Chapter 2
Hydrogenation of Renewables

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2.1 Introduction

Hydrogenation reactions have a variety of applications in the chemical industry which is shown by the corresponding products, such as ammonia, methanol, and polyamides. In petrochemistry, the addition of hydrogen is used to adjust properties of product mixtures, e.g. in the hydrocracking or hydrotreating. For renewables the same is already feasible or first proofs of concept were already shown. Therefore, hydrogenations indicate ways to increase the availability and enhance handling of products from natural resources. Heterogeneously catalysed hydrogenations with renewables are realised already in big scale, e.g. in the production of margarine or sorbitol.

In general, hydrogenation is the addition of hydrogen to C–C-, C–O-, C–N-, or N–O-multiple bonds. If the bond is broken, the reaction is referred to as hydrogenolysis [1]. Hydrogenation reactions are usually exothermic; therefore, low temperatures favour the reaction over its corresponding back reaction, which is dehydrogenation (Fig. 2.1).

Hydrogenations on industrial scale are mostly heterogeneously catalysed but lack of reactivity at mild reaction conditions or selectivity. Therefore, homogeneous catalysed hydrogenations are needed for more specialised reactions, which are required for the valorisation of renewables.

Common catalyst metals for homogeneous hydrogenations are platinum, palladium, rhodium, iridium, and ruthenium. But also non-precious metal systems as nickel, copper and other transition metals, such as molybdenum and cobalt have found applications in industrial processes. Frequently used homogeneous catalyst complexes in hydrogenation are as follows:

$$A + n\,\mathrm{H}_2 \rightleftharpoons B \quad \Delta H_r < 0$$

Fig. 2.1 General reaction equation of hydrogenation

A. Behr and A.J. Vorholt, *Homogeneous Catalysis with Renewables*,
Catalysis by Metal Complexes 39, DOI 10.1007/978-3-319-54161-7_2

- Wilkinson-type catalysts like $RhCl(PPh_3)_3$ and the corresponding ruthenium or iridium species
- Hydride species like $Rh(CO)_2(PPh_3)H$
- Chelate complexes with chiral ligands like the Binaphos (see Fig. 2.4)
- Ru-Carbene complexes
- Special pincer ligands have high activity in the hydrogenation of, for example, CO_2.

The present chapter is structured by the substrates of hydrogenation. In the first part, CO_2 as an inactive resource with carbon in a high oxidative state and with a low energy content as substrate is described. In this respect, homogeneous catalysts are able to gain valuable chemicals from this side product of burning or fermentation processes, e.g. methanol or formic acid.

The second part describes processing renewables, such as fatty acids and lignin via hydrogenation. These highly complex mixtures that contain various molecules and are oxygen rich compared to petrochemicals are defunctionalised or depolymerised via hydrogenation in order to gain more uniform blends.

2.2 Hydrogenations of Carbon Dioxide

Back in the 1980s, there were just a few research groups who dealt with the conversion of the “inactive” CO_2 [2–7]. The flashlight on carbon dioxide utilisation was set during the climate discussion and the impact of carbon dioxide to the greenhouse effect. Numerous efforts were put in the development of catalysts to process CO_2 as a chemical feedstock [8–11]. Beside this development, also photochemical and electrochemical reactions are in the statu nascendi with various materials from metal complexes, organic compounds, and transition metal electrodes [12–29]. The homogenously catalysed reduction of carbon dioxide focuses on formic acid and methanol as products. These C_1- molecules can act as hydrogen storage, as these molecules are liquid at ambient conditions. While formic acid contains 4.4 wt% of hydrogen, methanol contains 12.6 wt%. The stored hydrogen preferably originates from the electrolysis of water using solar energy from where a lot of effort is invested lately [27, 30–35]. The synthesis of formic acid [36] formate salts [37, 38] or methanol [39, 40] is entropically disfavoured, wherefore different bases are applied in the formation of formic acid (Fig. 2.2). If water is used as solvent, the carbonate/bicarbonate equilibrium also plays a role in the hydrogenations. Calculations showed that hydrogenation of the bicarbonate to formates is exergonic [41].

The formation of formic acid (FA) and formate amine salts was numerously studied in the last years. Also systems of hydrogenation and dehydrogenation with one catalyst system were developed. The following Table 2.1 gives an overview on several catalyst systems.

$$\mathrm{CO_2(g) + H_2(g) \rightleftharpoons HCO_2H(l)}$$

$$\Delta G^0 = 32.8\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^0 = -31.5\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^0 = -216\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$\mathrm{CO_2(g) + H_2(g) + NH_3(aq) \rightleftharpoons HCO_2^{-}\ (aq) + NH_4^{+}(aq)}$$

$$\Delta G^0 = -9.5\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^0 = -84.3\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^0 = -250\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$\mathrm{CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(l) + H_2O(l)}$$

$$\Delta G^0 = -9.5\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^0 = -131\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^0 = -409\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

Fig. 2.2 Gibbs energy of the hydrogenation of CO_2

First attempts to hydrogenate CO_2 were already made by Inoue in 1976 by applying triphenylphosphine with Ru-, Ir-, and Rh-complexes in benzene. The solvents applied in this hydrogenation of CO_2 play a crucial role for stabilising intermediate catalytic species. The Wilkinson complex has higher reaction rates in more polar solvents like methanol [43]. Also supercritical CO_2 itself as solvent in its state is possible, wherein also hydrogen is highly soluble [47]. The group of Jessop reported a TOF up to 95.000 h^{-1} with $RuCl_2(OAc)(PMe_3)_4$ as catalyst precursor with different amines and alcohols [48]. The role of these additives is still object of investigation, but it is reported that the formate generation needs a Lewis base, while the alcohol additive is proton donor.

