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PERSPECTIVE

Conversion of lignocellulose into renewable chemicals by heterogeneous catalysis

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Conversion of lignocellulose into renewable chemicals and fuels has received great attention for building up the sustainable societies. However, the utilisation of lignocellulose in the chemical industry has almost been limited for paper manufacturing because of the complicated chemical structure and persistent property of lignocellulose. Heterogeneous catalysis has the potential to selectively convert lignocellulosic biomasses into various useful chemicals, and this methodology has rapidly progressed in the last several years. In this perspective article, we outline our recent approaches on the heterogeneous catalysis for this challenging subject with related literatures.

Lignocellulose as a renewable resource

Conversion of biomass to renewable fuels and chemicals has attracted significant attention as a key technology for the sustainable societies.¹ Lignocellulose is the most abundant biomass resource, produced together with sugars and starch from carbon dioxide and water via the photosynthesis using sunlight and successive metabolism in plants. Lignocellulose is not digestible for human beings, which is an advantage over sugars and starch since the use of edible carbohydrates for the synthesis

of bioethanol fuel has competed with the food production, giving us a consensus that we should use non-food biomass as a feedstock to fuels and chemicals. Therefore, lignocellulose is one of the most attractive biomass resources in nature.

Lignocellulose in woods consists of cellulose (40–50%), hemicellulose (20–40%) and lignin (20–30%).² Cellulose is a water-insoluble polymer composed of glucose linked by β -1,4-glycosidic bonds (Fig. 1(a)) and forms robust crystal structures with inter- and intra-molecular hydrogen bonds, possessing high chemical stability.³ Hemicellulose is also a polysaccharide, but

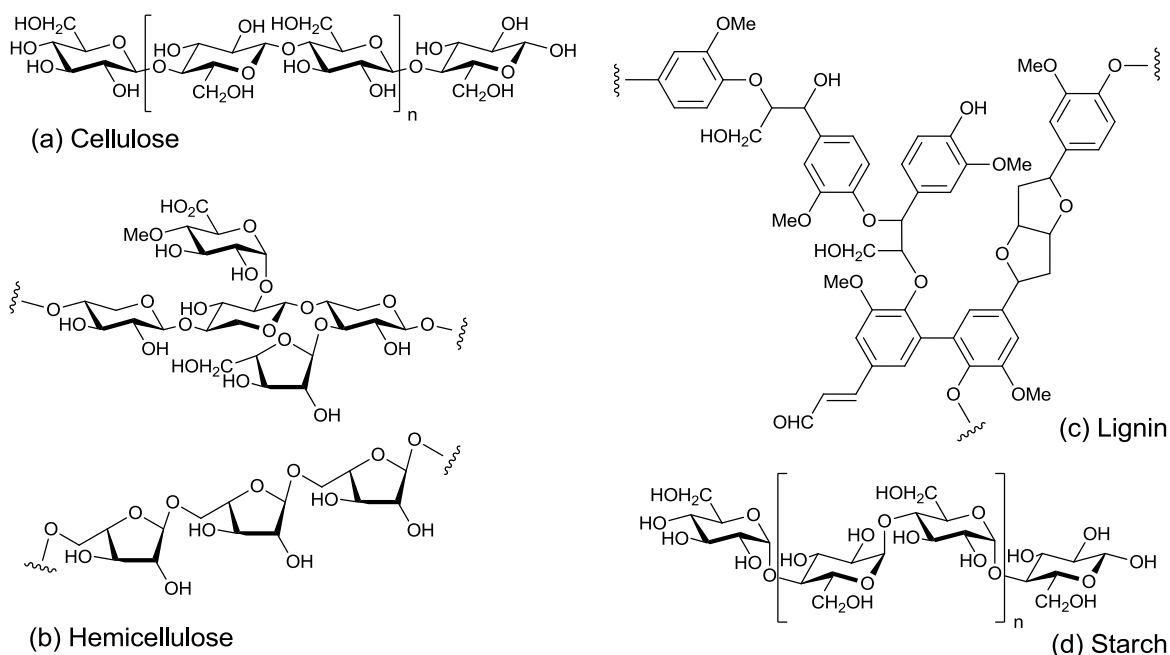
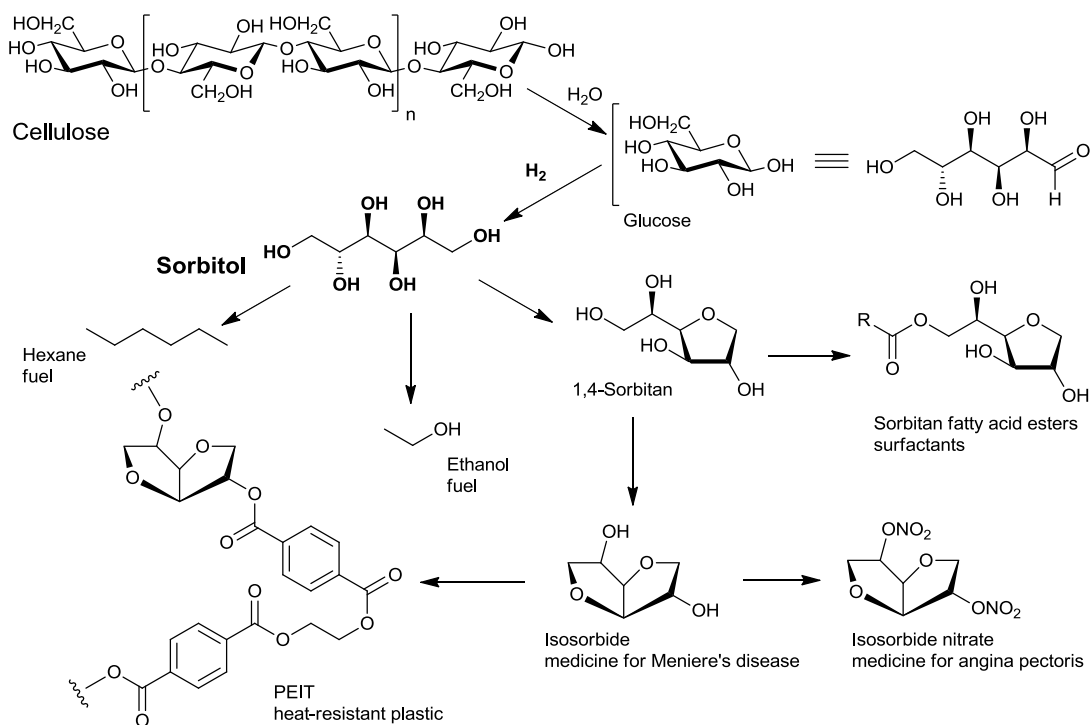


Fig. 1 Chemical structures of (a) cellulose, (b) hemicellulose (top: glucuronoarabinoxylan, bottom: arabinan), (c) lignin and (d) starch.



Scheme 1 Sorbitol as a platform chemical produced by the hydrolytic hydrogenation of cellulose.

includes pentoses and hexoses connected by several forms of glycosidic bonds, which results in amorphous structure.⁴ The components of hemicelluloses are varied depending on plants and their parts, and accordingly they have different names based on the feature, *e.g.* “glucuronoarabinoxylan” in grasses, consisting of xylose chain with glucuronic acid and arabinose residues, and “arabinan” in beetfibre, bearing a backbone of arabinose (Fig. 1(b)). Lignin is a three-dimensional aromatic polymer generated by the radical polymerisation of *p*-coumaryl alcohol, conipheryl alcohol and sinapyl alcohol (Fig. 1(c)).⁵ First of all, we focused on the catalytic conversion of cellulose, accounting for the largest part in lignocellulose and having a simple chemical structure like starch (Fig. 1(d)).

An extensive number of works have been devoted to the hydrolysis of cellulose to glucose,⁶ and sulphuric acid is known to be a typical catalyst for this reaction; however, this process suffers from the corrosive property of the acid and the product separation. Although cellulase enzymes can be used to selectively convert cellulose to glucose under ambient conditions,⁷ the driving down the cost of enzymes is a major issue in this field. Sub- and super-critical water has been applied for the hydrolysis of cellulose,⁸ but the low product selectivity can be pointed out as a subject. In contrast, heterogeneous catalysis has a potential to overcome these problems.⁹ In this scope, the catalytic gasification of cellulose to syngas and to pure hydrogen was reported,¹⁰ but the direct production of $\geq C_2$ compounds would be more effective in order to leverage the chemical structure of cellulose, *i.e.* C₆ polymer. In our work, we have studied the conversion of cellulose to sugar alcohols as well as glucose by supported metal catalysts and expanded to those of hemicellulose and lignin derivatives.

Hydrolytic hydrogenation of cellulose

Development of the catalytic system

Although the structures of cellulose and starch are similar except for the stereochemistry of 1,4-glycosidic bonds (Fig. 1(a, d)), cellulose is significantly more persistent than starch. Furthermore, cellulose is not soluble in water at lower than 590 K because of the inter- and intra-molecular hydrogen-bonding structure rigider than that of starch.^{8c} Thereby, cellulose is not hydrolysed to glucose under mild conditions outside of the enzymatic reactions, whereas glucose easily decomposes under harsh conditions because of the aldehyde group in its linear structure. In fact, our trial to hydrolyse cellulose by using zeolites and other oxides gave glucose in less than 4% yield, which was contrastive to the easy hydrolysis of starch¹¹. This trade-off relation is a key issue in the conversion of cellulose.

In 1950's, Ballandin and co-workers reported the hydrolytic hydrogenation of cellulose to sorbitol and sorbitan by mineral acids and supported Ru catalysts under H₂ pressure of 7 MPa (Scheme 1).¹² The important point for this methodology is that the *in-situ* hydrogenation of glucose to sugar alcohols having higher chemical stabilities resolves the trade-off problem by preventing the decomposition of glucose. Indeed, only 11% of glucose remained in water at 463 K for 3 h because of the decomposition to 5-hydroxymethylfurfural, furfural, and other compounds, whereas 99% of sorbitol was recovered under the same conditions in our tests. However, development of the process using only solid catalysts remained a challenge at that time, which had been due to the limited collision between the solid cellulose and the solid catalyst. On the other hand, Jacobs filed a patent for the one-pot conversion of starch to sorbitol

using Ru/USY in 1989, in which USY worked as a solid acid to hydrolyse soluble starch and Ru catalysed the reduction of glucose to sorbitol.¹³

In this situation, we reported the first hydrolytic hydrogenation of cellulose to sugar alcohols under aqueous conditions by supported metal catalysts without using soluble acids.¹⁴ Avicel (microcrystalline cellulose, Merck) was converted to sugar alcohols (total 31%; sorbitol 25% and mannitol 6%) by γ -Al₂O₃-supported Pt catalyst prepared from H₂PtCl₆, denoted as Pt(Cl)/ γ -Al₂O₃, in the presence of H₂ pressure of 5 MPa at 463 K for 24 h. The turnover number (TON) of bulk Pt for the production of sugar alcohols was 34. Ru/ γ -Al₂O₃ was also active, whereas Rh, Ir and Pd catalysts gave only small amounts of sugar alcohols.

