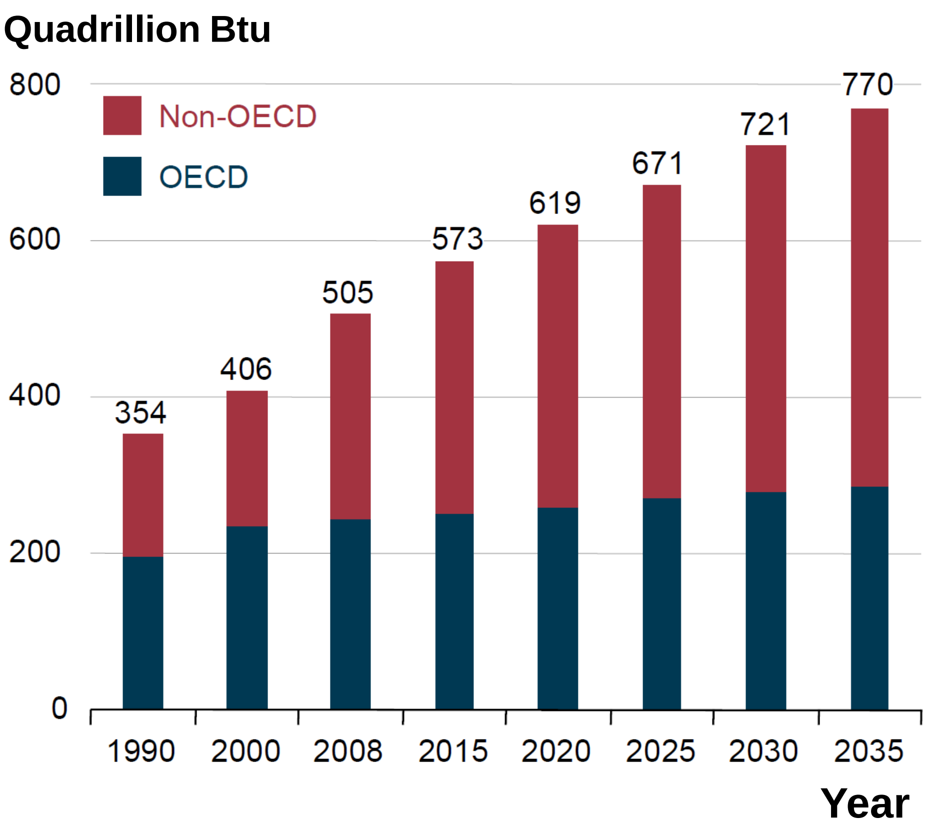
Lignocellulose Conversion toward
Green and Sustainable Society