The role of water in the solvent mixtures was investigated since faster reactions were reported if water was present [56]. Reactions in water were first shown in the

Table 2.1 Catalyst systems for the formation of formic acid and its salts from CO_2, for abbreviations see Figs. 2.4 and 2.5

Catalyst precursor	Solvent	Additive	*P* (H_2/CO) MPa	*T*/°C	Rct. time/h	TON	TOF/h^{-1}	References
		Phosphine ligand						
$RuH_2(PPh_3)_4$	C_6H_6	Et_3N/H_2O	2.5/2.5	rt	20	87	4	[42]
$RhCl(PPh_3)_3$	DMSO	Et_3N	2/4	25	20	2.500	125	[43]
$[Rh(cod)Cl]_2$/dppb	DMSO	Et_3N	2/2	rt	22	1.150	30–47	[44]
$RhCl(tppts)_3$	H_2O	$NHMe_2$	2/2	rt	12	3.440	290	[45, 46]
$l_2(PMe_3)_4$	$scCO_2$	Et_3N	8.5/12	50		7.200	1.040	[47]
$RuCl(OAc)\ (PMe_3)_4$	$scCO_2$	Et_3N/C_6F_5OH	7/12	50	0.33	32.000	95.000	[48]
$[RuCl_2(tppms)_2]_2$	H_2O	$NaHCO_3$	6/3.5	80	0.03		9.600	[49]
$Fe(BF_4)_2/PP_3$	MeOH	$NaHCO_3$	6/0	80	20	610	30	[50]
IrH_3(P1)	H_2O/THF	KOH	4/4	120	48	3.500.000	73.000	[51, 52]
RuH(Cl)(CO)(P3)	DMF	DBU	2/2	70	2	38.600		[53]
RuH(Cl)(CO)(P3)	DMF	DBU	3/1	120			11.00000	[54]
		Nitrogen ligand						
$[Cp^*Ir(DHPT)Cl]^+$	H_2O	KOH	3/3	120	48	222.000	(33.000)	[55]

early 1990 by Leitner with rhodium and sulfonated phosphine ligands (see Fig. 2.4), [57], and this concept was transferred to other ligands and metals [45, 49, 58–61]. TOFs of up to 9.600 h^{-1} were found with $[RuCl_2TPPMS_2]_2$. Besides, the sulfonated ligands also water-soluble amine-based ligands were used [62–65]. Beller and Laurenczy showed that if $[RuCl_2(C_6H_6)]_2$ is used also simple phosphine ligands such as TPP can form an active catalyst system in an aqueous $NaHCO_3$ solution. The ligand diphenylphosphinomethane DPPM showed TOFs of up to 1.260 h^{-1} but is fast deactivated. However, also phosphite ligands are reported [66].

The combination of ionic liquids (IL) and sulfonated ruthenium phosphine complexes was used to form a continuous operated process to gain pure formic acid under supercritical conditions (Fig. 2.3).

The optimisation of the process parameters was performed in a batch mode, especially the identification of the suitable IL. The 1-ethyl-3-methylimidazolium chloride (EMIMCl) was selected while the anion HCO_2^- showed the highest activity under continuous conditions. The extraction of the formic acid was the limiting factor of this system [67].

The group of Hicks established another concept of catalyst recycle by the immobilisation of Ir-complexes on mesoporous silica tethered surfaces. These concepts give a TON of 2800 after 20 h [68]. Laurenczy proved with the $[RuCl_2(PTA)_4]$ (see Fig. 2.4) the stability of the complex by producing FA without base under mild conditions. This system was recycled four times showing a constant activity [69].

Another step to a commercial hydrogenation of carbon dioxide is the use of non-precious metals as catalyst metal due to their lower cost. These opportunities were investigated by Beller with Co-precursors and PP_3 (see Fig. 2.4) as ligand which yield a TON of over 3.500 [70]. If very strong bases like the Verkade base are applied with 2 MPa CO_2/H_2, a TOF of 74.000 h^{-1} was achieved [71]. Also Fe complexes show activity in the hydrogenation with TONs of up to 7.500 [72].

