98] reported that acidic resins (e.g., Smopex-101 and Amberlyst-15) containing SO_3H groups could be used as efficient catalysts for the hydrolysis of arabinogalactans, which are hemicelluloses extracted from larch wood species. The yields of arabinose achieved over Smopex-101 and Amberlyst-15 were 85% and 50%, respectively, following a reaction of 24 h at 363 K. A further increase in the reaction time to 36 h led to an increase in the arabinose yield to 95% in the presence of Smopex-101. It is noteworthy that no degradation products, such as furfural or hydroxymethyl furfural, were observed during this reaction. It is highly likely that the differences in the structures of the two catalysts made a significant contribution to the differences in their activities. Smopex-101 is a fibrous non-porous material with a large external surface area and strongly acidic groups (SO_3H) on its surface that could be readily accessed by the reactants. In contrast, although the density of SO_3H groups of the surface of Amberlyst-15 is comparable with that of Smopex-101, the spherical morphology of this material and its small pore size could hinder the accessibility of the SO_3H groups to arabinogalactans, which would result in a lower arabinose yield. Several other acidic resins such as Amberlyst-70 and Amberlyst-35 have also been reported to be active for the hydrolysis of hemicellulose to xylose and arabinose, but significant leaching of the SO_3H groups occurred during these reactions, making it difficult to recycle these resin catalysts [99].

Chung et al. [100] reported that surface-functionalized mesoporous carbon nanoparticles (MCN) bearing weakly acidic sites could efficiently adsorb and hydrolyze the xylan polysaccharides extracted from *Miscanthus* biomass. A highly active catalyst with weakly acidic functional groups ($-\text{OH}$) representing 90% of its functionality was synthesized by the chemical oxidation of MCN with fuming sulfuric acid, followed by the desulfonation of the resulting product through a hydrothermal treatment process at 473 K. This catalyst was used to adsorb 76% of the xylan strands from an extract solution at a weight loading of 29% relative to the MCN. When the reaction was carried out over a 4 h period at 423 K, it afforded a xylose yield of 74%. A comparison with similar catalytic systems revealed that there was no direct correlation between the carboxylic acid sites and the performance of the catalyst, but that the phenolic OH sites could be contributing to the catalytic reaction. These active sites were found in a high local density on the surface, which might be present in pockets or nests and at defective sites. For such highly organized weakly acidic sites consisting of phenolic OH groups, hydrogen bonding interactions could play a critical role in lowering the pK_a values of the OH groups, which would favor the hydrolysis of the chemisorbed xylans.

Sahu et al. [101] investigated the conversion of hemicellulose in aqueous and biphasic media over several solids including zeolites (H-USY, H-Beta, H-MOR), clay (K10) and metal oxides (Al_2O_3 , Nb_2O_5). The results revealed that the product distribution could be tuned by regulating the reaction

media. When the reaction was performed in water for 1 h at 443 K, xylose, arabinose and several oligomers were isolated as the major products. Zeolites, especially H-USY and H-Beta, exhibited the highest yields towards xylose and arabinose (~60%), whereas K10 provided a total pentose yield of 31%. A furfural yield around 3% was also observed over these catalysts. Extending the reaction time to 6 h led to an increase in the yield of furfural to 18% over the H-USY catalyst. However, this strategy also led to decreased yields of xylose and arabinose (30%). In contrast, the use of a biphasic reaction system (water and *p*-xylene) appeared to favor the conversion of hemicellulose to furfural, with the yield reaching 56% over the H-USY catalyst. Several other biphasic systems such as water/toluene and water/MIBK (methyl isobutyl ketone) have also been reported to show similar results for the formation of furfural. It has also been suggested that organic solvents could be used to extract furfural from the water phase immediately after its formation to prevent it from being further degraded. This would lead to an increase in the selectivity of furfural.

4. Activation of C–O bonds in lignin and the related model compounds

4.1. Hydrolysis

Hydrolysis represents a simple route for the cleavage of the C–O linkages in lignin or lignin-derived molecules. The hydrolysis of guaiacol was investigated in subcritical and supercritical water without the addition of any catalyst [102]. Under the subcritical conditions (523 K, 8 MPa), the conversion of guaiacol reached only 6% after a reaction time of 2 h, and the yield to catechol from the C–O cleavage was less than 4%. When the reaction was performed in supercritical water (673 K, 40 MPa), the conversion of guaiacol increased significantly to 100%, with the yield to catechol reaching 42% following a reaction time of 2 h. This result therefore suggests that supercritical water is beneficial for the activation of the C–O bonds in guaiacol. Phenol and benzyl alcohol are both very reactive under hydrothermal conditions. The harsh reaction conditions required of these reactions could also result in the recondensation and repolymerization of the reaction intermediates and products, which would lead to a decrease in the product selectivity [102,103]. The development of new methods with milder reaction conditions and more efficient catalysts is therefore highly desirable to improve the conversion of guaiacol and the yield of the target product.

A variety of different model lignin compounds (e.g., guaiacol and benzyl phenyl ether) were recently investigated under mild conditions (448–548 K) in the presence of a series of water-tolerant Lewis acids to determine the nature of the decomposition pathways. The results revealed that indium triflate was an active catalyst for the cleavage of the C–O bond in guaiacol, with the conversion reaching 96% with a catechol yield of 70% following a reaction time of 2 h at 548 K [104]. For the cleavage of the weaker C–O bond in benzyl phenyl ether, indium triflate gave a conversion of 99% at a milder temperature (498 K). However, the selectivity of this reaction

towards the hydrolysis products was not high (~40%) because of the formation of oligomers via the rearrangement of phenol and benzyl alcohol [104].