2013/7/29 M2 Seki

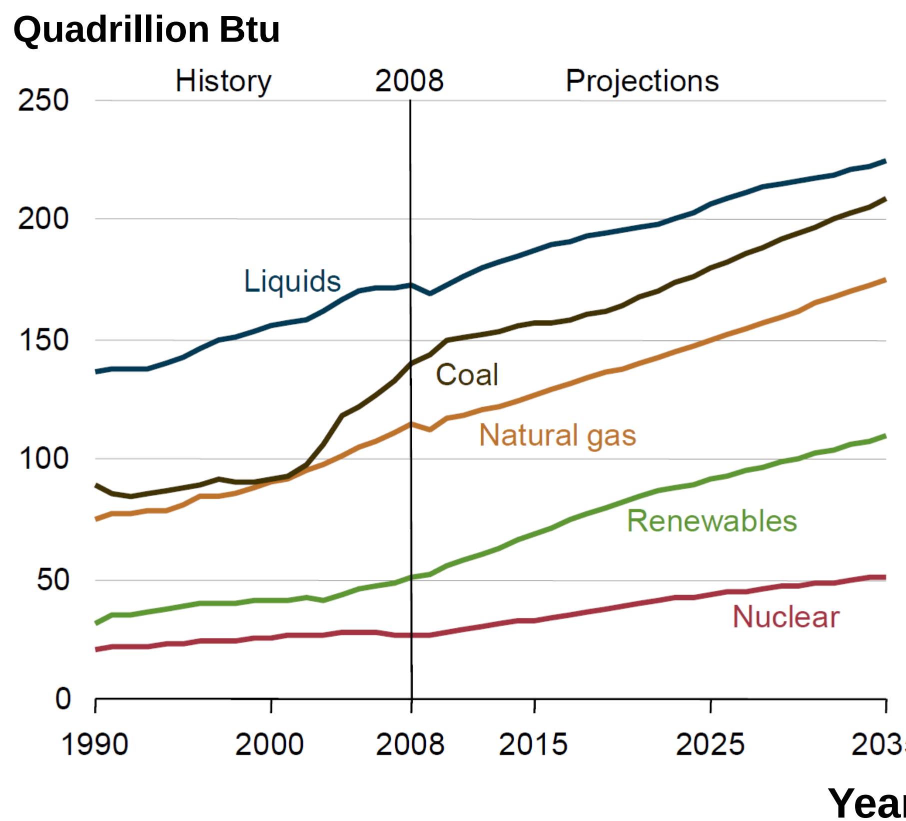
Contents

Contents

1-1. Energy demand

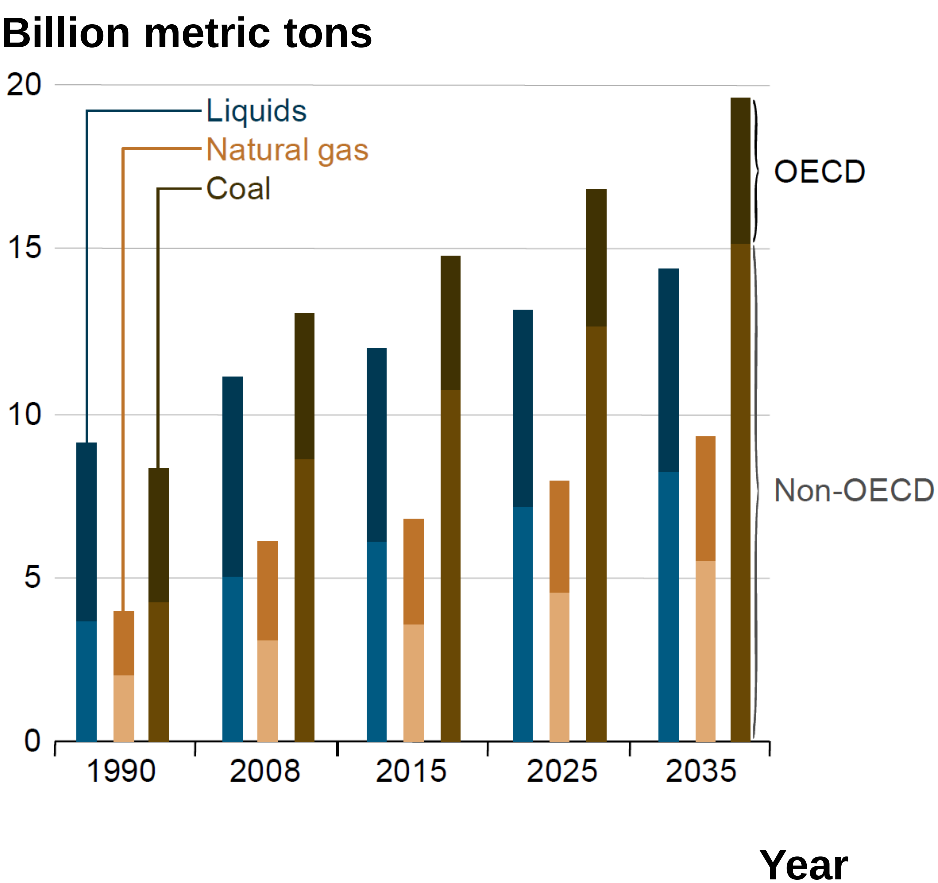


World energy consumption

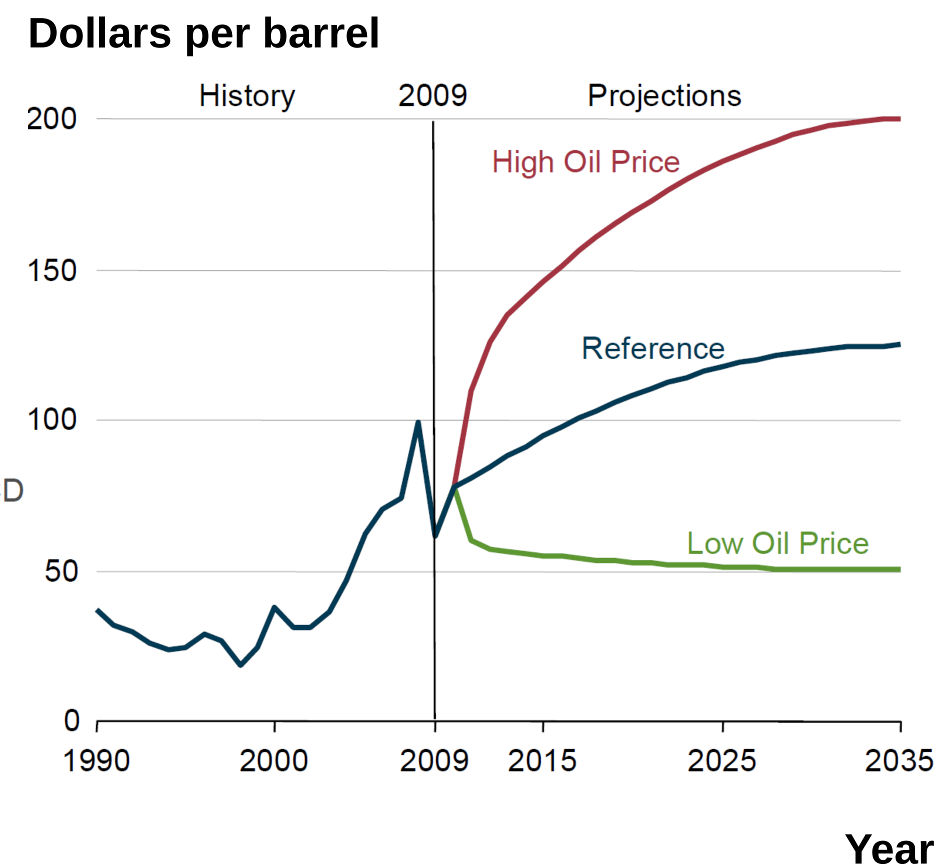


World energy consumption by fuel

1-2. Energy-related effects



World CO_2 emissions



World oil prices

1-3. Our task

Now there are sufficient amounts of oil reservoirs to satisfy our current needs even if the utilization of oil is on the verge of becoming uneconomical.

However…

We must think about how to develop new resources/methods to replace the current resources or at least to compensate its consumption in some percentage toward green and sustainable society.

1-4. Resources

Renewable energy

- Wind
- Hydro
- Solar energy
- Geothermal energy
- Biomass

1-5. Biomass

Biomass = Bio(Living thing) + Mass(Amount)