The produced sugar alcohols can be converted into various useful chemicals (Scheme 1).¹⁵ In the dehydrated products, sorbitan is a precursor to surfactants, and isosorbide is a feedstock to plastics¹⁶ including poly(ethylene-co-isosorbide) terephthalate (PEIT) as a remarkable PET analogue having high glass-transition temperature up to 470 K and also a commercial medicine for Meniere's disease. The nitric acid esters of isosorbide are used to treat angina pectoris. Hexane is produced from sorbitol by the hydrodeoxygenation using a metal-solid acid combined catalyst (Pt/SiO₂-Al₂O₃),¹⁷ and the product can be served as gasoline after the isomerisation to increase the octane number.

Optimisation of the catalytic system

Considering the practical applications, the yield of sugar alcohols (31%) in the cellulose degradation in our work needs to be increased, and one reason for the low yield is the persistent property of cellulose. A simple way to improve the reaction performance is pre-treatment of cellulose to break the rigid crystal structure as the depolymerisation of cellulose proceeds on the solid surface.¹⁸ By milling cellulose in a ceramic pot with ZrO₂ balls for 2 days, the crystallinity index of cellulose decreased from 81% to 22%, calculated from the X-ray diffraction (XRD) patterns,⁷ resulting in the reduction of number of hydrogen bonds in cellulose.¹⁹ The median diameter for the secondary particles of cellulose in water, determined by laser diffraction, also shrunk from 67 μ m to 42 μ m. Thus, we expected the improvement of the reactivity and used the ball-milled cellulose hereafter.

At first, we performed the hydrolytic hydrogenation of the milled cellulose by using 2 wt% Pt(Cl)/ γ -Al₂O₃ catalyst (Table 1 entry 1). Although the conversion of cellulose reached 89% because of the higher reactivity, yield of the sugar alcohols was 39% (sorbitol 32% and mannitol 7%). Accordingly, the selectivity for the sugar alcohols based on the conversion was 43%. The major by-products were 1,4-sorbitan (16%) and C₂-C₃ polyols (8%) including ethylene glycol, propylene glycol and glycerol. This result shows that the selective reduction of the hemiacetal/aldehyde group of glucose to alcohol is also important to achieve good yields of sugar alcohols, because the side-reactions, *e.g.* C-C hydrogenolysis, easily happen at the high temperatures required for the depolymerisation of cellulose. We prepared the catalyst from H₂PtCl₆ as described above, but Cl in the catalyst might affect the catalytic activity,²⁰ which prompted us to study the effect of catalyst precursors on the reaction. We utilised Cl-free γ -Al₂O₃ (JRC-ALO-2, Catalysis Society of Japan)

as the support in this work. The catalyst prepared from Pt(NH₃)₂(NO₂)₂, denoted as Pt(N)/ γ -Al₂O₃, gave higher yields of sorbitol (46%) and mannitol (5%) (entry 2), and the total selectivity (70%) was nearly doubled from that (43%) by Pt(Cl)/ γ -Al₂O₃ catalyst.²¹ It is implied that Cl-free precursors are suitable for the reaction. To elucidate the origin of the selectivity difference, we performed energy dispersive X-ray spectroscopy (EDX) analysis of the Pt catalysts to determine the content of Cl. Residual Cl in Pt(Cl)/ γ -Al₂O₃ catalyst was 1.1 wt%, whereas that in Pt(N)/ γ -Al₂O₃ was less than the detection limit (<0.01 wt%). Regarding the morphological property, both catalysts provided almost the same XRD patterns, CO uptake and N₂-adsorption isotherms. Consequently, a clear difference is the content of Cl, and it appears that the residual Cl induces the side-reactions by being adsorbed on the metal and/or by the formation of acidic species like HCl. In fact, the addition of HCl (Cl 1.1 wt% to Pt(N)/ γ -Al₂O₃) in the reaction mixture reduced the selectivity for the sugar alcohols (entry 3).

Table 1 Hydrolytic hydrogenation of cellulose by Pt catalysts.^a

Entry	Catalyst	Conv. of cellulose/%	Sugar alcohol yields /%C		
			Sorbitol	Mannitol	Total (Sel. ^b /%)
1	Pt(Cl)/ γ -Al ₂ O ₃ ^d	89	32	7	39 (43)
2	Pt(N)/ γ -Al ₂ O ₃ ^d	72	46	5	51 (70)
3	Pt(N)/ γ -Al ₂ O ₃ ^d +HCl	98	38	10	47 (48)
4	Pt(N)/BP2000 ^e	82	49	9	58 (70)
5 ^c	Pt(N)/BP2000 ^e	101 ^f	53	11	64 (63)
6 ^c	Pt(N)/BP2000 ^e	101 ^f	53	12	65 (64)

^a Cellulose (Merck, Avicel, ball-milled for 2 days) 324 mg, catalyst 195 mg (Pt 2.0 wt%), water 40 mL, reaction time 24 h, p(H₂) 5.0 MPa at r.t. ^b

Based on the conversion. ^c The residue of the previous entry number was used as the catalyst. The conversion and yields are based on fresh cellulose (324 mg). ^d γ -Al₂O₃: JRC-ALO-2, Catalysis Society of Japan. ^e BP2000: carbon black, Black Pearls 2000, Cabot. ^f "101%" was due to the degradation of cellulose that had remained in the previous reaction. See also footnote c.

Next, we focused on the durability of the catalysts: Pt(N)/ γ -Al₂O₃ catalyst selectively converts cellulose to sorbitol and mannitol (entry 2); however, the catalytic activity does not sustain in the reuse experiments owing to the transformation of γ -Al₂O₃ support to boehmite (AlO(OH)). In the screening tests of water-tolerant supports (TiO₂, ZrO₂ and C), we found that an easily available carbon black (BP2000, Cabot)-supported Pt(N) catalyst gives the sugar alcohols in 58%, 64% and 65%, respectively, in the reuse experiments of 3 times (entries 4–6). A total TON of Pt for the formation of sorbitol and mannitol was 175 in these reactions. In another way, Zhang *et al.* proposed an ordered mesoporous γ -Al₂O₃-C composite for the catalyst support affording both good interaction between Pt and Al₂O₃ and water-tolerant property derived from C.²² The γ -Al₂O₃ phase in the composite was thermally more stable than usual γ -Al₂O₃, but the reusability was not mentioned. A kinetic study of the Pt(N)/BP2000-catalysed reaction indicated that this reaction consists of two steps: the hydrolysis of cellulose to glucose *via* water-soluble oligosaccharides and the hydrogenation of glucose to sorbitol as expected.²¹ Although the former reaction, which is the rate determining step, proceeds even without catalysts under hydrothermal conditions,²³ it was found that the Pt catalyst

Table 2 Conversion of cellulose to sugar alcohols by solid catalysts in water.

Entry	Catalyst	Cellulose	T /K	P(H ₂) /MPa	Reaction time /h	Cellulose conv. /%	Sugar alcohol yields /%C			Ref.
							Sorbitol	Mannitol	Total (Sel. /%)	
7	2.0 wt% Pt(N)/BP2000 ^a	Microcrystalline	463	5.0	24	66	39	4	43 (66)	21
4	2.0 wt% Pt(N)/BP2000 ^a	Ball-milled	463	5.0	24	82	49	9	58 (70)	21
8	4.0 wt% Ru//AC ^b	Microcrystalline	518	6.0	0.5	86	30	10	39 (46)	26
9	1.0 wt% Ru/CNT ^c	Microcrystalline	458	5.0	24	-	36	4	40	27
10	1.0 wt% Ru/CNT ^c	H ₃ PO ₄ -treated	458	5.0	24	-	69	4	73	27
11	5 wt% Ru/C, Cs _{3.5} H _{0.5} SiW ₁₂ O ₄₀ ^d	Ball-milled	443	5.0	48	100	-	-	70 (70)	28a
12	1.0 wt% Ru/Cs ₃ PW ₁₂ O ₄₀	Ball-milled	433	2.0	24	-	43	2	45	28b
13	16 wt% Ni ₂ P/AC ^b	Microcrystalline	498	6.0	1.5	100	48	5	53 (53)	30
14	3.0 wt% Ni/CNF ^e	Microcrystalline	503	6.0	4.0	94	23	5	28 (29)	31
15	3.0 wt% Ni/CNF ^e	Ball-milled	463	6.0	24	93	50	6	57 (61)	31

^a BP2000: carbon black, Cabot. ^b AC: activated carbon. ^c CNT: carbon nanotube. ^d Pre-treated under hydrothermal conditions. ^e CNF: carbon nano-fibre.

unpredictably accelerates this step threefold. The catalyst has the hydrolysis activity and furthermore might produce protons by the heterolysis of H₂.^{14,24} The kinetic study also suggested that mannitol is predominantly derived from fructose generated by the isomerisation of glucose.

In the last few years, several groups have applied Ru/C catalysts to the hydrolytic hydrogenation of cellulose under aqueous conditions because of the superior activity of Ru/C for the hydrogenation of glucose to sorbitol.²⁵ Liu *et al.* employed Ru/activated carbon (AC) catalyst for the degradation of microcrystalline cellulose and gained the sugar alcohols in 39% yield (Table 2 entry 8).²⁶ Wang *et al.* showed that the products are obtained in 73% yield from H₃PO₄-pretreated cellulose by using Ru/carbon nanotube catalyst (entry 10).²⁷ Besides, Cs-substituted phospho- or silico-tungstates were utilised as solid acids to improve the hydrolysis step.²⁸ The reactions took place at lower temperatures (433–443 K) than those of usual cases (≥458 K), and the yield of sugar alcohols was up to 70% (entries 11, 12). Although the stability of the heteropolyacids in water and the effect of dissolved species are concerned, Sels *et al.* indicated that the hydrothermal treatment of the acid measurably improves the water-tolerance.^{28a} In addition, Wang and co-workers proposed that Cs₃PW₁₂O₄₀ also works as an acid catalyst by the heterolysis of H₂,^{28b} which might be a similar step to that proposed for Pt-SO₄/ZrO₂ in the production of alkylate gasoline.²⁹ However, W⁶⁺ species in heteropolyacids might be reduced to W⁵⁺ during the reaction (*e.g.*, [PW₁₂O₄₀]³⁻ + e⁻ → [PW₁₂O₄₀]⁴⁻, E° = +0.22 V).