Pincer ligands (see Fig. 2.5) are another highly promising aspect of hydrogenation of CO_2 since Nozaki reported on the trihydride iridium species with the PNP-pincer ligand (2,6-bis(diisopropylphosphinomethyl)pyridine) which showed the highest reported TOF (150.000 h^{-1}) and TON (3.5 mio after 48 h) at a temperature of 200 °C and 8 MPa in THF/water [51, 52]. In the following, also, other air-stable pincer ligands with lower activities were reported [73] and pincer ligands

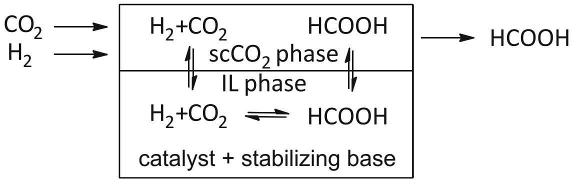


Fig. 2.3 Continuous-flow hydrogenation of CO_2 to formic acid based on a biphasic reaction system

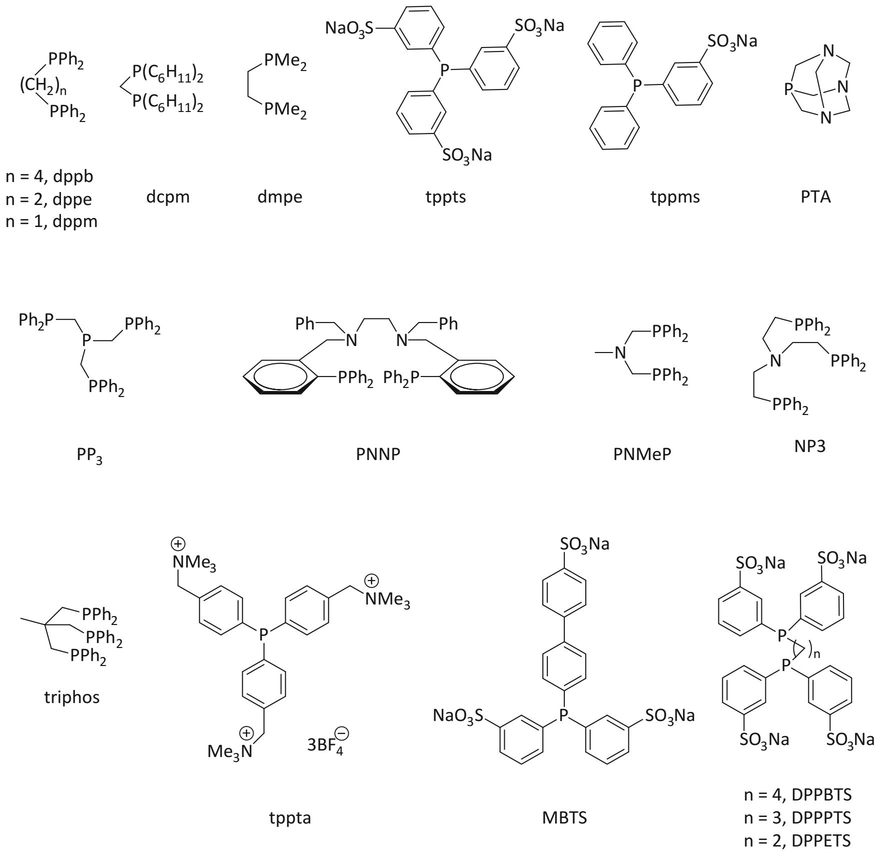


Fig. 2.4 Active phosphine ligands in the hydrogenation of CO_2

which use Fe as a catalyst metal [74]. Pidko reported on a Ru-based pincer catalyst which increases the TOF to 1.100.000 h^{-1} in a DMF/DBU system [54].

Like in other filed of homogeneous catalysis, N-heterocyclic carbenes were applied also in this field. The electron-donating ligands [75] showed with iridium TONs of up to 190.000 at 200 °C and 6 MPa in 75 h [76, 77].

Only a few examples of N,N- or N,C-Ligands were reported so far [78–80]. These complexes are highly pH sensitive in respect of activity and solubility. The iridium-4DHBP catalyst complex [Cp*Ir-(4DHBP)Cl]Cl can be attributed to TOF of 42,000 h^{-1} and TON of 190,000 at 120 °C and 6 MPa. Noteworthy is activity of the catalyst at ambient temperature and pressure with the TOF of 7 h^{-1}. The pH switch can also be used as a trigger to precipitate such catalyst complexes in order to recycle them [81, 82]. While $[Cp^*Ir(4DHBP)(OH_2)]^{2+}$ is still soluble in the water phase (1 ppm) even at optimised pH conditions, $[Cp^*Ir(DHPT)(Cl)]^+$ has a very low solubility in the product mixture of acidic FA/formate solution in a pH range of 4–7 (lowest concentration at pH 5 with 100 ppb). The filtration of the catalyst had

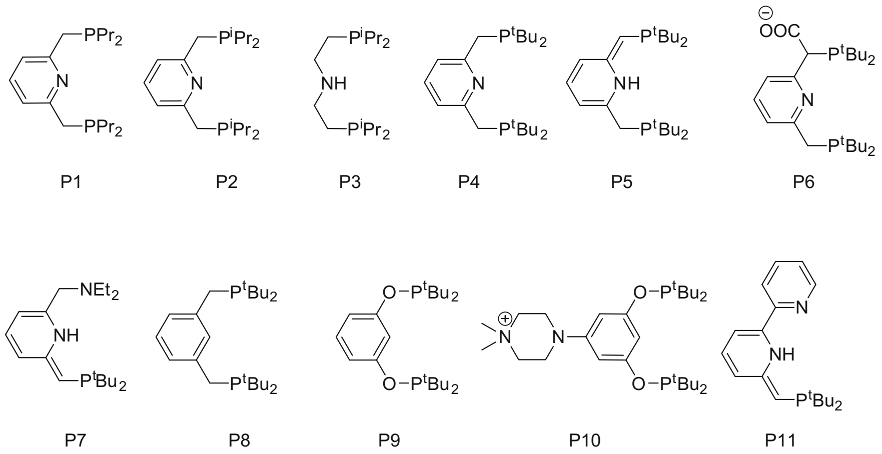


Fig. 2.5 Hydrogenation active pincer ligands

an efficiency of 91% after three runs, and the activity was retained over these recycling runs [55].