Besides acid catalysts, several base catalysts have also been reported to be capable of activating the C–O bonds in lignin and lignin model compounds under hydrothermal conditions [105–108]. Lercher and co-workers studied the alkali carbonate-catalyzed hydrolysis of diphenyl ether, which was used as a simple model of the repeating units in lignin, in subcritical water [105]. Compared with Li_2CO_3 and Na_2CO_3 , K_2CO_3 provided a higher phenol selectivity (100%) and yield (73%) at 673 K. Further studies revealed that the formation of phenol proceeded via an ionic mechanism, which was initiated via the polarization of the ether bond by an alkaline cation. The high ionic product of the solution would therefore favor ionic reactions, leading to higher phenol selectivity (100%). In contrast, a low ionic product for the solution could facilitate reactions initiated with homolytic bond cleavage, which would lead to lower phenol selectivity. Given that K_2CO_3 is more soluble than Li_2CO_3 and Na_2CO_3 in subcritical water, more K^+ cations would be dissolved in the solution, which would result in an increase in the ionic product of the solution because of the higher concentration of salts. A phenol selectivity of 100% was also achieved over a ZrO_2 -supported K_2CO_3 catalyst. For the hydrolysis of lignin, stronger bases such as NaOH and KOH could be used as catalysts, and the products became much complicated [107,109]. Several monomers such as syringol and its derivatives are the primary hydrolysis products. Furthermore, it has been reported that the formation of monomers is directly proportional to the concentration of NaOH in the aqueous solution. Increasing the concentration of NaOH from 2 wt% to 4 wt% led to an increase in the monomer yield from 2% to 7%. The excess amount of NaOH could facilitate the conversion of hydroxyl groups in phenolic and catechol compounds to alcohols. Reactions of this type therefore lead to a decrease in the number of internal hydrogen bonding interactions between the hydroxyl groups, which consequently lead to an increase in the accessibility of the lignin ether bonds by the catalyst. However, the alkali metal could also enhance some of the secondary reactions such as the recombination or rearrangement of the monomer intermediates, which would lead to the formation of high molecular-weight compounds. To inhibit the concurrent oligomerization and polymerization of reactive phenolic hydroxyl groups it would be crucial to improve the yields of the target products. Boric acid could react with the phenolic hydroxyl groups to form the corresponding esters. Thus, the addition of boric acid to the base-catalyzed hydrolysis of lignin shifted the product distribution towards lower-molecular-weight compounds and increased the yield of target product to >85 wt% [107].

A recent study demonstrated that Ni loaded onto hydrotalcite (HT), which is a solid base, could be used as an efficient catalyst for the conversion of 2-phenoxy-1-phenethanol (PE) in supercritical water at 543 K. In this particular study, PE was used as a model compound for lignin because it contains a similar β -O-4 linkage to those found in

lignin [108]. Under these conditions, PE was completely converted to a mixture of phenol and acetophenone over the Ni/HT catalyst (5 wt%). The yields of the two products obtained from this C–O bond cleavage were comparable to those obtained for the NaOH-catalyzed transformation of PE. A subsequent comparison of the results obtained for the nickel salt or HT in isolation revealed much lower PE conversions of 23% and 28%, respectively, which indicated that they were working in synergy to convert PE. The Ni/HT catalyst was also used for the conversion of Organosolv-derived and ball-milled lignin into monomers and small molecules, although it was not possible to identify some of the products resulting from this reaction. Upon completion of the catalytic reaction, the structure of Ni/HT remained unchanged from its starting structure, and no significant leaching of Ni, Mg or Al was observed. Subsequent analysis revealed that nickel oxide was the dominant component in this catalytic reaction. It has been suggested that the nickel species in this system provide a strong binding sites for the aryl ether bonds of the model lignin compounds or biomass-derived lignin polymers, and that the hydroxide anions in the HT interlayers then act as active sites for the cleavage of the C–O bonds.

Stahl and co-workers developed a novel strategy for the selective transformation of lignin into low-molecular-weight aromatic compounds under mild conditions [110]. The strategy described in this study involved the oxidation of the alcohol at the C_α position of lignin to give the corresponding ketone, followed by the hydrolysis of β -O-4 linkages. The aerobic oxidation of the C_α alcohol of lignin was achieved at a mild temperature of 318 K in the presence of 4-acetamido-TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) to give the corresponding C_α ketone in high yields of up to 94%. The oxidized lignin was then readily hydrolyzed in the presence of formic acid/sodium formate to give low-molecular-weight aromatic compounds with a yield of more than 60 wt%. In contrast, the conversion of un-oxidized lignin only resulted in a 7.2 wt% yield of low-molecular-weight aromatic compounds. The results of mechanistic studies on the conversion of model lignin molecules have suggested that the oxidation of lignin could contribute to the polarization of the C_β -H bond through the benzylic carbonyl group and therefore lower the barrier for the elimination of H (Fig. 8). The results of these mechanistic studies also indicated that the coexistence of formic acid and formate was beneficial for the cleavage of the C–O bonds of lignin. The inclusion of a base favored the removal of the protons, whereas the acid assisted in the release of the formate. Furthermore, the formic acid generated during the reaction could be readily recovered by evaporation from the reaction medium, resulting in no net consumption of formic acid. The high efficiency and environmentally friendly nature of this sustainable approach make it particularly attractive for the direct utilization of lignin for the production of aromatic compounds.