Recently, base metal catalysts have been studied for the conversion of cellulose as alternatives for noble metals. Zhang *et al.* demonstrated that 16 wt% Ni₂P/AC catalyst produces sorbitol (48% yield) and mannitol (5%) from microcrystalline cellulose (entry 13).³⁰ Although the activity of the fresh catalyst was superior to those for 16 wt% Ni/AC catalyst and the mixture of 16 wt% Ni/AC and H₃PO₄ (*ca.* <10% yield), the catalyst was not durable in reuse experiments because of the phosphorus leaching. Sels and co-workers reported that reshaped Ni metal catalyst at the tip of carbon nano-fibres on γ-Al₂O₃ (3 wt% Ni/CNF),³¹ produced in methane decomposition,³² provides 50% yield of sorbitol and 6% of mannitol in the conversion of ball-milled cellulose (entry 15), whereas 3 wt% Ni/AC catalyst prepared by simple impregnation methods is ineffective for the production of the sugar alcohols. They suggested that the reshaping of Ni crystals lifted up from the original support (Al₂O₃) by the formation of CNF in the decomposition of methane is the major

factor for inhibiting the bond-breaking side-reactions. It is known that Ni crystals grow at the initial stage of the methane decomposition.^{32b} In addition, Ni/CNF catalyst was stable in the reuse reactions.

Also in the combination of metal catalysts and homogeneous acids, many works have been devoted to improve the yield and to overcome the drawbacks. Sels *et al.* demonstrated the quantitative degradation of cellulose to the sugar alcohols (85%) and sorbitan (15%) in only 1 h by using H₄SiW₁₂O₄₀.³³ Mizuno and co-workers also utilised heteropolyacids for this reaction, and 54% yield of sorbitol was obtained at a low temperature (333 K) and hydrogen pressure (0.7 MPa).³⁴ Heteropolyacids are recoverable by recrystallisation or extraction.³⁵ Moreover, Sels *et al.* reported that highly-diluted HCl (0.0177 wt%, pH=2.3) accelerates the hydrolysis step, and 60% yield of sugar alcohols and 33% of sorbitan are obtained.³⁶ Some types of stainless steel can be used as a reactor even in the presence of HCl at low concentrations.

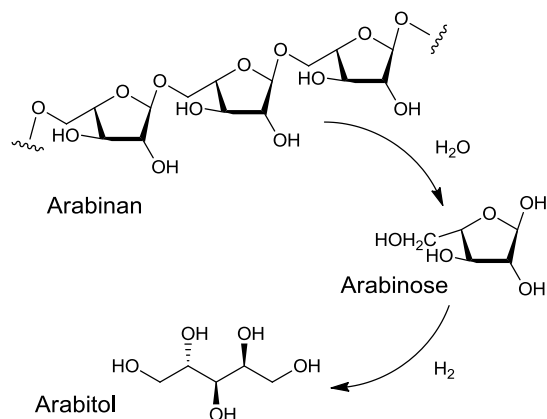
Hydrolytic hydrogenation of hemicellulose

Hemicellulose is depolymerised more quickly than cellulose, but the products, C₅ sugars, are more reactive than glucose.³⁷ Consequently, enzymes or soluble acids have been required to gain good yields of sugars, whereas solid catalysts have afforded less than *ca.* 50% yields of monosaccharides.³⁸

Hence, the hydrolytic hydrogenation method is also useful for the conversion of hemicellulose. Moreover, C₅ sugar alcohols such as xylitol are not only the sweeteners that do not induce dental caries, but also potential precursors to ethylene glycol and propylene glycol.³⁹ However, homogeneous acids or multistep reaction have been used for this reaction as far as we know.^{12a,40} Thus, we applied the heterogeneous catalysis to the one-pot conversion of hemicellulose.⁴¹ In this study, we chose beet fibre (Nippon Beet Sugar Manufacturing) as an actual agricultural waste in the production of sucrose from sugar beet, whose annual production has been about 200-300 Mt. The beet fibre contains 23 wt% hemicellulose principally composed of arabinan, which is a polymer of arabinose mainly linked by 1,5- α -glycosidic bonds (Scheme 2). Accordingly, the hydrolytic hydrogenated product from beet fibre is arabitol. We found that 2 wt% Ru/AC catalyst converts beet fibre to arabitol in 83 wt% yield based on the weight of hemicellulose at 428 K for 24 h under H₂ pressure of 5 MPa.^{41b} Assuming that the hemicellulose part is approximately pure arabinan, the carbon-based yield is 72%.

Very recently, Murzin *et al.* reported Pt/MCM-48 catalyst for

the conversion of a bleached birch kraft pulp, and they obtained small amounts of sorbitol and xylitol.⁴²



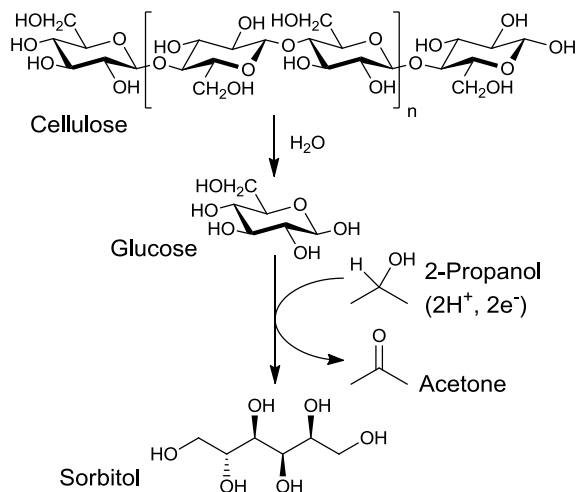
Scheme 2 Synthesis of arabitol from beet fibre containing arabinan.

Hydrolytic transfer hydrogenation of cellulose

The hydrolytic hydrogenation has been shown as an effective methodology for the selective conversion of cellulose and hemicellulose as described above. However, one of the disadvantages was that all the systems needed pressurised H₂ of ≥ 4 MPa, and lower pressures were preferred for the efficient synthesis of sugar alcohols. Thus, we aimed for the conversion of cellulose to sugar alcohols without using high H₂ pressures.

As a substitute for H₂ molecule, the sources supplying 2H⁺ and 2e⁻ can be used for the reduction of sugar intermediates to sugar alcohols like the conversion of glucose to sorbitol on cathodes by electrochemical potential (2e⁻) with water (2H⁺).

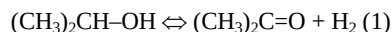
Zhu *et al.* reported ionic liquid-stabilised Ru nano-particles and a reversible binding boron agent for the conversion of cellulose to sorbitol, in which formates were used for the reduction step.⁴³ As a simple and solid-catalytic system, we investigated the conversion of cellulose to sugar alcohols in water using 2-propanol as a reductant by supported metal catalysts (Scheme 3), which is the hydrolytic transfer hydrogenation of cellulose.⁴⁴ In the screening tests of various catalysts, 2 wt% Ru/C catalysts (C: AC(N), CMK-3, C-Q10)⁴⁵ prepared from RuCl₃ by a typical impregnation method with H₂-reduction at 673



Scheme 3 Transfer hydrogenation of cellulose to sorbitol.

K gave the highest yields of the sugar alcohols (43–46%) with the generation of H₂ from 2-propanol (*vide infra*). In contrast, Ru/ γ -Al₂O₃ catalyst, which is active for the hydrolytic hydrogenation under 5 MPa of H₂, was completely inactive for the transfer hydrogenation (0% yield), implying the difference of Ru active species. Regarding the durability, Ru/AC(N) catalyst was reusable only twice (total TON=170), which might be due to strong adsorption of by-products as EDX and XRD analyses showed no change of the structure of Ru species before and after the deactivation. In addition, no Ru leaching was detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement, and filtrate after the first reaction did not catalyse the transfer hydrogenation reaction. We concluded that the Ru/carbons are heterogeneous catalysts for the hydrolytic transfer hydrogenation of cellulose.

When the Ru/C catalysts were used for the reaction, H₂ was evolved during the reaction and the pressure became constant at 0.8 MPa in the initial period of 0.5 h, meaning the chemical equilibrium (eqn (1)). Considering this phenomenon, we expected that the hydrolytic hydrogenation of cellulose occurs with 0.8 MPa of H₂ without using 2-propanol. In fact, Ru/AC(N) catalyst provided 38% yield of the sugar alcohols in this reaction, whereas Ru/ γ -Al₂O₃ catalyst was inactive, suggesting that the active Ru species on C and Al₂O₃ are different. Note that very recently Mizuno and co-workers reported the hydrolytic hydrogenation of cellulose to sorbitol by Pt nano-particles catalyst under 0.7 MPa of H₂ as described above, although a concentrated solution of H₄SiW₁₂O₄₀ and a large amount of Pt (24 mol% to the substrate based on the number of glucose-unit) were required.³⁴



We performed physicochemical analyses for Ru/CMK-3 as an active catalyst and Ru/ γ -Al₂O₃ as an inactive one to reveal the active Ru species. XRD pattern for Ru/CMK-3 catalyst exhibited no diffraction lines derived from Ru metal ($2\theta=43^\circ$) even when the Ru loading was increased to 10 wt%, indicating that the Ru species on carbons are not metal crystalline particles. Thus, we carried out temperature programmed reduction (TPR), O₂ uptake, transmission electron microscopy (TEM), Ru 3p_{3/2} XPS and Ru K-edge X-ray absorption fine structure (XAFS) measurements.⁴⁷ Finally, we concluded that RuCl₃ supported on CMK-3 is reduced to Ru metal nano-particles (*ca.* 1 nm) during H₂ reduction in the catalyst preparation, but that they are easily oxidised to an oxide species RuO₂·2H₂O, which has a one-dimensional chain structure (Fig. 2),⁴⁸ by exposure to air even at r.t. because of the remarkably high dispersion. On the other hand, XRD pattern of

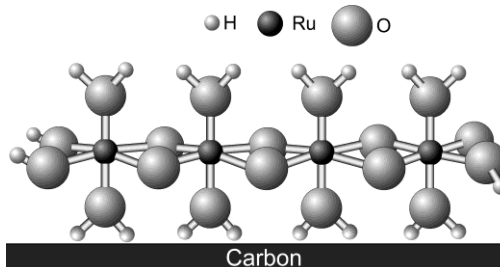
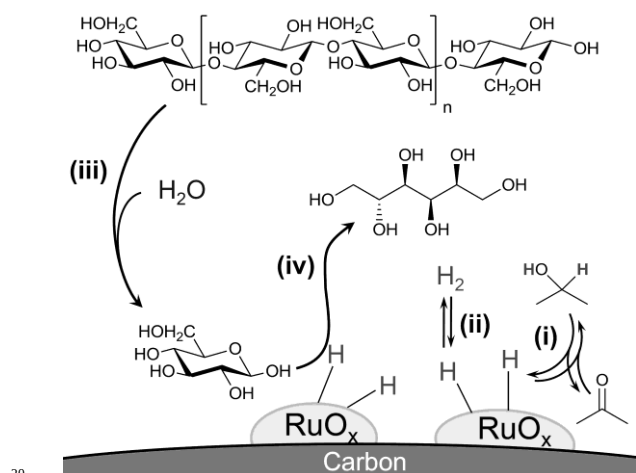


Fig. 2 Possible structure of Ru/CMK-3 catalyst.