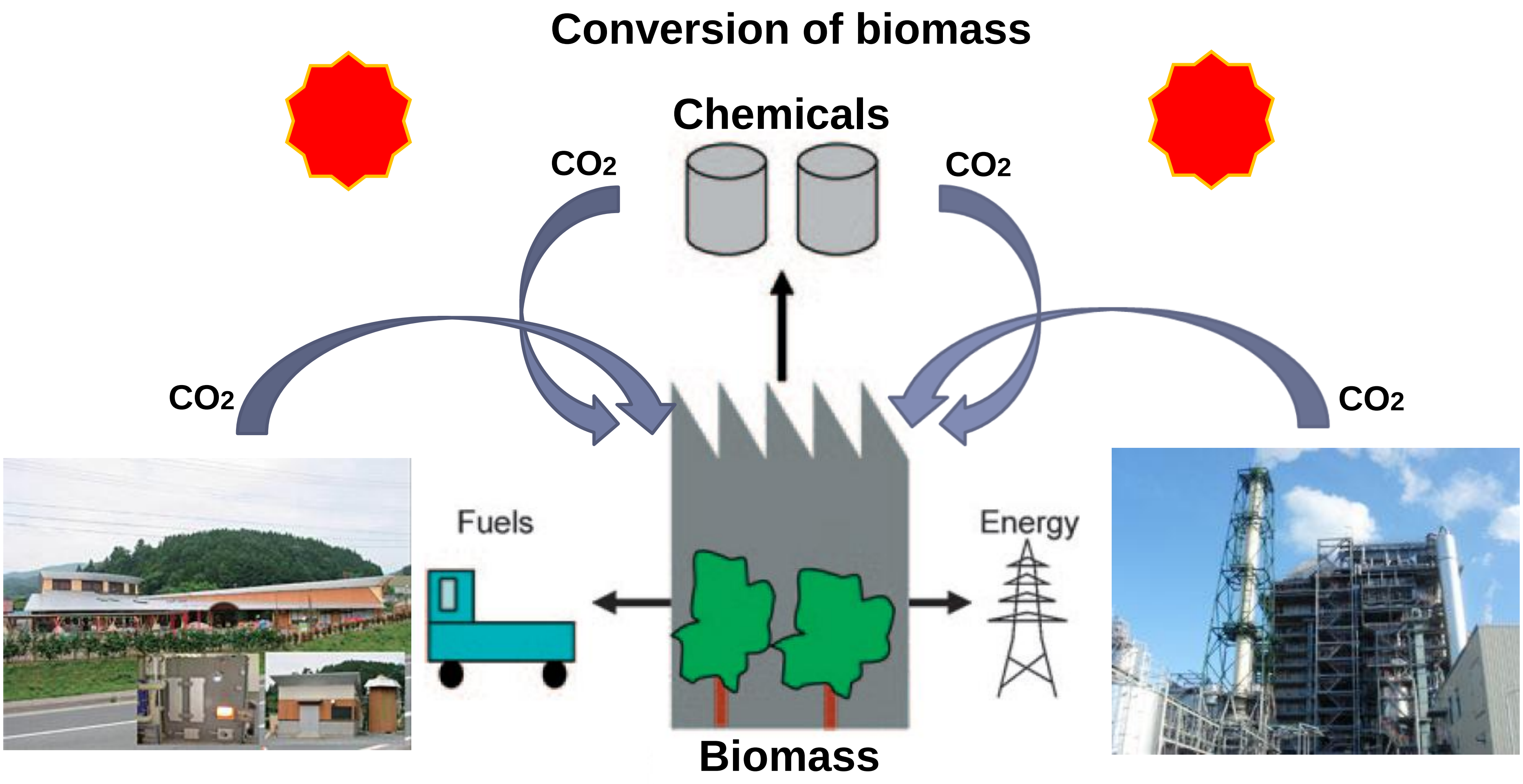
Biomass = Biological materials derived from living, or recently living organisms.