In a later study, Westwood and co-workers [111] described the development of another catalytic system based on a combination of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)/tBuONO/ O_2 , which was used for the pre-oxidation of

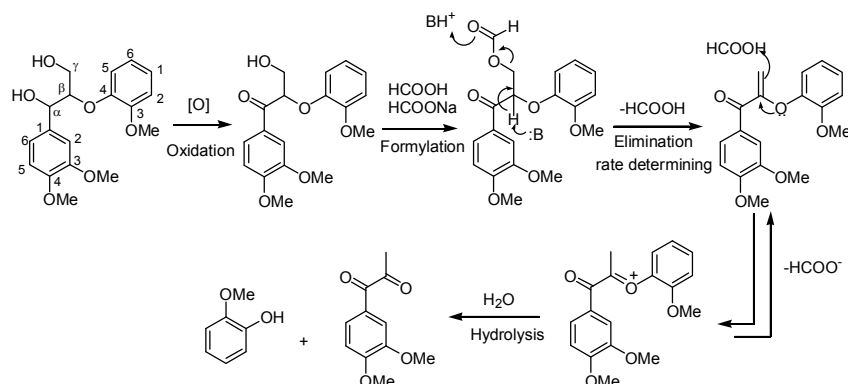


Fig. 8. Proposed mechanism for the cleavage of the β -O-4 linkage in a model lignin compound.

the C_α hydroxyl groups in lignin. The subsequent treatment of the pre-treated material with Zn/NH₄Cl allowed for the cleavage of β -O-4 linkages. This catalytic system performed effectively for the conversion of various model lignin compounds containing β -O-4 linkages at a mild temperature of 353 K to give monomer yields in the range of 80%–92%. The application of this system for the conversion of birch lignin resulted in phenolic monomers with a yield of 5%.

4.2. Hydrogenolysis

Hydrogenolysis has been extensively exploited for the transformation of lignin into high-value aromatic compounds. Metal catalysts are generally required for hydrogenolysis reaction to activate molecular hydrogen or some other source of hydrogen and promote the cleavage of the C–O bonds. Numerous homogeneous metal catalysts based on Ni [112–114], Fe [115] and Ru [116,117] complexes have been developed as efficient systems for the conversion of model lignin compounds under mild conditions. For instance, a Ni(COD)₂ (COD, 1,5-cyclooctadiene) catalyst with *N*-heterocyclic carbene ligands (e.g., SIPr) has been developed for the quantitative conversion of diphenyl ether at 393 K. Notably, the selectivity of the system towards benzene and phenol was close to 99% [112]. The substrate scope of this Ni complex catalyst (Ni-SIPr) was subsequently evaluated under a variety of different conditions, and the results revealed that it could be expanded to a wide range of benzyl esters, where the phenyl ring was substituted with different alkyl or alkyloxy groups. The use of the Ni catalyst in the absence of dative ligands (SIPr) revealed a different performance profile with a greater tendency towards the cleavage of C–O bonds in electron-rich diaryl ethers [113]. The conversion of the di-*o*-anisyl ether (bearing electron donor groups on its phenyl ring) to the corresponding arene and aryl alcohol reached up to 100% with a ligand-free Ni catalyst in the presence of *t*-BuONa, while a much lower conversion of 75% was obtained using the Ni-SIPr system under the same conditions. In contrast, the Ni-SIPr system gave a conversion of 100% for the trifluoromethyl-substituted ether (bearing an electron withdrawing group on its phenyl ring), whereas the ligand-free Ni catalyst gave a much lower conversion of 41% and produced compounds resulting from the cleavage of both the C–O and C–F bonds of

the substrate. It is therefore envisaged that Ni-based catalytic systems of this type could find numerous applications for the transformation of lignin using ligand-containing or ligand-free catalysts.

Ren et al. [115] found that iron (III) acetylacetonate could catalyze the selective cleavage of the aryl C–O bonds in aryl methyl ethers. In the presence of LiAlH₄, a variety of model lignin compounds were successfully converted to the corresponding monomeric aromatic compounds, with yields of up to 100%. When H₂ was used as a reducing agent in the presence of this catalyst for the reaction of hydroxyethylbenzyl phenyl ether, the β -O-4 linkage was also cleaved. However, the yield of the aromatic compounds was much lower (~81%). A Ru complex with a bidentate phosphine ligand (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphine) also catalyzed the conversion of 2-aryloxy-1-arylethanol to give the corresponding C–O bond cleavage products with yields in the range of 62%–98% [116].

Very recently, Feghali et al. [118] attempted to hydrolyze model lignin compounds using metal-free catalysts. Using B(C₆F₅)₃ as a catalyst and inexpensive Et₃SiH, PMHS and TMDS hydrosilanes as reductants, various alkyl aryl ethers containing α -O-4 and β -O-4 linkages were quantitatively converted to the corresponding alkyl alcohols and phenols at room temperature.

The homogeneous catalytic systems described above showed encouraging results for the selective conversion of aryl ethers into the corresponding aromatic monomers. The mechanisms of these reactions were also elucidated to develop a deeper understand of the fundamental processes underlying the activation of the C–O bonds in lignin. However, the recovery and reuse of these homogeneous catalysts remains problematic. Some of these catalytic systems are also very sensitive to air or moisture, especially those involving the use of LiAlH₄ and *t*-BuONa. Furthermore, most of these homogeneous catalytic systems are limited to the conversion of model lignin molecules.