Ru/ γ -Al₂O₃ catalyst clearly displayed the presence of Ru metal nano-particles with an average diameter of 9 nm. Therefore, we proposed that RuO₂·2H₂O is the precursor to the active species for the transfer hydrogenation and the low pressure hydrogenation reaction, and that Ru metal nano-particles are inactive for the reactions. The difference in chemical structure of Ru dramatically affects the catalytic activity.

RuO₂·2H₂O might be reduced to RuO_x species ($x < 2$) during the reaction,⁴⁹ due to the reducing atmosphere. The *in-situ* generated species should be the real active species, whose characterisation with *in-situ* XAFS is being under investigation by us. We propose the reaction mechanism as follows (Scheme 4): (i) 2-propanol is transformed to acetone to give active hydrogen species on the Ru oxide active species. (ii) The active hydrogen species is in the chemical equilibrium with H₂ molecules, which allows both 2-propanol and H₂ gas to be used as reductants. (iii) Cellulose is hydrolysed to glucose by hot compressed water and by the Ru/C catalysts. (iv) Glucose is reduced to sorbitol by the active hydrogen species.



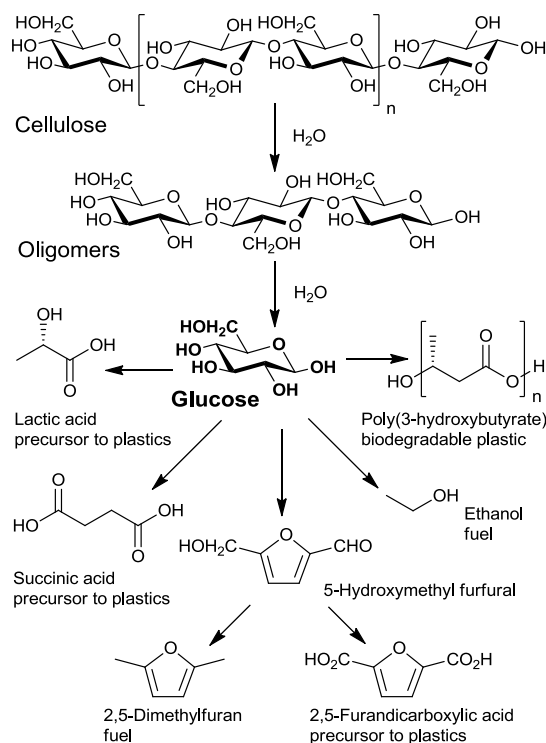
Scheme 4 Possible reaction pathway for the transfer hydrogenation of cellulose.

Hydrolysis of cellulose

Supported metal catalysts for the hydrolysis of cellulose

Selective and efficient hydrolysis of cellulose to glucose is an extremely difficult issue as described above; however, glucose is a fascinating feedstock to plastics and fuels (Scheme 5), and solid catalysts have been applied to this reaction in the last few years. Hara *et al.* demonstrated that a sulphonated carbon made from carbohydrates hydrolyses cellulose to glucose and oligosaccharides at a low temperature of 373 K and is reusable for 25 times without losing the activity.⁵⁰ Generally the sulphonic groups on large graphene sheets are easily hydrolysed to sulphuric acid, but they indicated that the small size of graphene (*ca.* 1 nm) and electrophilicity of surface carboxylic groups on the carbon afford the water-tolerant property. In addition, they mentioned that surface phenolic or carboxylic groups adsorb 1,4- β -glucan chains to make opportunities of the hydrolysis by sulphonic groups in the model experiments using cellobiose and cellohexaose.⁵¹ Besides the catalysis, their reactor is also important;^{50c,d} the staggered shear wings attached to the reactor efficiently mix the catalyst and cellulose to promote the

hydrolysis reaction under the concentrated conditions: *e.g.* cellulose 3 g and the catalyst 3 g in water 2.25 mL. According to Onda and co-workers, a sulphonated carbon prepared from a commercial AC is also effective and gives 40% yield of glucose with 5 TON of SO₃H at 423 K for 24 h.⁵² Similarly, a silica/carbon nano-composite and a mesoporous carbon CMK-3⁴⁶ treated by concentrated sulphuric acid produced glucose in 50% (8 TON) and 75% yields (12 TON), respectively.^{53,54} Utilisation of catalysts containing ferrites was also proposed to separate catalyst/substrate by using magnets.⁵⁵ In addition, ionic liquids are utilised as the reaction media,⁵⁶ because some of them dissolve cellulose and increase the reactivity.⁵⁷ Schüth *et al.* showed that a sulphonated polystyrene resin (Amberlyst 15DRY) hydrolyses cellulose in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl); however, the cation exchange happened to release H₃O⁺.^{56b,c}



Scheme 5 Hydrolysis of cellulose to glucose and the potential chemicals derived from glucose.

Immobilised sulphonic acids have been well studied for the hydrolysis of cellulose as outlined above, whereas the catalysis of supported metals has not been elucidated. Since we found that supported metal catalysts accelerate the hydrolysis step in the hydrolytic hydrogenation of cellulose, we retried the hydrolysis of cellulose by using this type of catalysts.⁵⁸ In our study, we used 4-day-milled cellulose (Avicel, Merck) as the substrate. To achieve both the high reaction rate and the inhibition of glucose decomposition, rapid heating and cooling conditions were utilised,^{23b} *i.e.* the reactor was heated from 298 K to 503 K in 15 min and then cooled down to 298 K by blowing air. In the screening tests of catalysts, we found that 2 wt% Ru/CMK-3 catalyst prepared from RuCl₃ with H₂-reduction at 673 K hydrolyses cellulose to glucose in 24% yield (Fig. 3). This catalytic system can produce glucose over a short period. The

TON of Ru for the formation of glucose was 15 with excluding the glucose yield obtained by CMK-3 (see below). The conversion of cellulose was 56%, and thereby the selectivity for glucose was 43%. Other products were water-soluble oligosaccharides (16%) and glucose derivatives such as fructose (2%), mannose (1%), levoglucosan (1%), 5-hydroxymethylfurfural (5-HMF; 3%) and furfural (0.4%). The sugar compounds should be carefully analysed because they sometimes overlap in the chromatographs.^{9e} This catalyst was reusable at least 5 times with retaining the activity.

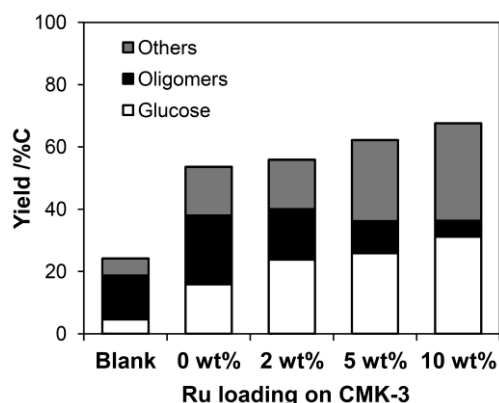
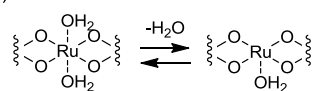


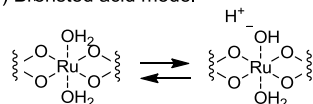
Fig. 3 Hydrolysis of cellulose by Ru/CMK-3 catalyst under rapid heating and cooling conditions. Cellulose (Merck, Avicel, ball-milled for 4 days) 324 mg, catalyst 50 mg, water 40 mL. "Blank" entry shows the reaction without catalysts. "Others" = (conversion of cellulose) – ("Glucose" + "Oligomers").

We conducted control experiments to clarify the detail of the catalysis. A blank test without catalysts gave small amounts of glucose (5%) and oligosaccharides (14%), but CMK-3 gave 16% yield of glucose and 22% yield of oligosaccharides, indicating that the carbon has hydrolytic activity. By increasing Ru loading from 0 wt% to 10 wt%, the yield of glucose was smoothly raised from 16% up to 31%, whereas that of oligosaccharides decreased from 22% to 5%. The conversion of cellulose was slightly improved by increasing the content of Ru. It is thus indicated that the Ru species hydrolyses both cellulose and oligosaccharides, and especially shows high activity for the latter substrate. In fact, the hydrolysis of cellobiose to glucose by Ru/CMK-3 catalyst took place 5 times more quickly than that by CMK-3 at 393 K. The catalytic activity of the Ru species is intriguing, and we determined that the Ru species is $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ by means of several analytical techniques (Fig. 2, *vide supra*).⁴⁷ Regarding the mechanism for the hydrolysis, one possibility is that the $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ species on CMK-3 might desorb the hydrated water