Waste biomass

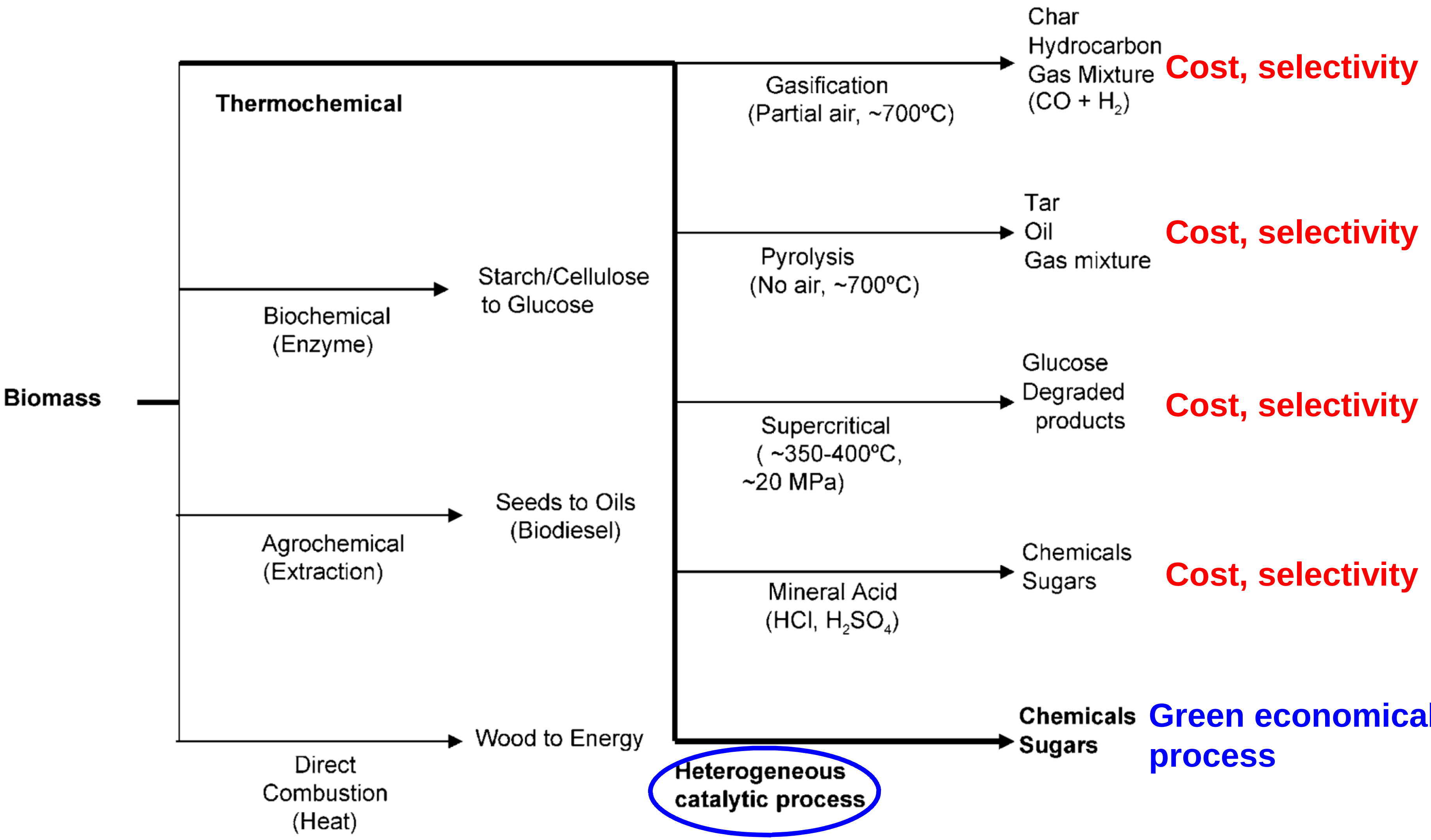
Unused biomass

Resource crops

1-6. Biorefinery



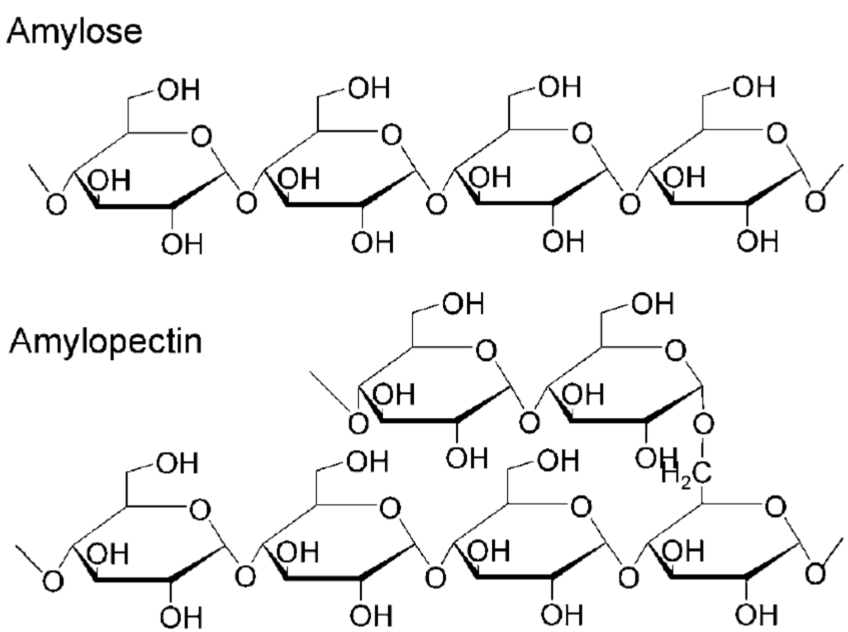