Heterogeneous metal catalysts have attracted considerable attention for the conversion of lignin and model lignin compounds. Non-noble metal catalysts, including Ni [119–129], Cu [130–135] and Mo [136–139] catalysts have been used extensively for the hydrogenolysis of lignin and model lignin compounds with molecular H₂ or some other source of hydrogen because of their low cost and availability. For

example, Wang et al. [121] evaluated the catalytic performance of Raney Ni for the hydrogenolysis of diphenyl ether in a variety of different solvents. The results revealed that the basicity of the solvent had a significant impact on the selectivity for the different products. In non-basic solvents (e.g., methylcyclohexane), the Raney Ni catalyst exhibited high hydrogenolysis and hydrogenation activities. In these cases, the diphenyl ether substrate was mainly converted to cyclohexane and cyclic alcohols. In contrast, the use of a basic solvent (e.g., methanol and 2-propanol) led to a decrease in the activity of catalyst, but the conversion became much more selective for the hydrogenolysis reaction, with the product profile shifting towards phenols and unsaturated products.

Song et al. [122] found that supported Ni catalysts worked efficiently for the conversion of lignosulfonate to phenols. A conversion of 68% was attained with 86% selectivity for the phenol products (4-propyl-guaiacol and 4-ethyl-guaiacol) over an AC-supported Ni catalyst at 473 K. The conversion of lignosulfonate and the product selectivity could be further increased to 91% and 90%, respectively, by raising the mass ratio of the catalyst to lignosulfonate from 0.1 to 0.2. Subsequent studies on model lignin compounds revealed that the metallic nickel not only worked as the active species for the hydrogenolysis of both aryl-alkyl (C–O–C) and hydroxyl (–OH) bonds, but that it was also responsible for the reduction of the sulfonate groups to H₂S. The same group also compared the performance of this nickel catalyst with those of several precious metal catalysts for the conversion of phenethyl phenyl ether [123]. The selectivity for the C–O bond cleavage products was 85% over the Ni catalyst, which was higher than the values observed over the Ru/C (40%) and Pd/C (69%) catalysts. The Ni-based catalyst also performed much more effectively for the conversion of birch wood lignin into monomeric aromatic compounds via a fragmentation-hydrogenolysis process in alcoholic solvents [124]. For this process, the birch wood lignin was initially fragmented into smaller oligomers consisting of several benzene rings, which were dissolved in the alcohol solvent. Several alcohols, including methanol, ethanol and ethylene glycol were evaluated in this study and shown to behave as nucleophilic reagents for the cleavage of the C–O–C linkages. The oligomers generated during this process were then subjected to a hydrogenolysis reaction over a nickel catalyst, which led to the formation of monomeric phenols. In the second of these two steps, the alcohol functioned as a source of active hydrogen. Under the optimized reaction conditions (i.e., 0.1 MPa of Ar pressure at 473 K for 6 h in ethylene glycol), the highest selectivity to monomeric phenols was 97% with a birch wood lignin conversion of 50%. Isotopic labeling experiments indicated that the conversion of smaller lignin fragments into monomeric phenols proceeded via sequential β -H elimination, dehydration and hydrogenation reactions for C _{α} and C _{β} followed by a hydrogenolysis reaction for C _{γ} .

Lercher and co-workers [125] studied the cleavage of model lignin compounds containing three different C–O bonds (i.e., α -O-4, β -O-4 and 4-O-5 bonds) over Ni/SiO₂ catalyst under aqueous conditions at 393 K. Cyclohexanol and ethylbenzene

were formed as the primary products following the conversion of 2-phenethyl phenyl ether (a model lignin molecule containing a β -O-4 bond) over the Ni/SiO₂ catalyst, with both products being formed with 50% selectivity during the initial stage of the reaction. After a reaction time of 10 h under the same conditions, the selectivity of the conversion for both products decreased slightly (only 2%). The subsequent conversions of phenol and ethylbenzene over the Ni/SiO₂ catalyst revealed that the rate of the hydrogenation of phenol in water at 393 K (TOF, 130 h⁻¹) was two orders of magnitude larger than that of ethylbenzene (TOF, 0.8 h⁻¹). This result therefore indicated that the hydrogenolysis of the substrate followed by the hydrogenation of the resulting phenol was the dominant reaction pathway for the conversion of 2-phenethyl phenyl ether (Fig. 9). Phenol and toluene were formed as the main products following the conversion of benzyl phenyl ether (a model lignin molecule containing an α -O-4 bond) over the Ni/SiO₂ catalyst. The rate of the reaction for the conversion of benzyl phenyl ether containing an α -O-4 bond was faster than that for the conversion of 2-phenethyl phenyl ether containing a β -O-4 bond. This difference in the rates was attributed to the relatively low energy barrier for the activation of the α -O-4 bond (218 kJ/mol) compared with the activation of the β -O-4 bond (289 kJ/mol) [121]. The products from the conversion of diphenyl ether (a model lignin molecule containing a 4-O-5 bond) included cyclohexanol, benzene, cyclohexyl phenyl ether and cyclohexane, which suggested that the cleavage of the 4-O-5 bonds resulted in the formation of complex networks [125]. Lercher and co-workers [126,127] further investigated the catalytic mechanism for the cleavage of the C–O bonds in di-aryl ethers over the Ni/SiO₂ catalyst under aqueous conditions. The cleavage of the C–O bond on the Ni surface proceeded via parallel hydrogenolysis and hydrolysis reactions. Several experiments were conducted to determine the effect of H₂ pressure on the rate of C–O bond cleavage, and the results revealed that H₂ competed with the organic reactant for the adsorption sites and that the rate-determining step involved the cleavage of C–O bond on the Ni surface. The use of a low H₂ pressure led to an increase in the surface area covered by the H species, which may have resulted in the observed increase in hydrogenolysis rate. In contrast, the use of a high H₂ pressure led to a decrease in the rate because of the lack of any reactants.