2.2.1 Interconversion of CO_2/Formic Acid as Hydrogen Storage

In order to use the hydrogenation of CO_2 as liquid hydrogen storage not only the reaction to formic acid (FA) is important, but also the dehydrogenation of FA plays an important role [83, 84]. The concept of interconversion with one catalyst system was first realised by Leitner who used a Rh/DPPB catalyst system in a FA/NEt_3/acetone mixture in order to gain a hydrogenation TOF of 54 h^{-1} and a dehydrogenation TOF of 40 h^{-1} [85]. The very effective NPN Pincer iridium catalyst system for the hydrogenation is not active in the dehydrogenation [52]. If other additives like triethanolamine or NaOH are used, TOFs of up to 1.000 h^{-1} were observed for the dehydrogenation (Fig. 2.6).

The systems can be switched from hydrogenation to dehydrogenation by temperature and pressure [86, 87] or pH value [88]. Olah and co-workers presented a temperature controlled reversible hydrogen storage system in which a Ru pincer complex catalysed the hydrogenation of CO_2 in a water/THF system at 70–85 °C and 4–8 MPa. The dehydrogenation is executed at 69 °C with the same catalyst complex. The recovery of the formed FA was completed after 4.5 h with 90% yield and could be repeated for six times with a total TON of 11.500.

The pH-controlled system is using the circumstance that at high pH values the hydrogenation is favoured while at low pH the dehydrogenation is faster (Fig. 2.7). This behaviour was shown with the $[(Cp^*IrCl)_2(THBPM)]^{2+}$ complex which is

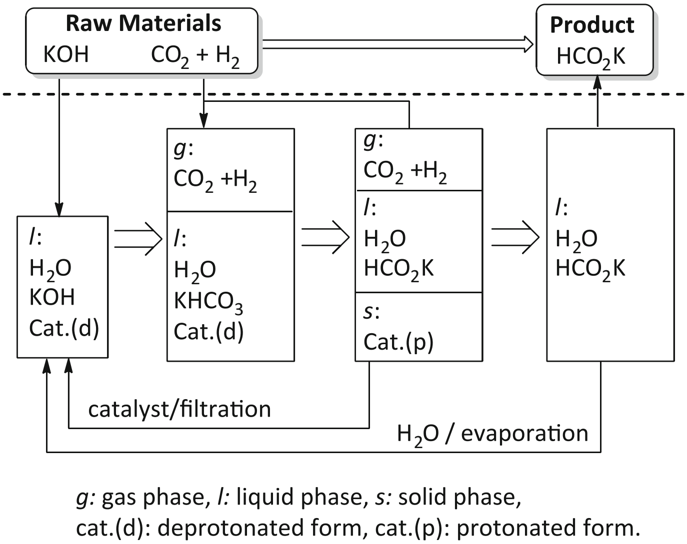


Fig. 2.6 Recycling system for the conversion of CO_2/H_2 into HCO_2K using $[Cp^*Ir(DHPT)(Cl)]^+$ in aqueous KOH solution

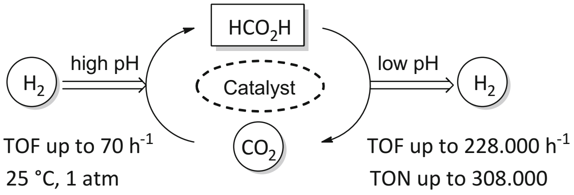


Fig. 2.7 pH-controlled hydrogen storage

active at ambient conditions with a TOF of 70 h^{-1} towards the FA and a TOF for the dehydrogenation of 228.000 h^{-1} at 90 °C and low pH value. This cycle was repeated twice by adding acid or base to the system, respectively.

2.2.2 Methanol

The hydrogenation of formic acid, urea, or CO_2 can also be used to yield methanol in a more sustainable fashion in comparison with the route via syngas, which is gained from the partial oxidation of naphtha or steam reforming of methane. The

$$3HCO_2H(aq) \rightarrow CH_3OH(aq) + H_2O(aq) + 2CO_2(g)$$

$$\Delta G^0_{298} = -23.5 \text{ kcal mol}^{-1}$$

Fig. 2.8 Disproportionation of formic acid to methanol

examples to use homogeneous catalysis in this case are rare, but these examples are qualified by high efficiency.

For urea derivatives, organic carbonates, carbamates, and formates as products from carbon dioxide, Milstein showed that a PNN-Ru(II) pincer complexes [Ru(P7)(H)-(CO)] and [Ru(P11)(H)(CO)] produce methanol under mild conditions [89]. The high TON of 4.400 for the substrate dimethyl carbonate at 5 MPa, H_2 at 110 °C, is a promising example on the indirect hydrogenation [89].