1-7. Conversion of biomass



1-8. Plant-derived biomass

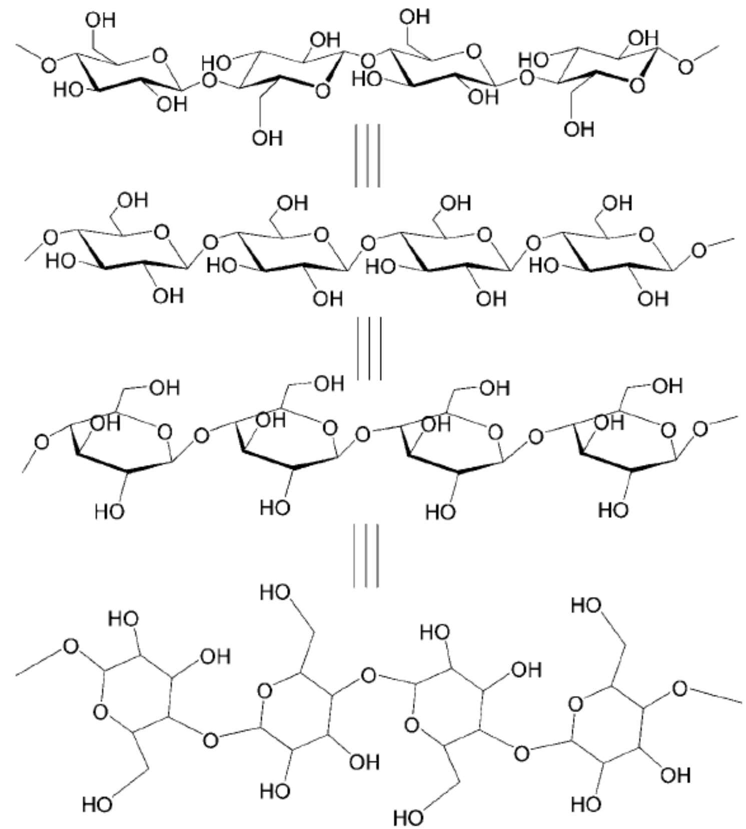
Plants produce carbohydrates such as starch, cellulose, hemicellulose, lignin.