A nickel/titanium nitride (Ni-TiN) composite was reported to be a stable and efficient catalyst for the hydrogenolysis of diaryl ethers in ethanol at 373–423 K [128]. This catalyst gave a

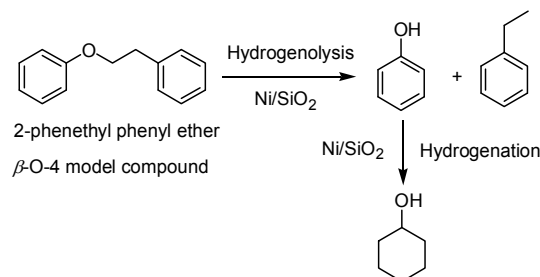


Fig. 9. Reaction pathway for the conversion of 2-phenethyl phenyl ether over Ni/SiO₂.

conversion of more than 99% for benzyl phenyl ether at 398 K, with the total selectivity for the C–O bond cleavage products approaching 100%. In contrast, Ni alone afforded a conversion of less than 20%, whilst TiN was almost inactive. It was therefore proposed that the formation of a strong interaction between TiN and Ni led to the observed high levels of activity and excellent selectivity of the composite catalyst [128]. Zaheer et al. [129] reported that the introduction of Ni nanoparticles into a hierarchical porous SiC support led to an efficient Ni/SiC catalyst for the hydrogenolysis of model lignin compounds under aqueous conditions. The Ni/SiC catalyst allowed for the quantitative cleavage of C–O bonds in phenethoxybenzene (a model lignin molecule containing a β -O-4 bond) and diphenyl ether (a model lignin molecule containing a 4-O-5 bond) in the presence of *t*-BuOK, which provided aromatic compounds exclusively. Subsequent studies revealed that the hierarchical porous structure of SiC, which could favor the diffusion of reactants and the desorption of products, contributed to the excellent activity of this catalyst.

Ford and co-workers [130] developed a copper-doped porous metal oxide (MgAlO_x , denoted as PMO) for the conversion of the model lignin compound dihydrobenzofuran in methanol. The temperature of this reaction was 573 K, which is higher than the supercritical temperature of methanol (512.6 K). At this temperature, the reforming of methanol was catalyzed by the Cu-doped PMO catalyst and afforded H_2 for the subsequent hydrogenolysis reaction, which meant that there was no need for additional H_2 . Although this Cu catalyst showed good activity for the cleavage of C–O bonds, it showed poor selectivity for the formation of aromatic compounds (2%), with cycloalkanes being formed as the major products. This result suggested that the arene ring was being over-hydrogenated over the Cu catalyst. The same catalyst was also evaluated for the conversion of Organosolv-derived lignin and wood samples in supercritical methanol [131,132]. The products of these reactions were complex and contained various cyclohexyl derivatives. These products also had the potential to be further processed for the production of liquid hydrocarbons and fuel additives. Under milder reaction conditions (413–493 K), the Cu-doped PMO was found to be useful for the conversion of Organosolv-derived lignin into simple mixtures of aromatic products [133,134]. The lignin conversion at 453 K was >90%, whilst the yield to the aromatic monomers (catechol derivatives) was >71%.

The Cu-doped PMO catalyst was also used for one-step conversion of soda lignin in supercritical ethanol [135]. In this case, the catalyst performed efficiently for the hydrogenolysis of various C–O bonds, but showed low activity for the hydrogenation of arene rings, leading to the formation of aromatic compounds as the main products with a yield of 23 wt%. Phenolic hydroxyl groups were found to be reactive in the presence of this catalyst, leading to the repolymerization of the monomers to form chars. Further research revealed that ethanol could be used as a capping agent for this reaction. In this way, it was possible to protect the highly reactive phenolic intermediates from O- and C-alkylating the hydroxyl and aromatic rings, respectively. The effectiveness of this strategy

was confirmed by 2D HSQC NMR analysis. The use of ethanol was significantly more effective in producing monomers and avoiding char formation than the use of methanol.

Weckhuysen and co-workers studied a commercial sulfided-CoMo/ Al_2O_3 catalyst for the extensive hydrodeoxygenation of model lignin compounds under 5 MPa of H_2 pressure at 573 K in dodecane [136]. The use of this catalyst for the conversion of 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)ethane (a model lignin compound with a β -O-4 bond) resulted in the exclusive formation of monomeric aromatic compounds, including phenol, guaiacol and syringol derivatives. The total yield of these products was 33% after reaction of 4 h. The same group combined the sulfided-CoMo/ Al_2O_3 catalyst with a liquid phase reforming process (LPR) for the direct conversion of Organosolv, kraft and sugarcane bagasse lignin to monomeric aromatic compounds [137]. In the first step of the LPR process, lignin was subjected to a depolymerization reaction over a Pt/ γ - Al_2O_3 catalyst at 498 K in alkaline ethanol-water mixture, which led to the formation of numerous low-molecular-weight compounds. In the subsequent step, the mixture was transformed by the sulfide-CoMo/ Al_2O_3 catalyst at 573 K. This two-step process led to the formation of a mixture of monomeric products with a total yield of 9%, 25% of which consisted of oxygen-free products such as benzene, toluene, xylene and ethylmethylbenzene.