The use of the above-described FA route in combination with the followed disproportionation of FA yields methanol [90] (Fig. 2.8). After the first investigation with iridium catalysts [90], Cantat reported a significantly improved precursor [Ru(cod)(methylallyl)$_2$], with triphos ($CH_3C(CH_2PPh_2)_3$) as ligand and MSA (methanesulfonic acid) as catalytic system [91].

The direct hydrogenation of CO_2 without any intermediates is also part of the efforts of the academic community. At first, a tandem reaction was designed consisting of three steps: hydrogenation of CO_2 to FA (a); esterification to the formate ester (b); hydrogenation of the formate ester to methanol (c) [92]. The total TON for the whole cascade reaction was 2.5 in respect of methanol in a one-pot reaction (Fig. 2.9).

The direct hydrogenation of CO_2 was initially shown by the Leitner group while the hydrogenation to methanol is conducted within one catalytic cycle (Fig. 2.10).

The ligand triphos is the game-changer in this synthesis and in cooperation with the additives gives a TON for the ruthenium complex of 603. The activity of this catalyst system is comparable to the heterogeneous catalyst systems.

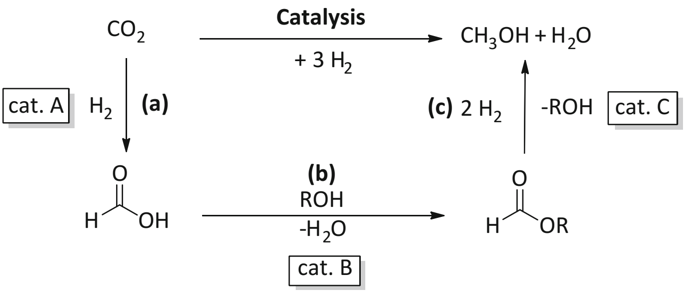


Fig. 2.9 Three-step tandem catalysis

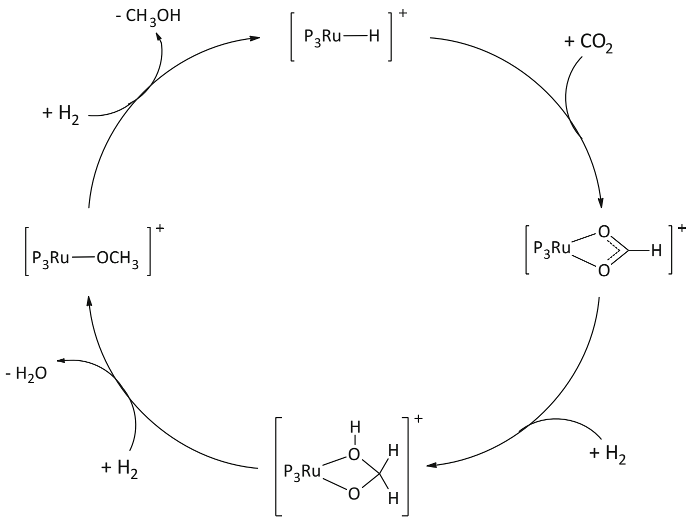


Fig. 2.10 MeOH production from direct catalytic hydrogenation of CO_2 and proposed mechanism

2.3 Lignin

As lignin is a complex three-dimensional amorphous polymer that consists of methoxylated phenylpropanoids (see Chap. 1.3.4), it is a hard task to generate valuable chemical products or products blends [93]. Since lignin is the only widespread renewable with aromatic moieties, several approaches were made to depolymerise lignin as alternative to the petrochemically produced aromatics [94, 95]. Hydrotreating is one possibility to produce chemicals with low molecular weight from lignin. These processes are also named hydrodeoxygenation, hydrogenation, and hydrogenolysis depending on the molecular structure to be cleaved. The monomers from lignin are usually linked by ether or by C–C bonds. The majority of almost two-thirds or more are ether bonds. The review of Zhang beautifully shows differences of the linkages (Fig. 2.11) [96].

The big challenge in the valorisation of lignin is the different linkages of the polymeric structure and the big variety of the compositions of lignin depending on plant type, part of the plant, etc. [97, 98].

The homogeneous-based systems for hydrogenation of lignin compounds are relatively rare in comparison with the heterogeneous catalyst systems [99]. Table 2.2 shows recent examples of homogeneous catalysts with model substrates. Only few catalyst systems are ready to work with processed lignin from, e.g., the Kraft process.

Hu hydrogenated lignin model compounds such as 4-propylphenol, eugenol, 1,2-dimethoxy-4-propylbenzene, and 2,6-dimethoxy-4-propylphenol at 298 K with a di-μ-chlorobis(η^4-1,5-hexadiene)-dirhodium(I) complex. In a solvent system of hexane/water, mostly double bond and the aromatic rings were hydrogenated. This