Structure of starch molecules



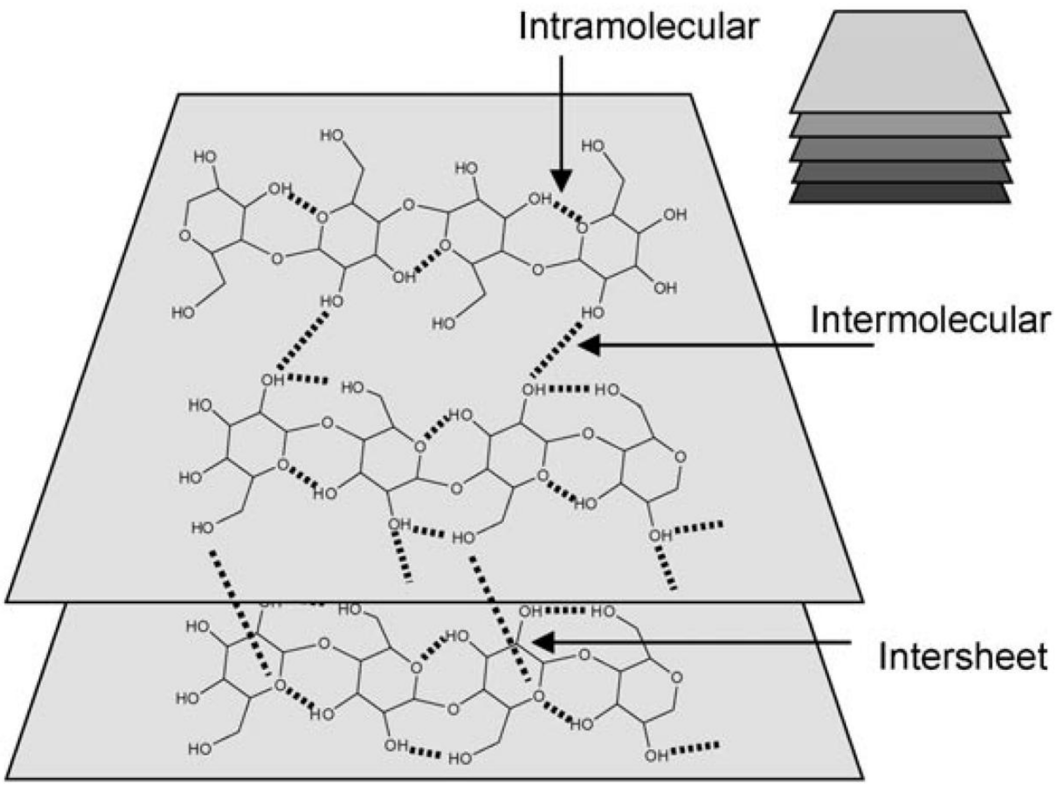
α-1,4 or α-1,6 linkages, constituent of food materials

Structure of cellulose molecules



β-1,4 linkages, constituent of wood

1-9. Plant-derived biomass



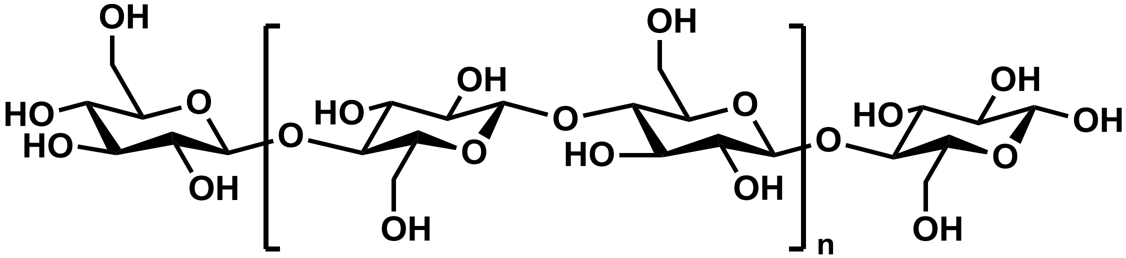
Characterization tools such as

X-ray diffraction (XRD),
NMR spectroscopy

are generally used to check the crystallinity of cellulose.