Hicks and co-workers [138] reported the development of an FeMo phosphide catalyst for the cleavage of the ether bonds of aryl ethers at 673 K. This catalyst afforded total selectivity values of up to 88% towards the formation of C–O bond cleavage products (including benzene, ethylbenzene and phenol), and an almost quantitative conversion (>99%) of ethylphenol ether. A Mo carbide catalyst was recently disclosed by Li and co-workers for the conversion of kraft lignin in supercritical ethanol [139]. In this case, the kraft lignin was converted into high-value low-molecular-weight chemicals with a yield of 1.64 g/g of lignin. These products consisted of C_6 - C_{10} esters, alcohols, arenes, phenols and benzyl alcohols with an overall heating value of 36.5 MJ/kg. Further evaluation revealed that the supercritical ethanol affected the depolymerization of the lignin to give small molecules and fragments with molecular masses in the range of 700–1400, which were subjected to a hydrogenolysis reaction over the Mo carbide catalyst. Notably, this process did not give rise to any oligomers or chars.

Noble metals such as Pt, Ru, Pd and Rh have been used extensively to catalyze the hydrogenolysis reactions of lignin and model lignin compounds under mild conditions because of their excellent ability to activate small molecules such as H_2 and O_2 [140–143]. Jones and co-workers investigated the depolymerization of Organosolv switchgrass over a Pt/C catalyst in ethanol [141]. Formic acid was used as a hydrogen source in this case. After reaction of 4 h at 623 K, 21 wt% of the switchgrass lignin was converted to phenolic monomers using a combination of Pt/C and formic acid. Extending the reaction time to 20 h led to a significant increase in the formation of liquid products with a 76% decrease in the average molecular

weight. The O/C ratio decreased by 50%, whilst the H/C ratio increased by 10% compared with the original switchgrass lignin. Samec and co-workers [142] reported the use of a supported Pd catalyst in combination with formic acid for the cleavage of the C–O bonds of 2-aryloxy-1-arylethanol. The formation of specific products (i.e., ketones, alcohols or alkanes) could be regulated by slightly modifying the reaction conditions such as the base amount or the reaction time (Fig. 10). The isolated yields to these cleaved products were 92%–98%.

A bimetallic Pd-Zn/C catalyst for the cleavage of the β -O-4 bonds in model lignin dimers was reported by Paesell et al. [143]. This reaction was carried out at a relatively mild temperature (423 K) and H₂ pressure (2 MPa) using methanol as a solvent. The model compound, guaiacylglycerol- β -guaiacyl ether, was completely converted over the Pd-Zn/C catalyst (5 wt%). The major products, which were identified as guaiacol and 2-methoxy-4-propylphenol, were formed with a yield of 85%. This Pd-Zn/C catalyst also afforded a high yield (86%) for the conversion of a β -O-4 lignin polymer (molecular mass number of 3390), with the methoxy substituted propylphenol resulting from the cleavage of the C–O bond being formed as the major product. Zhang et al. [144,145] reported that the addition of a noble metal such as Au or Ru to a Ni catalyst could significantly enhance the performance of the catalyst for the cleavage of the C–O bonds in lignin. The authors also compared the activity of a variety of monometallic catalysts, including Ru, Rh, Pd, Pt, Ir, Ag, Au, Cu, Fe, Co, Ni, Re and Sn for the hydrogenolysis of 2-phenoxy-1-phenylethanol (a model lignin compound containing a β -O-4 bond) at 403 K in water. Among these monometallic catalysts, Ni showed the highest selectivity towards the formation of monomers, which suggested a high selectivity for the hydrogenolysis of β -O-4 bonds. Although noble catalysts (Rh, Ru, Pt, Ir) were very active, they mainly catalyzed the hydrogenation of the benzene ring. However, some of the other catalysts, including Au, Pd, Cu, Fe and Sn showed no activity or selectivity towards the formation of monomers. The introduction of 20% Ru, Rh, Pd, Pt or Au to the Ni catalyst had a significant promoting effect, leading to the near quantitative conversion of 2-phenoxy-1-phenylethanol after reaction of 2.5 h. The highest monomer yield of 72% was achieved over the Au-Ni catalyst. Further studies on the

hydrogenation of the adsorbed phenoxy (ArO*) intermediates on the Au-Ni and Ni catalysts revealed that the addition of Au to Ni could lead to a marked increase in the activation of the ArO* species and a decrease in the reaction barrier from 161 to 140 kJ/mol. Furthermore, the rate coefficient was increased 500-fold when the reaction was conducted at 403 K. This Au-Ni bimetallic catalyst also exhibited high activity for the hydrogenolysis lignin, leading to the formation of 14 wt% aromatic monomers from Organosolv lignin at 443 K in water.

5. Conclusions and outlook

The development of efficient methods for the selective cleavage of the C–O bonds in cellulose, hemicellulose and lignin or their model compounds is critical for the facile conversion of lignocellulosic biomass into value-added chemicals or fuels under mild conditions. This review has highlighted recent advances in the development of new catalysts and novel strategies for the selective cleavage of the glycosidic bonds in cellulose, its carbohydrate derivatives and hemicellulose, as well as the C–O linkages in lignin and its model compounds.