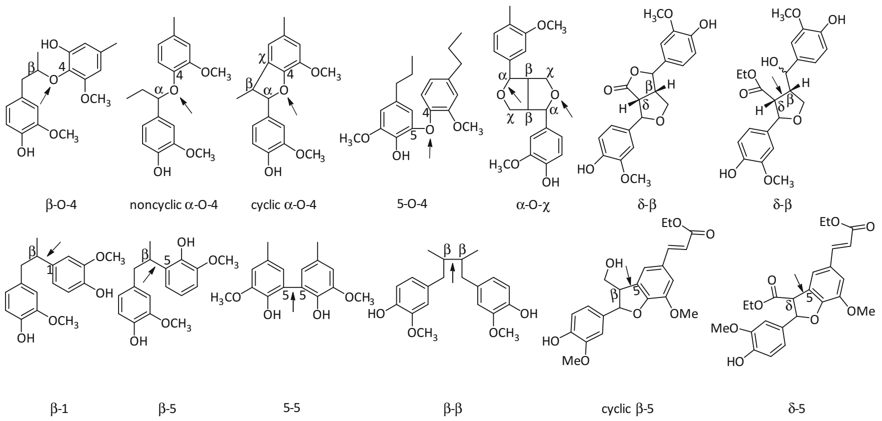


Fig. 2.11 Typical linkages between the primary units of lignin

reactivity is not beneficial due to the point that no cleavage has occurred and hydrogen has been consumed. Further examples used other model substrates, such as phenol, anisole, and anthracene [102–105, 108, 109].

The group of Nagy used besides Raney Ni, Pt/C, and $NaBH_4/I_2$ also the homogeneous hydrogenation catalyst $Ru(PPh_3)_3Cl_2$ in the hydrogenation of organosolv lignin in order to significantly reduce the molecular weight of the lignin. This catalyst was able to cleave 4-O-5- and aryl-O-aliphatic linkages to decrease oxygen content in the product mixture [106].

Nickel complexes with a N-heterocyclic carbene (SIPr·HCl) and NaOtBu as an additive are also active in the hydrogenolysis of diaryl ethers [107]. At 0.1 MPa, H_2 yields of 54–99% for the corresponding phenols and arenes were reported by Hartwig. The cleavage activity for aromatic C–O bonds of this system is in the order of $Ar–OAr \gg Ar–OMe > ArCH_2–OMe$. Comparable heterogeneous Ni catalyst showed different selectivities to the diol instead of the phenol (Fig. 2.12) [110].

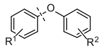
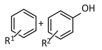
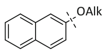
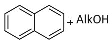
The group of Marks developed a nice way to process aliphatic ethers or furans with a tandem strategy of homogenous and heterogeneous catalysis. The homogeneous catalyst is a transition metal triflate that decyclises the C–O bond in the furan while the supported Pd nanoparticle catalyst hydrogenates the resulting double bond. This reaction is conducted in a stabilising IL and yields linear alcohols with no loss of any aromaticity (Fig. 2.13) [111, 112].

These reactivities are dedicated to cleave β-O-4 ethanol aryl ethers and do not affect the aromatic rings in the substrates [113, 114]. Popular catalyst systems are $Ru(Cl)_2(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$, and Ru-Xantphos, as shown in Fig. 2.14.

A new reactivity was lately shown by Leitner by addressing the C–C Bond in β-O-4-linked molecules. The Ru triphos complex showed again, as already shown in the CO_2 hydrogenation, a unique reactivity (Fig. 2.15) [115].

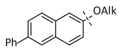
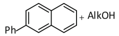
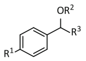
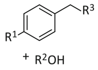
Different substrates were applied with high selectivities for the cleavage of the C-C bonds. These developments show the possibility to address several linkages in lignin by homogeneous catalysis.

Table 2.2 Homogeneous catalytic systems for the hydrogenation of lignin and their corresponding model substrates

	Reaction conditions							
Catalyst	T (K)	P (MPa)	t (min)/solvent	Substrate	Products	Conv. (%)	Notes	References
(1,5-hexadiene) RhCl dimer[a]	[f]	0.1	[g]	Phenol	cyclohexanol	[g]		[100]
Colloidal rhodium	[f]	5	[g]	Methylanisole	Methylcycohexane, 1-methyl-2-methoxycyclohexane[h] Mmethylcyclo-hexanone	100		[101]
[(1,5-C_6H_{10}) $RhCl]_2$[b]	[f]	0.1	3000	2-methoxy-4-propylphenol	*cis*-2-methoxy-*cis*-4-propylcyclohexanol, *cis*-2-methoxy-*trans*-4-propylcyclohexanol	100		[102]
Oxo-trirhodium (III)acetate[c]	313	0.1	[g]	Anthracene	1,2,3,4-tetrahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene	[g]	[i]	[103]
$[(C_6H_6)_4Ru_4H_4]Cl_2$[d]	363	6	14	Acetophenone	Methylcyclohexylketone, Phenylethanol, Cyclohexylethanol	64		[104]
$[(C_6H_6)_4Ru_4H_4]Cl_2$[d]	363	6	14	Anisole	Methoxycyclohexane	22		[104]
Rhodium nanoparticles[e]	348	4	600	4-methoxyphenol	4-methoxy-cyclohexanol, 1-methoxy-4-cyclohexenol	21		[105]
$RuCl_2(PPh_3)_3$	[f]	5	[g]	Ethanol organosolv lignin	Lower Mw lignin	[g]	[j]	[106]
$Ni(COD)_2$, SIPr• HCl	120	0.1	*m*-Xylene			>85	R=H, Me, *m*-OMe, CF_3	[107]
$Ni(COD)_2$, SIPr• HCl	120	0.1	*m*-Xylene			100	Alk=Hexyl, Me	[107]