(a) Lewis acid model



(b) Brønsted acid model

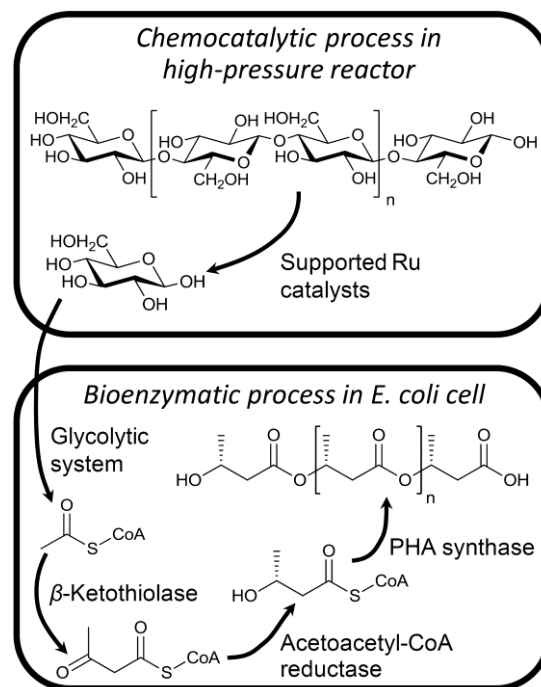


Scheme 6 Speculated mechanisms for the formation of acid sites on Ru/CMK-3 catalyst.

to give a Lewis acid site (Scheme 6a), as it has been proposed that a Ru polyoxometalate depolymerises cellulose to glucose.^{35a} Another hypothesis is that the Ru species works as Brønsted acid by the heterolysis of water molecules on Ru (Scheme 6b), because it is known that $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ has a low pK_a (2.9 at 298 K).⁵⁹

Synthesis of bio-plastics from the hydrolysate of cellulose

The hydrolysate of cellulose is expected to be an actual source for the production of value-added chemicals. Significant targets are polyhydroxyalkanoates (PHAs), which are representative bio-based and bio-degradable plastics produced from sugars by extensive strains of bacteria, and therefore promising as alternatives of conventional petroleum-based plastics.⁶⁰ Although cellulose is an attractive source for PHAs, most bacteria cannot ferment cellulose directly. Accordingly, the hydrolysis of cellulose to glucose is an essential step for the conversion of cellulose into PHAs. Along this line, sulphuric acid was used for the hydrolysis of cellulose and hemicellulose to generate glucose and xylose for the synthesis of PHAs,⁶¹ but complicated purification of the sugars was required before the fermentation as microbes are sterilised principally by sulphuric acid. In contrast, the hydrolysis reaction mixtures produced by supported metal catalysts are easily separated by filtration, and the solutions do not contain strong acids or salts, which allows the direct utilisation of the hydrolysate without complicated handlings. Herein, we tried the production of poly(3-hydroxybutyrate) (P(3HB)) as one of the major PHAs by a recombinant *Escherichia coli* (*E. coli*) from the hydrolysate with no neutralisations or purifications (Scheme 7).⁶²



Scheme 7 Conversion of cellulose to poly(3-hydroxybutyrate) using chemical and biological systems.

There are two key factors on the synthesis of cellulose hydrolysate for the fermentation process. (1) The *E. coli* requires at least 2 g L⁻¹ glucose in the culture medium to accumulate

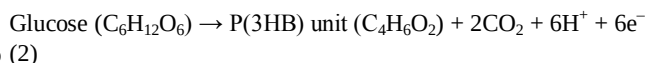
P(3HB). This point can be achieved by increase of the concentration of cellulose. (2) The growth of the microbes is mainly inhibited by 5-HMF,⁶³ indicating that a high molar ratio of glucose to 5-HMF is required. Since 5-HMF was formed by the successive thermal decomposition of glucose, we expected that a lower conversion of cellulose by dropping the reaction temperature would give a higher glucose/5-HMF ratio. As the first trial, we used Ru/ γ -Al₂O₃ as a catalyst and carried out the hydrolysis of cellulose at a cellulose concentration of 130 g L⁻¹ using the rapid heating to 488 K (15 K lower than the typical hydrolysis temperature) and cooling conditions, where substrate/catalyst (S/C) ratio based on mol-glucose units to g-atom-Ru was 740. The major products were glucose (12% yield), corresponding to the concentration of 16 g L⁻¹, oligosaccharides (5.2%), fructose (2.1%) and 5-HMF (1.1%). The concentration of glucose and the glucose/5-HMF ratio of 10 were sufficiently high for the fermentation, which prompted us to conduct the microbial synthesis of P(3HB) using the hydrolysate by collaborating with biochemists.

E. coli (JM109 strain) harbouring a plasmid pGEM-CAB, which bore the P(3HB) synthesis genes from *Ralstonia eutropha* that encoded β -ketothiolase, acetoacetyl-CoA reductase and PHA synthase, was cultured for 72 h at 303 K in LB media containing the reaction solution of the cellulose hydrolysis in various fractions to be aimed concentrations of glucose (2–10 g L⁻¹) (Table 3). Terminal growth of the *E. coli* improved from 2.1 g L⁻¹ to 3.9 g L⁻¹ based on the dried cell weight with increasing the concentration of glucose in the range of 2–7 g L⁻¹, and the accumulated weight of P(3HB) was also raised from 7 wt% to 42 wt% in the dried *E. coli* cells at the same time (entries 1–6). Therefore, the production amount of P(3HB) reached 1.6 g L⁻¹ at 7 g L⁻¹ glucose, which corresponds to 49% efficiency based on the theoretical maximum yield (3.4 g L⁻¹) calculated from eqn 2. A higher concentration of glucose gains a better productivity of P(3HB). However, the *E. coli* did not swell at ≥ 8 g L⁻¹ glucose (entries 7, 8) because the concentrations of harmful by-products for the bacteria, in which 5-HMF was the major one, were proportional to that of glucose and reached the threshold for inhibiting the cell growth. If we can improve the glucose/5-HMF ratio of the hydrolysate, the fermentation should proceed at larger concentrations of glucose.

Table 3 Production of P(3HB) from hydrolysate of cellulose by using recombinant *E. coli*.^a

Entry	Glucose ^b /g L ⁻¹	<i>E. coli</i> ^c /g L ⁻¹	P(3HB) content ^d /%	P(3HB) amount /g L ⁻¹ (Yield ^e /%)
1	2.0	2.1	7.0	0.15 (15)
2	3.0	2.3	24	0.55 (38)
3	4.0	3.1	23	0.71 (37)
4	5.0	3.4	26	0.88 (37)
5	6.0	3.9	31	1.2 (42)
6	7.0	3.9	42	1.6 (49)
7	8.0	0.0	-	0.0 (0.0)
8	10	0.0	-	0.0 (0.0)

^a 303 K, incubation time 72 h. ^b The cellulose hydrolysate containing glucose 86 mM (16 g L⁻¹) was added to condensed LB media to be each concentration of glucose by changing the mixing ratio. ^c Terminal growth of the *E. coli* based on the dried weight. ^d In dried cells of the *E. coli*. ^e P(3HB) yield based on eqn 2.



We compared the productivity of P(3HB) by using pure glucose to that by using the hydrolysate, which resulted in the same cell growths and accumulation amounts of P(3HB) at respective concentrations of glucose (2–7 g L⁻¹). Furthermore, the weight-average molecular weights (*M*_w) of the P(3HB)s produced from the hydrolysate and pure glucose were similar (1.6×10⁶, 2.4×10⁶, respectively) and sufficiently high for the practical use. Thus, by-products in the hydrolysis of cellulose such as 5-HMF have critical concentrations for the life activity of the *E. coli*, but they do not affect both the cell growth and the production of P(3HB) below the threshold. We demonstrated that the cellulose hydrolysate synthesised by using supported metal catalysts can be used for the production of the bio-plastic without neutralisation or purifications.

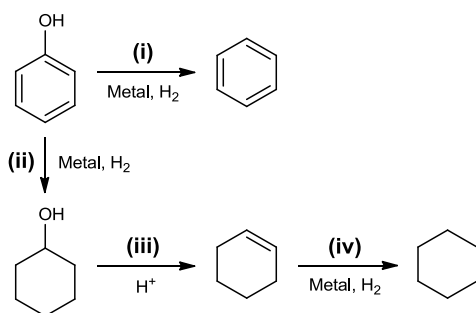
The above strategy was applied to synthesise poly(3-hydroxybutylate-co-3-hydroxyvalerate) (P(3HB-co-3HV)),⁶⁴ which has higher strength and flexibility than P(3HB).⁶⁵ P(3HB-co-3HV) is producible with using propionate based on the mechanism for the formation of P(3HB), whose key step is the condensation of propionyl-CoA with acetyl-CoA to 3-ketovaleryl-CoA by β -ketothiolase. Since it was found that *E. coli* LS5218 is more resistant to 5-HMF than JM109, the concentration of the cellulose hydrolysate in the LB media was increased to 10 g L⁻¹ of glucose. 0.5–3.8 g L⁻¹ of sodium propionate was added into the mixture, and then pH of the solution was adjusted to 7 because the concentration of the base (propionate) was different in each experiment, which could affect the results. The microbes converted glucose and propionate to a plastic, and the amount was up to 2.1 g L⁻¹. The plastic surely contained 3HV fraction in the range of 5.6–40 mol%.

Hydrodeoxygenation of lignin derivatives

Degradation of lignin

Lignin is the second most abundant biomass next to cellulose and is a highly cross-linked, oxygenated aromatic polymer consisting of methoxylated phenylpropane units, which is a potential resource of aromatic compounds from biomass (see, Fig. 1(c)).⁶⁶ Catalytic conversion of lignin has attracted much attention for the production of biofuels and value-added chemicals as well as simple aromatic compounds such as BTX (benzene, toluene and xylene).⁶⁷ However, lignin is very difficult to decompose because of its robust structure, limiting the industrial application of lignin except for energy production by the direct combustion.⁶⁷ Many efforts have been made over the recent years to achieve effective degradation of lignin.^{66–70} Among them, pyrolysis is one of the most investigated methods for converting lignin into low-molecular-weight fractions, in which the chemical bondings in lignin are thermally broken down to yield liquid products, named bio-oils.^{68,69} The lignin-derived oils contain various kinds of oxygenated species (phenols, furans, carboxylic acids, alcohols, aldehydes, ketones and esters), which are chemically unstable and have some undesirable properties for further applications.⁶⁹ Therefore, the upgrading is necessary for the utilisation of lignin-derived materials.⁶⁹

Catalytic hydrodeoxygenation (HDO) is one of the most important reaction for converting lignin and lignin-derived materials such as bio-oils into hydrocarbons.^{66,71} HDO studies often employ lignin models, especially phenol derivatives, rather than lignin and bio-oil themselves to get better understanding of reaction pathway and intermediates in lignin conversion. The HDO of phenols involves two reaction pathways; (i) one is the direct hydrogenolysis of the C–O bond in phenols leading to deoxygenated aromatic products, and the other provides aliphatic hydrocarbons *via* (ii) the hydrogenation of aromatic ring, (iii) the dehydration of cycloalkanols to cycloalkenes and (iv) the hydrogenation of cycloalkenes (Scheme 8).^{71,72} The former route is important not only for bio-fuel production but also as an alternative to petrochemical-based routes for the production of bulk aromatic compounds such as BTX.⁷³ The latter route consumes more hydrogen to produce aliphatic hydrocarbons but is more promising for the production of biofuels with lower aromatics contents satisfying an environmental demand.⁷⁴



Scheme 8 Reaction pathway for the HDO of phenol.