The hydrolytic cleavage of the glycosidic bonds in cellulose leads to the formation of glucose or related oligomers. Because of the low stability of glucose under stringent hydrothermal conditions, the development of efficient acid catalysts for the hydrolysis of cellulose under mild conditions is crucial. Strong homogeneous Brønsted acids (e.g., mineral acids and heteropolyacids) exhibited high catalytic performances. Solid acids bearing SO₃H groups were also efficient for the hydrolysis of glycosidic bonds, although the overall utility of these catalysts was compromised by the leaching of the SO₃H groups, which limited the recyclability of these catalysts. Recent studies have demonstrated that several catalysts (especially carbon-based materials) bearing functional groups capable of forming hydrogen-bonding interactions with cellulose enhanced the performance of these catalysts. The design of robust solid acid materials with synergistic effects for their acidic and hydrogen-bonding sites represents a challenging area of research for the selective transformation of cellulose via hydrolysis.

The use of an alcohol to replace water for the conversion of cellulose to corresponding alkyl glucosides, which are more stable than glucose, represents an efficient strategy to accelerate the selective activation of glycosidic bonds. Polyoxometalates have been identified as efficient catalysts for this process, and the development of recyclable solid acids for the alcoholysis of glycosidic bonds in cellulose represents an interesting area of future research. The combination of hydrolysis with hydrogenation or oxidation could allow for the direct conversion of cellulose into stable, value-added chemicals, including polyols and organic acids. A variety of bifunctional catalysts have been reported based on the combination of liquid or solid acids for hydrolysis with noble metal particles (e.g., Ru, Pt and Au) for hydrogenation or oxidation. The combination of a heteropolyacid or sulfonic acid-bearing solid material with supported Ru or Au nanoparticles represents a promising strategy for the

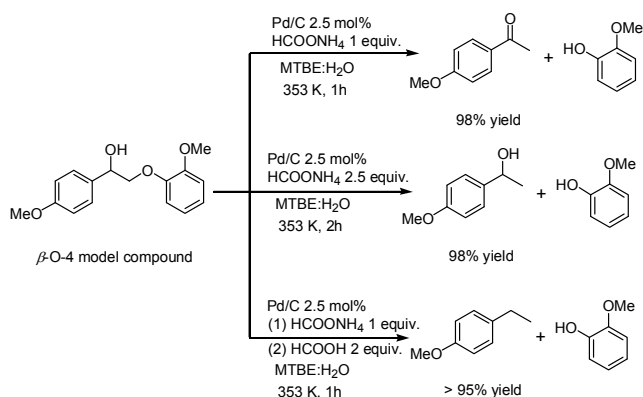


Fig. 10. Selective conversion of model lignin compounds containing a β -O-4 linkage into different aromatic compounds over a Pd/C catalyst.

production of hexitols or gluconic acid. Significant interest has been directed towards the use of metal nanoparticles loaded on solid materials without intrinsic acidity, which can catalyze the direct conversion of cellulose into hexitols in water under H_2 . The reversible generation of protons in high-temperature water could effectively generate Brønsted acids in these systems. Moreover, molecular H_2 -derived Brønsted acidic sites (i.e., protons generated by the dissociation of H_2 on metal nanoparticles followed by their spillover on to a support with electron-exchanging ability) are attractive for the transformation of biomass to polyols.

The hydrolysis of hemicellulose in the presence of an acid catalyst could result in the cleavage of glycosidic bonds, to give xylose, arabinose and several other monosaccharides under mild conditions. Sulfuric acid was efficient for the hydrolysis of hemicellulose, but it also catalyzed the further dehydration of monosaccharides into furfural and its derivatives. Weakly acidic dicarboxylic acids (e.g., maleic acid and oxalic acid) exhibited high selectivity towards monosaccharides. Solid acids, including acidic resins and zeolites were efficient for the hydrolysis of hemicellulose. However, the leaching of the acidic groups from these resin catalysts remains a significant problem in need of a solution.

Hydrolysis and hydrogenolysis are two major types of reaction for the catalytic activation of C–O bonds, including the β -O-4, α -O-4 and 4-O-5 linkages in lignin or model lignin compounds. Acids and bases can both catalyze the hydrolysis of lignin and its model compounds to give the corresponding monomeric aromatic compounds, although harsh reaction conditions are generally required to ensure a high level of conversion. Strategies involving the pre-oxidation of the C_{α} -OH bonds in lignin, followed by the hydrolysis of the pre-oxidized products using $HCOOH/HCOONa$ have been demonstrated to be successful for the transformation of model lignin model compounds and Organosolv-derived lignin into aromatic compounds under mild conditions. The hydrogenolysis of lignin and model lignin compounds can be catalyzed by homogeneous metal complexes, such as Ni, Fe and Ru complexes. Heterogeneous supported non-noble metal (such as Ni, Cu or Mo) or

noble metal (e.g., Pt, Ru, Pd or Rh) catalysts have also been shown to perform efficiently for the hydrogenolysis of the C–O bonds in lignin and its model compounds to give the corresponding monomeric aromatic compounds. In some cases, the cleavage of the C–O bonds was accompanied by the hydrogenation of the arene rings to provide complex mixtures of the corresponding cyclohexane derivatives. The design of efficient catalysts with enhanced hydrogenolysis abilities but the ability to suppress the hydrogenation is therefore needed to enhance the production of aromatic compounds.