(continued)

Table 2.2 (continued)

	Reaction conditions							
Catalyst	*T* (K)	*P* (MPa)	*t* (min)/solvent	Substrate	Products	Conv. (%)	Notes	References
Ni(COD)$_2$, SIPr• HCl	120	0.1	*m*-Xylene			85	Alk=Hexyl	[107]
Ni(COD)$_2$, SIPr• HCl	120	0.1	*m*-Xylene			>85	R^1=^{t}Bu, H; R^2=Ph, Me; R^3=H, Et	[107]

[a]With phase transfer catalyst. [b]With Bu_4NHSO_4 phase transfer agent. [c]Active after reduction with H_2. [d]Biphasic conditions. [e]In ionic liquids. [f]Room temperature. [g]Not specified. [h]Two isomers. [i]Extremely air sensitive. [j]More hydroxyl groups. SIPr*HCl = 1,3-Bis(2,6-diisopropylphenyl)imidazolidinium chloride

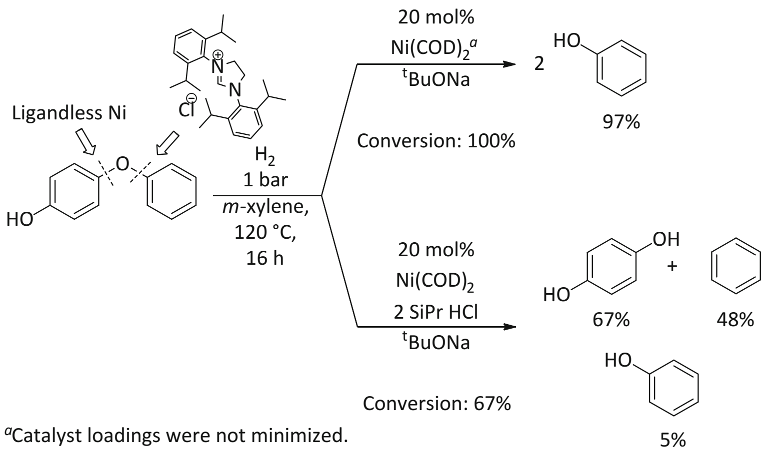


Fig. 2.12 Selectivities in nickel-catalysed hydrogenation

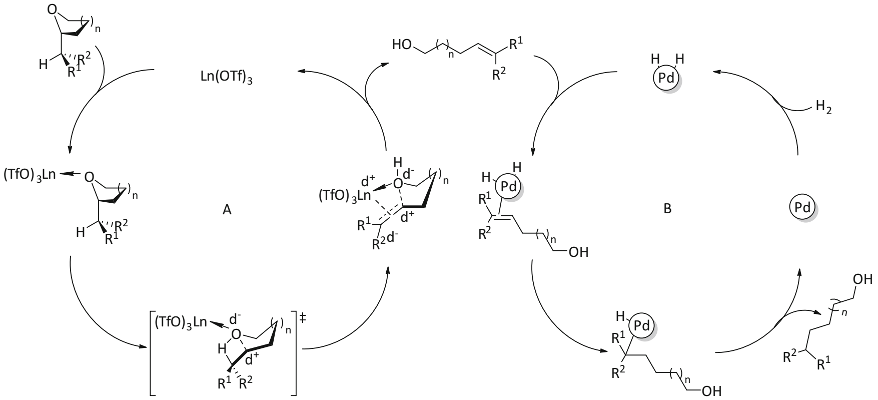


Fig. 2.13 Proposed tandem pathway for lanthanide triflate/Pd nanoparticle-mediated etheric C–O bond hydrogenolysis

2.4 Sugars

The conversion of cellulose, starch, or the corresponding oligo- and mono-sugars by hydrogenation with homogeneous catalysts is rarely reported. Hydrogenation of carbohydrates can be divided into the conversion of polymers into degraded products or monomers and further processed derivatives like HMF. The depolymerisation of cellulose is acid catalysed hydrogenolysis to fermentable sugars [116]. For the conversion of mono-sugars such as glucose in big scale processes to yield, e.g. the sweetener sorbitol, heterogeneous catalyst are used.