Conventional HDO catalysts

Most investigated catalysts in the HDO process are sulphided Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃, which are industrially successful hydrodesulphurisation (HDS) catalysts.⁷⁵ It is proposed that the catalytically active sites in the sulphided catalysts are exposed Mo ions with sulphur vacancies (coordinatively unsaturated sites) presented on the edge of MoS₂ slab.^{75,76} Thus, the MoS₂ structure must be maintained by adding a sulphur source (*e.g.* H₂S and CS₂) into the feedstock.⁷⁷ In HDO without adding a sulphur source, these sulphided catalysts are rapidly deactivated by the reduction of sulphided Co and Ni to the zero-valent states followed by the coke formation because of the low sulphur contents of the HDO feedstocks. Furthermore, these systems suffer from sulphur contamination and water-induced catalyst deactivation. For these reasons, non-sulfided catalyst systems have been developed for the HDO of lignin and related model compounds.

Development of non-sulphided HDO catalysts

Noble metal catalysts, which are highly active for hydrogenation and hydrogenolysis, have been studied in the HDO of lignin derivatives (Table 4). Gutierrez *et al.* reported various ZrO₂-supported noble metal catalysts consisting of Rh, Pt and Pd for the HDO of guaiacol in *n*-hexadecane under pressurised H₂ at 373–573 K.⁷⁸ All the catalysts promoted the reaction at 573 K to give benzene as a major product (entry 1). Under the conditions, the ZrO₂-supported catalysts were more stable to carbon

deposition than conventional sulphided Co-Mo/ γ -Al₂O₃ catalyst. Jones *et al.* found that Pt supported on HY zeolite (SiO₂/Al₂O₃ = 12) worked as a metal/acid bifunctional catalyst for the HDO of aqueous phenol (H₂O content: 5 wt%) in a fixed-bed reactor at 523 K under 4 MPa H₂, affording cyclohexane as a predominant product (entry 2).⁷⁹ In this case, the Pt/HY also produced small amounts of bicyclic products such as cyclohexyl phenol, cyclohexyl cyclohexanone and bicyclohexyl by metal/acid catalysis. Resasco *et al.* investigated the gas-phase HDO of anisole over Pt/HBeta catalyst at 673 K under atmospheric H₂, giving benzene (51% yield), toluene (28%) and xylene (11%) (entry 3).⁸⁰ The reaction includes Brønsted acid-catalysed demethylation/methyl transfer and Pt-catalysed HDO, where the synergistic effect of Pt and HBeta was observed. Fang *et al.* reported that Pt catalyst supported on mesoporous ZSM-5 was more effective in the gas-phase HDO of dibenzofuran to bicyclohexyl than Pt/ZSM-5, assuming a positive contribution of the mesoporous structure in the catalyst (entry 4).⁸¹ Kou and Dyson *et al.* developed a remarkably active bifunctional catalyst system based on noble metal nanoparticles (Rh, Ru, Pt and Pd NPs) and ionic liquids (ILs) bearing Brønsted acid functionality, which facilitated the HDO of phenols into cycloalkanes under 4 MPa H₂ at surprisingly low temperature (403 K) (entry 5).⁸² It is suggested that Brønsted acidic ILs catalyse the rate-determining dehydration of cycloalkanols into cycloalkenes and that hydrophobicity allows the generated water to be removed from the reaction system. Besides, Sheu *et al.* examined the upgrading of a pine pyrolytic oil by using a Pt/Al₂O₃/SiO₂ catalyst at 673 K in a trickle-bed reactor to give hydrotreated oil with reduced oxygen content (entry 6).⁸³ De Wild *et al.* performed the HDO of a fast pyrolytic oil from Alcell lignin in *n*-dodecane at 623 K under 10 MPa H₂ using a Ru/AC catalyst (entry 7).⁸⁴ After the reaction, all phenolic species in the pyrolytic oil were converted to cycloalkanols, cycloalkanes and linear alkanes. With a variety of noble metal catalysts (Ru/AC, Ru/TiO₂, Ru/ γ -Al₂O₃, Pt/AC and Pd/AC), Heeres *et al.* studied the hydrotreating of a beech fast pyrolytic oil at 623 K, and found that Ru/AC was superior to the conventional hydrotreating catalysts (sulphided Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃) in terms of both liquid product yield (up to 60 wt%) and deoxygenation level (up to 90 wt%) (entry 8).⁸⁵ As described above, noble metal catalysts show high activity and selectivity, especially for ring-saturated products. However, the noble metal catalysts have not been applied to the large-scale HDO due to the high cost of processing.

Recent efforts have been focused on developing low-cost, base metal catalysts with high activity and selectivity in the HDO process. Bell reported that γ -Mo₂N was an effective catalyst for the gas-phase HDO of benzofuran at 723 K under 1 atm H₂ to give a mixture of aromatic products (ethylbenzene, toluene and benzene) (entry 9).⁸⁶ The reaction involves hydrogenation of the furan ring, hydrogenolysis of the C–O bonds and hydrogenolysis/dealkylation of the alkyl group. With a series of metal carbide and nitride catalysts (VN, Mo₂N, TiN, VC, Mo₂C, WC, NbC), Oyama studied the hydroprocessing of a model liquid feed mixture (3000 ppm dibenzothiophene, 2000 ppm quinoline, 500 ppm benzofuran, 20 wt% tetralin and balance aliphatics) in a trickle-bed reactor at 643 K.⁸⁷ Among the catalysts tested, VN showed the best activity to give ethylbenzene (entry 10), while

Table 4 HDO of lignin derivatives by non-sulphided catalyst systems.^a

Entry	Catalyst	Substrate	Reactor	$P(\text{H}_2)$ /MPa ^b	T/K	Reaction time /h	Conv. of the substrate /%	Main product (Sel. /%)	Ref.
1	Rh/ZrO ₂	Guaiacol	Batch	8 ^c	573	3	ca. 100	Benzene	78
2	Pt/HY	Phenol	Fixed-bed	4 ^c	523	20 ^d	100	Cyclohexane (94)	79
3	Pt/HBeta	Anisole	Fixed-bed	0.1	673	0.33 ^e	100	Benzene (51), toluene (28), xylene (11)	80
4	Pt/m-ZSM-5 ^f	Dibenzofuran	Fixed-bed	— ^g	473	6 ^h	— ^g	Bicyclohexyl (83)	81
5	Rh/Ru NPs, IL ⁱ	4-Ethylphenol	Batch	4	403	4	99	Ethylcyclohexane (99)	82
6	Pt/Al ₂ O ₃ /SiO ₂	Pine pyrolytic oil	Trickle-bed	10 ^c	673	2 ^d	— ^g	Phenols, aromatics, alkanes	83
7	Ru/AC ^j	Alcell lignin fast pyrolytic oil	Batch	10	623	1	— ^g	Cycloalkanol, cycloalkanes, linear alkanes	84
8	Ru/AC ^j	Beech fast pyrolytic oil	Batch	2	623	4	— ^g	Phenols, aromatics, alkanes	85
9	γ-Mo ₂ N	Benzofuran	Microreactor	0.1	723	— ^g	ca. 100	Benzene (37), toluene (30), ethylbenzene (33)	86
10	VN	Benzofuran (in a model liquid feed mixture)	Trickle-bed	3.1 ^c	643	5 ^h	63	Ethylbenzene	87
11	Ni-Mo/γ-Al ₂ O ₃	Phenol	Batch	2.8	723	1	100	Benzene (60), cyclohexane (16)	88
12	Ni-Mo/γ-Al ₂ O ₃	2,3-Dihydrobenzofuran	Fixed-bed	— ^g	553	— ^g	ca. 100	Ethylcyclohexane (ca. 70), methylcyclohexane (ca. 30)	89
13	Ni-Cu/CeO ₂	Anisole	Fixed-bed	1 ^c	573	1 ^h	100	Cyclohexane (>99)	90
14	Co-Mo-B	Phenol	Batch	4 ^c	548	10	100	Cyclohexane (>95)	91
15	Ni-Mo-B	Phenol	Batch	4 ^c	498	7	81	Cyclohexane (81), benzene (12)	92
16	La-Ni-W-B	Phenol	Batch	4 ^c	498	4	95	Cyclohexane (36), cyclohexene (37) cyclohexanol (25)	93
17	Ni-W(P)/AC ^{jk}	Phenol	Fixed-bed	— ^g	523	0.5 ^d	100	Cyclohexane (>95)	94
18	MoO ₃	4-Methylphenol	Batch	4.8 ^c	648	1.7	100	Toluene (ca. 60)	95
19	Ni/SiO ₂ ^l	Phenol	Fixed-bed	0.1	573	0.73 ^e	— ^g	Benzene (99)	96
20	Ni ₂ P/SiO ₂	Guaiacol	Packed-bed	0.1	573	— ^g	80	Benzene (60), phenol (30), anisole (10)	97
21	Cu-PMO ^m	2,3-Dihydrobenzofuran	Batch	— ⁿ	573	13	100	2-Ethylcyclohexanol (68), methylethylcyclohexanol (24)	98
22	Cu-PMO ^m	Poplar organosolv lignin	Batch	— ⁿ	573	24	100	Monomeric cyclohexyl derivatives	99
23	Pd/AC ^j /H ₃ PO ₄	4-Propylphenol	Batch	5	523	0.5	100	Propylcyclohexane (96)	101
24	RANEY Ni, Nafion/SiO ₂	4-Propylphenol	Batch	4	473	0.5	100	Propylcyclohexane (99)	102
25	Pt/AC or Pd/AC ^j , H ₃ PO ₄	White birch wood lignin	Batch	4	473–523	2–4	— ^g	C ₈ –C ₉ alkanes, C ₁₄ –C ₁₈ alkanes, methanol	103
26	Pt/AC(N) ^o	4-Propylphenol	Batch	4	553	2	100	Propylcyclohexane (>99)	104

^a Selected examples from each reference. ^b initial H₂ pressure at rt. ^c H₂ pressure at reaction temperature. ^d Weight hourly space velocity (WHSV /h⁻¹). ^e W/F (h) = catalyst mass (g)/feed rate (g/h). ^f mesoporous ZSM-5. ^g Not specified. ^h Liquid hourly space velocity (LHSV /h⁻¹). ⁱ 1-Methyl-3-(4-sulphobutyl)imidazolium trifluoromethanesulphonate. ^j AC: activated carbon. ^k Ni-W/AC prepared using H₃[P(W₃O₁₀)₄]·xH₂O as a tungsten precursor. ^l the Ni particle diameter is 3.7 nm. ^m Cu-PMO: hydrotalcite-derived porous metal oxide doped with Cu. ⁿ Methanol as a solvent and H₂ source. ^o AC(N): activated carbon (Norit).

the conventional sulphided Ni-Mo/γ-Al₂O₃ catalyst produced ethylcyclohexane as a major product.