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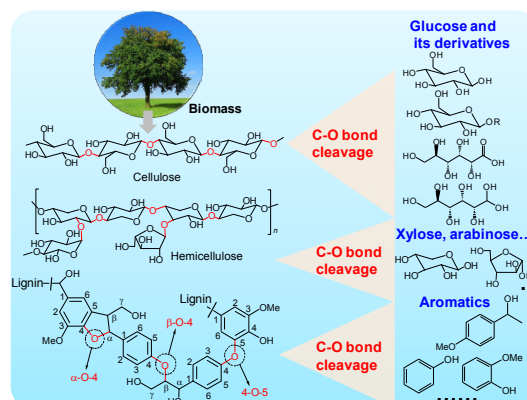
Graphical Abstract

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Selective activation of the C–O bonds in lignocellulosic biomass for the efficient production of chemicals

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Recent advances in the development of new catalysts and novel strategies for the selective cleavage of the C–O bonds in cellulose, hemicellulose and lignin have been reviewed. Key factors and mechanisms for the formations of glucose, glucose derivatives, xylose, arabinose and aromatics have been discussed.



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木质纤维素中C–O键选择性活化和高效转化制化学品

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摘要: 高效转化来源丰富且可再生的木质纤维素制备化学品和燃料对建立可持续发展社会具有重要意义。木质纤维素利用的一条理想途径是将其主要成分纤维素、半纤维素和木质素在温和条件下高选择性地催化转化为关键平台化学品。本文综述了近年报道的有关纤维素、半纤维素和木质素或其模型分子中C–O键选择性活化生成葡萄糖、葡萄糖衍生物(包括葡萄糖苷、六元醇和葡萄糖酸)、木糖、阿拉伯糖和芳香化合物的新催化剂和新策略,阐述了决定催化性能的关键因素。本文还讨论了相关反应机理以深入理解C–O键选择性活化。

纤维素由葡萄糖单元通过 β -1,4-糖苷键连接而成,通过水解反应,选择性切断这些糖苷键可以获得葡萄糖或其低聚物。鉴于葡萄糖在水热条件下不稳定,发展纤维素温和条件下水解的酸催化剂至关重要。众多研究表明,均相酸催化剂(如无机酸,杂多酸等)具有强Brønsted酸,在该水解反应中显示高的催化活性。另一方面,拥有强酸性基团-SO₃H的固体酸也表现出优异的水解糖苷键性能,但是-SO₃H官能团易于流失,限制了这类固体酸催化剂的循环使用。最近研究显示,一些催化剂尤其是碳材料上引入能够与纤维素形成氢键的官能团时,其催化纤维素水解性能显著增强。设计合成这类具备酸性位和氢键位协同效应的稳定固体酸催化剂是纤维素水解转化的一个颇具前景的研究方向。

以醇替代水为溶剂实施纤维素醇解制葡萄糖苷是高效活化石糖苷键的有效策略。杂多酸被证实为该醇解反应的高性能催化剂。在相同反应条件下,醇解产物葡萄糖苷较水解产物葡萄糖更为稳定,因此可以获得高的葡萄糖苷收率。开发稳定可重复利用的固体酸催化剂是纤维素醇解的关键。耦合水解与加氢或氧化反应可以直接将纤维素转化为相对稳定且具有广泛用途的多元醇或有机酸。目前已有系列多功能催化剂被报道,这些催化剂通常组合了具备水解功能的液体酸或固体酸和具备加氢或氧化功能的贵金属或过渡金属(譬如Ru, Pt, Ni和Au)。其中杂多酸盐或含有磺酸官能团的固体酸负载Ru或Au多功能催化剂显示出优异的生成六元醇或葡萄糖酸的催化性能。

半纤维素由葡萄糖、甘露糖、木糖、阿拉伯糖、半乳糖等单糖单元通过糖苷键连接而成,糖苷键选择性活化可生成各种单糖混合物。硫酸可以有效水解半纤维素,但是同时也易于催化所生成的单糖深度转化为呋喃及其衍生物。较之硫酸,酸性较弱的有机酸特别是二元羧酸(例如马来酸、草酸等)具有较高的单糖选择性。固体酸如酸性树脂,分子筛等亦可催化半纤维素水解反应,但树脂类催化剂中官能团的流失问题有待解决。

木质素是由含甲氧基等取代基的苯丙烷单元通过一系列化学键连接而成的复杂大分子,其芳香单元间包括 β -O-4, α -O-4和4-O-5等三种主要连接方式,选择性切断这些C–O键可获得高附加值的芳香化合物。水解和氢解是两类普遍用以活化木质素及其模型化合物C–O键的反应。酸和碱均可催化木质素及其模型化合物水解,但是通常需要苛刻条件获取高转化率。近期研究显示,通过对木质素C_α-OH预氧化,再以HCOOH/HCOONa实施水解反应,可以成功实现温和条件下有机溶剂提取木质素及其模型化合物的高效转化。另一方面,均相金属络合物(如Ni, Fe和Ru)或多相负载型金属催化剂(如Ni, Cu, Mo, Pt, Ru, Pd或Ru等)均可有效催化木质素及其模型化合物中C–O键氢解,获得芳烃化合物。在部分多相催化剂体系中,除C–O键活化断裂外,还伴随芳环深度加氢反应,产生较多环己烷衍生物。因此,设计合成具备氢解功能同时抑制过度加氢功能的催化剂是获得芳烃化合物的关键。

关键词: 生物质; 纤维素; 半纤维素; 木质素; 碳-氧键活化

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