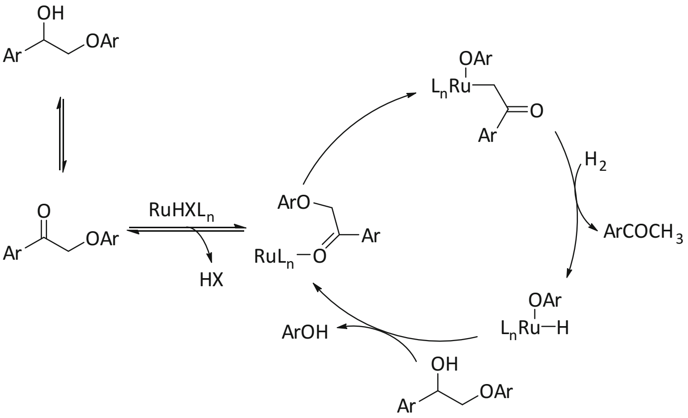


Fig. 2.14 Mechanism of Ru-catalysed C–O-bond cleavage of lignin-related polymers

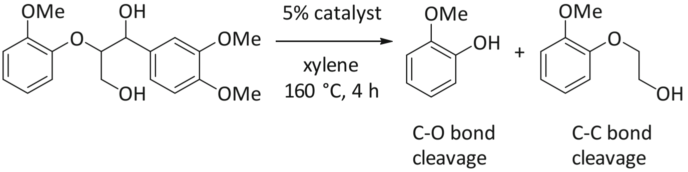


Fig. 2.15 Hydrogenation of lignin surrogate by Ru triphos

An example using homogeneous catalysis for depolymerisation was shown by Jiang to yield alcohols by applying 80–120 bar hydrogen with nickel salts. The intermediates glucose and xylose were hydrogenated in one pot to sorbitol and xylitol in yields up to 87.9% [117] (Fig. 2.16).

Furthermore, homogeneous reactions with platform intermediates from sugar are reported, as like HMF [118] to caprolactam. Also fragrances and pharmaceuticals can be synthesised incorporating homogenous catalysis [119].

2.5 Fats

The hydrogenation of unsaturated fats and oils is a well-established process in oleo chemistry and is called “hardening”. This process is used in the nutrition industry for producing margarine. Liquid unsaturated oils are converted into their corresponding saturated fats. The common catalyst for this process is Raney nickel, while some processes also use palladium particles [1]. A more challenging transformation is the selective conversion of polyunsaturated fatty acids into mono-unsaturated compounds (Fig. 2.17).

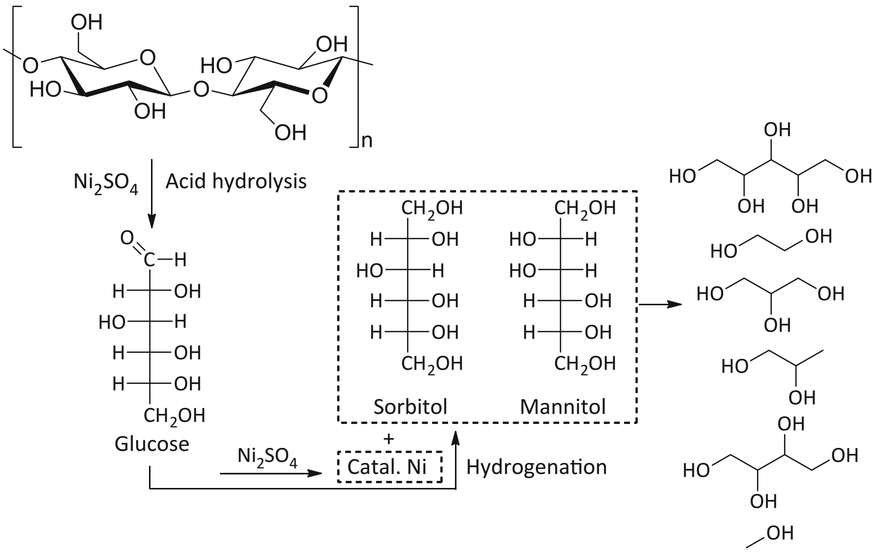


Fig. 2.16 Hydrogenation of cellulose to corresponding degradation products

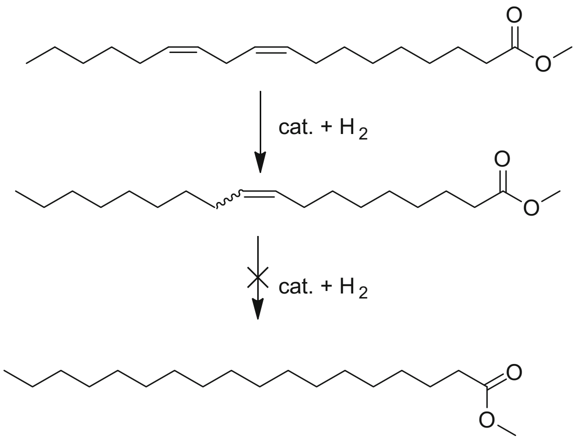


Fig. 2.17 Selective hydrogenation of methyl linoleate to C18:1—acid methyl ester

These reactions are catalysed by palladium carbonyls, platinum-tin systems, iron, and cobalt or nickel salts, which are activated by triethylaluminium [120–123]. Good results are observed with precious metal phosphine catalyst, for example, Wilkinson's catalyst [124]. High conversions of linoleic esters can be easily obtained with a palladium nanocatalyst. The catalytically active nanoparticles (diameter: 4 nm) are obtained by reducing palladium dichloride with hydrogen in DMF or propylene carbonate and an aqueous buffer. Sunflower oil with a linoleic acid content of 70% is converted into 92% oleic acid with no detectable content of linoleic acid. These palladium nanoparticles are also suitable for recycling using a liquid/liquid technique [125–127].

2.6 Conclusions

In conclusion, the hydrogenation of renewables with homogeneous catalyst addresses several points for future greener chemistry. The upgrade of raw renewable polymers such as lignin or sugars is of high importance to use more of these good available feedstocks. Furthermore also defined high value molecules can be yielded by hydrogenation of the renewables. Specially, the hydrogenation of CO_2 will gain more importance in the future as possible energy storage or as starting point for C_1-building blocks.

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