Recently, it is presumed that the presence of coordinatively unsaturated sites in non-sulphided catalysts is important for the HDO of lignin-related compounds. Kallury *et al.* tested the HDO activity of a non-sulphided Ni-Mo/γ-Al₂O₃ catalyst for various phenol derivatives in a fixed-bed reactor at 623–773 K under 2.8 MPa H₂.⁸⁸ The reaction of phenol at 723 K afforded benzene and cyclohexane in 60% and 16% yields, respectively (entry 11). The deoxygenation activity was greatly decreased in the presence of water (14% conversion, benzene in <1% yield), suggesting the interaction of the oxygen atoms with the active sites. Ozkan *et al.* investigated the use of Ni-Mo/γ-Al₂O₃ catalysts for the gas-phase HDO of benzofuran derivatives (entry 12).⁸⁹ The reduced Ni-Mo/γ-Al₂O₃ showed good hydrogenation activity to give saturated hydrocarbons, suggesting the formation of Ni- and Mo-associated anionic vacancies during the reaction. In contrast,

hydrogenation activity of the sulphided catalyst was decreased by adding sulphur source. Yakovlev *et al.* found that Ni-Cu catalysts supported on metal oxides were effective for the gas-phase HDO of anisole and biodiesel.⁹⁰ When Ni-Cu/CeO₂ was used as a catalyst at 573 K under 1 MPa H₂, anisole was fully converted to cyclohexane (entry 13). The authors explain that Cu facilitates the reduction of nickel oxide and catalyst support, and the reduced Ni activates hydrogen whereas the oxide support serves for an additional activation of the C–O group in oxygen-containing compounds. Yang *et al.* studied the HDO of phenol in dodecane with amorphous Co-Mo-B,⁹¹ Ni-Mo-B⁹² and La-Ni-W-B⁹³ catalysts (entries 14, 15 and 16). The reactions may involve the adsorption of phenol on the acid sites of MoO₂ and WO₃ via the donation of a lone pair of the C–O group as well as the activation of hydrogen by Ni and Co. Similarly, Echeandia *et al.* found that the Ni-W/AC catalysts prepared from heteropolyacids were active in the gas-phase HDO of phenol at 523 K to afford

cyclohexane with high selectivity (entry 17).⁹⁴ Smith examined the gas-phase HDO of 4-methylphenol at 648 K under 4.8 MPa H₂ over unsupported MoO₃, MoO₂, MoS₂ and MoP catalysts. The MoO₃ catalyst showed highest activity to yield toluene as a major product (entry 18).⁹⁵ Keane reported the HDO of methanolic solution of phenol using a Ni/SiO₂ catalyst (Ni particle diameter: 3.7 nm) at 573 K under atmospheric H₂ flow in a fixed-bed reactor to give benzene in 99% selectivity (entry 19).⁹⁶ The product ratio of benzene/cyclohexane greatly depends on the Ni particle size and the reaction temperature. Oyama *et al.* investigated the gas-phase HDO of guaiacol at 573 K under atmospheric H₂ using SiO₂-supported metal phosphides (Ni₂P, Fe₂P, MoP, Co₂P, WP) as catalysts.⁹⁷ Among the catalysts tested, Ni₂P/SiO₂ showed the highest activity (80% conversion) to form benzene, phenol and anisole in 60%, 30% and 10% selectivities, respectively (entry 20). Under the conditions, commercial sulphided Co-Mo/ γ -Al₂O₃ deactivated quickly by coking and showed almost no activity for the HDO of guaiacol. As outlined above, various heterogeneous catalysts have been developed for the conversion of lignin derivatives, providing valuable information about designing a new catalyst for HDO reaction.

HDO of lignin derivatives via hydrogen transfer

The above-described HDO reaction is an effective process for the selective conversion of lignin and related compounds, but the system usually needs pressurised H₂. Recently, Ford *et al.* found that a Cu-doped porous metal oxide (PMO) catalysed the sequential hydrogenolysis-hydrogenation of 2,3-dihydrobenzofuran at 573 K via hydrogen transfer from supercritical methanol, giving 2-ethylcyclohexanol as a major product (68% yield) (Table 4, entry 21).⁹⁸ The reaction involves the catalytic formation of H₂ equivalents from methanol solvent itself followed by the hydrogenolysis and hydrogenation of 2,3-dihydrobenzofuran. Large amounts of methylethylcyclohexanol (24% yield) was also formed as a by-product via the methyl transfer from methanol solvent during the reaction. This transfer hydrogenolysis/hydrogenation approach was further utilised to the degradation of organosolv lignin from poplar sawdust and subsequent HDO reaction in a one-pot reaction (entry 22).⁹⁹ Hydrogen transfer from methanol to organosolv lignin affords the complete hydrogenolysis of the phenyl ether bonds, coupled with the hydrogenation of aromatic rings. The final product mixture contained almost no aromatic species and had highly reduced oxygen content. In addition, no char formation was observed in this system.

Aqueous-phase HDO of lignin derivatives

Metal/Acid-catalysed system

For utilising insoluble solid biomass such as lignin, it is important to develop a catalyst system that effectively works in a liquid phase, especially in water. The advantage of water-based system includes not only the easy separation of organic products from water but also the potential use of hot compressed water for the degradation of lignin.¹⁰⁰ Recently, Lercher *et al.* reported the highly selective HDO of phenols into cycloalkanes in water by using commercial noble metal catalysts (Pd/AC, Pt/AC, Rh/AC and Ru/AC) with a liquid acid (0.5 wt% H₃PO₄ aq., pH = 2.1) at 523 K under 5 MPa H₂ (Table 4, entry 23).¹⁰¹ The reaction

consists of metal-catalysed hydrogenation of aromatic ring/cycloalkene and acid-catalysed dehydration of cycloalkanol to cycloalkene. No direct hydrogenolysis of phenol to benzene was observed. The Pd/AC catalyst was reused twice for the reaction of simulated bio-oil mixture (4-propylphenol, 4-propylguaiacol, 4-acetonylguaiacol and 4-allyl-2,6-dimethoxyphenol). The HDO of phenols in water was also studied by RANEY Ni with a solid acid catalyst (Nafion/SiO₂).¹⁰² 4-Propylphenol was easily converted to propylcyclohexane in 99% yield at 473 K (entry 24), while the reaction of guaiacol and syringol derivatives needed higher reaction temperature (573K). Besides, Kou *et al.* reported the selective degradation of white birch wood lignin over noble metal catalysts with a strong liquid acid in a two-step process (entry 25).¹⁰³ In the first step, selective cleavage of the C–O bonds in lignin was observed under optimised conditions (Pt/AC, 1 wt% H₃PO₄, H₂O/dioxane, 473 K, 4 h, 4 MPa H₂) without disrupting the C–C linkages and the methoxy groups, affording four phenolic monomers and some dimers. In the second step, these compounds were completely hydrodeoxygenated under optimised conditions (Pd/AC, 5 wt% H₃PO₄, H₂O, 523 K, 2 h, 4 MPa H₂) to give 42 wt% C₈–C₉ alkanes, 10 wt% C₁₄–C₁₈ alkanes and 11 wt% methanol from the actual wood lignin.

Acid-free Pt-catalysed system

In the course of the HDO study, we found that readily available carbon-supported Pt catalysts showed high activity and durability in the aqueous-phase HDO of phenols without adding any acid catalysts (Table 4, entry 26, the details are as follows).¹⁰⁴ The Pt/carbon catalysts (2 wt% Pt loading) were prepared by an impregnation method using an aqueous solution of H₂PtCl₆ with different types of carbon materials such as AC(N) and AC(W) (activated carbons from Norit and Wako), MWCNT (multi-walled carbon nanotube, TCI), CMK-3⁴⁶ (mesoporous carbon) and BP2000 (carbon black, Cabot). The catalysts were reduced by H₂ at 673 K for 2 h. Characterisation of the catalysts was performed by N₂ adsorption, XRD and TEM analyses. Pt catalysts supported on AC(N), AC(W), CMK-3 and BP2000 have large BET surface areas of ca. 1000 m² g⁻¹. On the other hand, Pt/CNT has a much lower surface area (94 m² g⁻¹). TEM analyses of Pt/AC(N), Pt/CMK-3 and Pt/BP2000 revealed that the Pt nanoparticles of 1–2 nm were formed on the supports. The Pt particle sizes of Pt/AC(W) and Pt/MWCNT were also determined to be ca. 2 nm by XRD and TEM analyses. The Pt/carbons were employed as catalysts in the HDO of 4-propylphenol (4-PrPhOH) in water at 553 K under 4 MPa H₂ for 1 h (Table 5). Readily available Pt/AC(N) showed excellent catalytic activity and gave propylcyclohexane (PrCyH) in 97% yield (entry 1). Pt/MWCNT and Pt/CMK-3 were also effective in this reaction, affording PrCyH in slightly lower yields (entries 6, 7). Pt/AC(W) yielded PrCyH and 4-propylcyclohexanol (4-PrCyOH) in 73% and 16% yields, respectively (entry 5). In contrast, Pt/BP2000 gave much lower conversion (16%) and yield of PrCyH (9%) probably due to the reduction of catalytic activity by the sulfur impurity of BP2000 support (entry 8).¹⁰⁵ Since Pt/AC(N) showed high activity, a reaction of 4-PrPhOH on a gram-scale was performed with a high substrate to catalyst molar ratio (S/C) of 1000 at 553 K for 2 h, which gave PrCyH in >99% yield (entry 2). Pt/AC(N) also promoted the large-scale

Table 5 Aqueous-phase HDO of 4-propylphenol (4-PrPhOH) by supported metal catalysts under acid-free conditions.

Entry	Catalyst	Yield /%					Conv. /%
		PrCyH ^m	4-PrCyOH ⁿ	4-PrCyO ^o	PrPhH ^p	Others ^q	
1	Pt/AC(N) ^e	97	<1	0	0	3	100
2 ^{a,b}	Pt/AC(N) ^e	>99	0	0	0	0	100
3 ^{a,c}	Pt/AC(N) ^e	>99	0	0	0	0	100
4 ^{a,d}	Pt/AC(N) ^e	>99	0	0	0	0	100
5	Pt/AC(W) ^f	73	16	<1	0	11	100
6	Pt/MWCNT ^g	92	1	<1	0	7	100
7	Pt/CMK-3	92	0	0	0	8	100
8	Pt/BP2000 ^h	9	1	0	1	5	16
9	Pt/CeO ₂ ⁱ	83	<1	0	8	9	100
10	Pt/TiO ₂ ^j	77	2	0	3	18	100
11	Pt/ZrO ₂ ^k	66	<1	0	10	24	100
12	Pt/ γ -Al ₂ O ₃ ^l	0	0	0	0	0	0
13	Ru/AC(N) ^e	55	<1	0	0	45	100
14	Rh/AC(N) ^e	83	<1	0	0	17	100
15	Pd/AC(N) ^e	22	57	2	<1	3	84

Reaction conditions: 4-PrPhOH 272 mg (2.0 mmol), catalyst (2 wt% metal, S/C = 200), water 40 mL, 553 K, reaction time 1 h, $p(\text{H}_2)$ 4.0 MPa at r.t. ^a 4-PrPhOH 1.36 g (10 mmol), S/C = 1000. ^b 553 K, 2 h. ^c 513 K, 10 h. ^d 553 K, 4 h, without water. ^e Activated carbon, SX Ultra (Norit). ^f Activated carbon (Wako). ^g Multi-walled carbon nanotube (TCI). ^h Carbon black Black Pearls 2000 (Cabot). ⁱ JRC-CEO-2 (JRC: Japan Reference Catalyst, Catalysis Society of Japan). ^j P-25 (Degussa). ^k JRC-ZRO-2. ^l JRC-ALO-2. ^m Propylcyclohexane. ⁿ 4-Propylcyclohexanol. ^o 4-Propylcyclohexanone. ^p Propylbenzene. ^q Gaseous hydrocarbons, etc.

reaction even at 513 K, affording PrCyH in excellent yield (>99%) after 10 h (entry 3). Furthermore, 4-PrPhOH was efficiently converted into PrCyH without water-solvent (entry 4), which shows that the catalyst can be used both in water and under water-free conditions. Besides, oxide-supported Pt/CeO₂, Pt/TiO₂ and Pt/ZrO₂ were also examined as catalysts for this reaction, giving PrCyH in 66–83% yield (entries 9–11). In these reactions, propylbenzene (PrPhH) was also formed in 3–10% yield probably via the direct hydrogenolysis of 4-PrPhOH. In stark contrast, Pt/ γ -Al₂O₃ showed no catalytic activity because of the structural change of γ -Al₂O₃ into boehmite (AlO(OH)) during the reaction (entry 12). Ru/AC(N), Rh/AC(N) and Pd/AC(N) were not very effective for the reaction of PrPhOH, affording lower yields of PrCyH than the Pt/AC(N) catalyst (entries 13–15).

Pt/AC(N) was also effective for the aqueous-phase HDO of guaiacols (4-propylguaiacol, 4-allylguaiacol and 4-acetonylguaiacol) and a syringol derivative (4-allyl-2,6-dimethoxyphenol) under the standard conditions in Table 5, giving PrCyH (58–78% yield based on carbon) and methanol (2–3%) after 6 h. In these cases, propylcyclopentane (5–10%) was also formed possibly via skeletal isomerisation and hydrogenolysis of cycloalkane.^{101,102} These results suggest that this water-based catalyst system is applicable to the HDO of various phenolic compounds, including lignin and bio-oil.

The reuse experiments of Pt/AC(N) were carried out for the HDO of 4-PrPhOH at 553 K in water with the S/C ratio of 1000 for the reaction time (10 min) that provided ca. 60% yield of PrCyH in the first run to check the durability (Fig. 4(a)). The catalyst was recovered by centrifugation and was reused twice in water, which afforded PrCyH in stable chemical yields (61–65%). The XRD analysis of the Pt/AC(N) after the 3rd run showed that the Pt particles retained their small sizes (< 2 nm). In addition, the pH of the aqueous solution after the 1st run was neutral (pH =

7.0), showing no leaching of acid components from the catalyst. These results indicate that the Pt/AC(N) catalyst is durable under the catalytic conditions. In contrast, the reuse experiments under the water-free conditions showed that the catalytic activity was reduced during the repeated catalytic runs probably due to coke formation (Fig. 4(b)). Hence, the aqueous conditions are suitable to keep the catalytic activity.

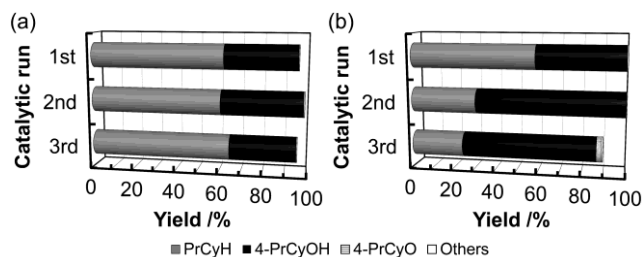


Fig. 4 Reuse experiments of Pt/AC(N) catalyst in the HDO of 4-PrPhOH (a) in water and (b) water-free conditions. Reaction conditions: 4-PrPhOH 1.36 g (10 mmol), 2 wt% Pt/AC(N) 98 mg (S/C = 1000), 553 K, 10 min (in water) or 30 min (water-free conditions). Abbreviations: see Table 5.

The HDO of 4-PrCyOH was investigated to reveal the reaction pathway from 4-PrPhOH to PrCyH (Fig. 5). In the absence of catalyst, 4-PrCyOH was dehydrated to give 4-propylcyclohexene (4-PrCHE) in 11% yield (15% conversion). It is suggested that the dehydration is catalysed by *in-situ* generated protons from hot compressed water.^{100,106,107} Hence, the reaction of 4-PrCyOH into 4-PrCHE was completely suppressed by the addition of a base (CaCO₃, pH = 10). On the other hand, Pt/AC(N) easily facilitated the conversion of 4-PrCyOH to PrCyH in 95% yield. Even under the basic conditions, Pt/AC(N) afforded PrCyH in a good yield (58%). Besides, NH₃-TPD profile showed that Pt/AC(N) had no acidity. These results suggest that this reaction is promoted not by acid-catalysis but by the direct C-O bond hydrogenolysis of 4-PrCyOH with Pt/AC(N).

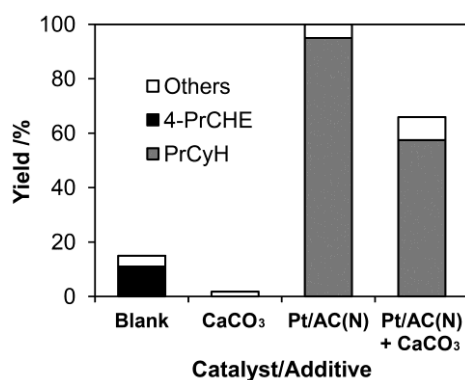
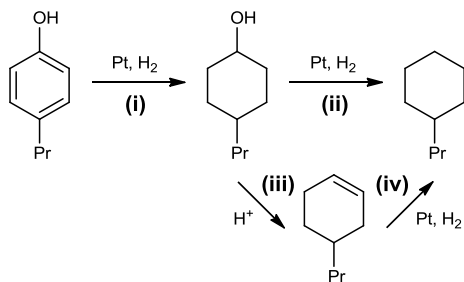


Fig. 5 HDO of 4-PrCyOH in water by Pt/AC(N). 4-PrCyOH 2.0 mmol, 2 wt% Pt/AC(N) 98 mg, CaCO₃ 4.0 mmol, water 40 mL, 553 K, 1 h, 4 MPa H₂ at r.t. “Blank” entry shows the reaction without catalyst. PrCHE: 4-propylcyclohexene. Other abbreviations: see, Table 5.

Scheme 9 shows the proposed reaction pathways for the HDO of 4-PrPhOH to PrCyH by Pt/AC(N) catalyst. (i) First, the aromatic ring of 4-PrPhOH is hydrogenated to give 4-PrCyOH. (ii) 4-PrCyOH is converted to PrCyH by the direct C-O bond hydrogenolysis, which is the main pathway from 4-PrCyOH to PrCyH. (iii) When the HDO is performed in water, the reaction includes the dehydration, as a minor pathway, of 4-PrCyOH to 4-

PrCHE by *in-situ* generated protons from hot compressed water. (iv) Subsequent hydrogenation of 4-PrCHE affords PrCyH. Therefore, the addition of acid catalysts is not necessary in this reaction.



Scheme 9 Putative reaction mechanism for the HDO of 4-PrPhOH into PrCyH by Pt/AC(N) without additional acid catalysts.

Conclusions

The conversion of lignocellulose to renewable chemicals is the one of the challenging subjects in green and sustainable chemistry. We have studied the hydrolytic hydrogenation, transfer hydrogenation and hydrolysis of cellulose by using supported metal catalysts. This strategy has also been extended to the conversion of hemicellulose and bio-oils from lignin. These approaches have succeeded in gaining good yields of platform chemicals such as sugar derivatives and alkanes. The obtained sugar is directly useful for the production of bio-plastics.

In the utilisation of the lignocellulose conversion, the separation of heterogeneous catalysts from a solid mixture containing lignin is a problem. Since the extraction of lignin has been established in the paper industry, one possible way is the separation of lignocellulose into carbohydrates and lignin followed with the successive catalytic reactions. Another route is the direct transformation of whole lignocellulose to chemicals using multifunctional catalytic steps.

As various types of solid catalysts can be designed and wide ranges of reaction conditions are applicable to the catalytic systems, we believe that further progress of solid catalysis overcomes this tough issue for the practical applications. One of such catalysts would be different from previous ones that possess strong acidic sites. Very recently, it has been demonstrated that silanols (average $pK_a=7$) can cleave glycosidic bonds by optimising the configurations.¹⁰⁸

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