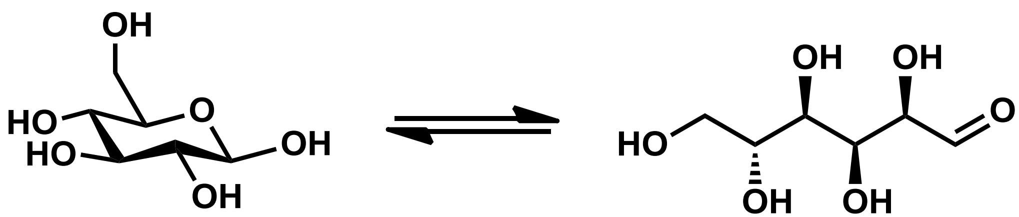
Hydrogen bonding in cellulose

1-10. Conversion of cellulose



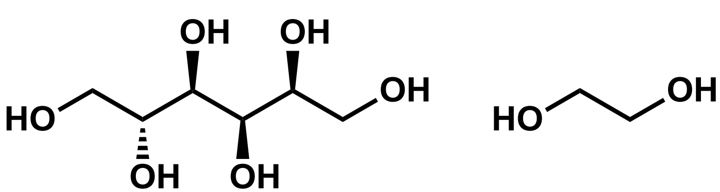
Cellulose

Hydrolysis Chapter 2



Glucose
Chemicals, fuels, foods, medicine

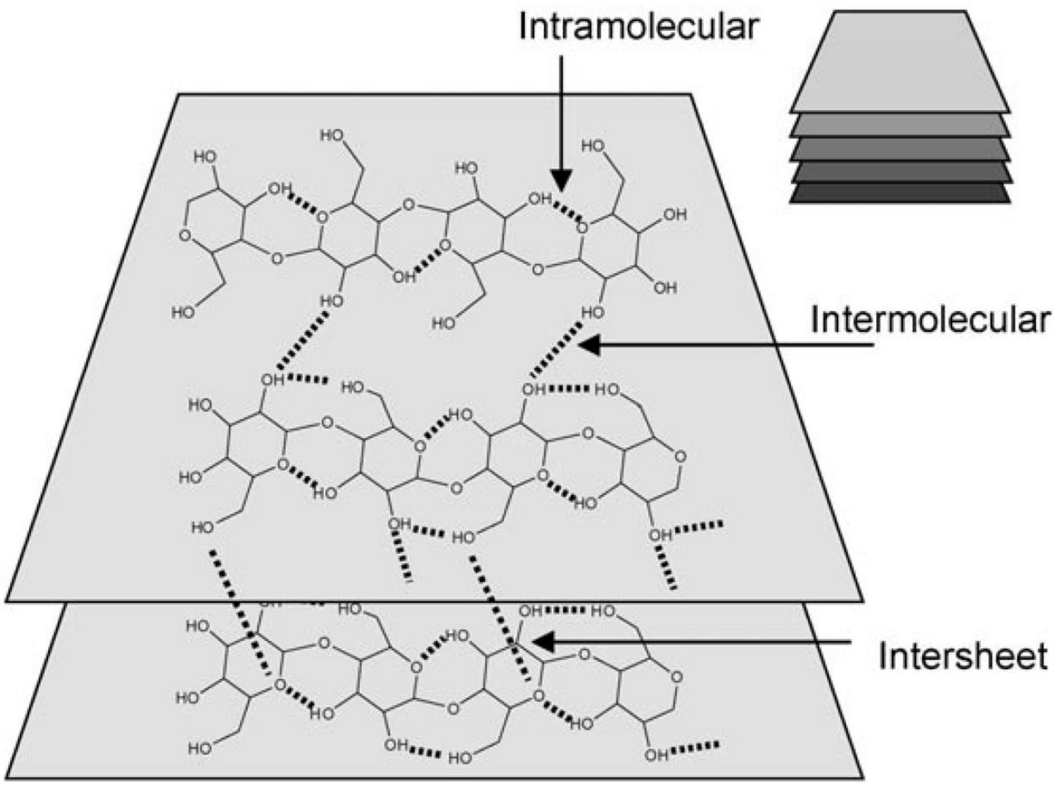
Hydrocracking Chapter 3



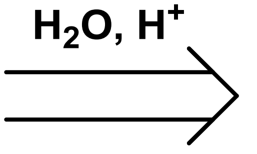
Sorbitol, Ethylene glycol
Chemicals, fuels, medicine, PET

Contents

2-0. Hydrolysis of cellulose

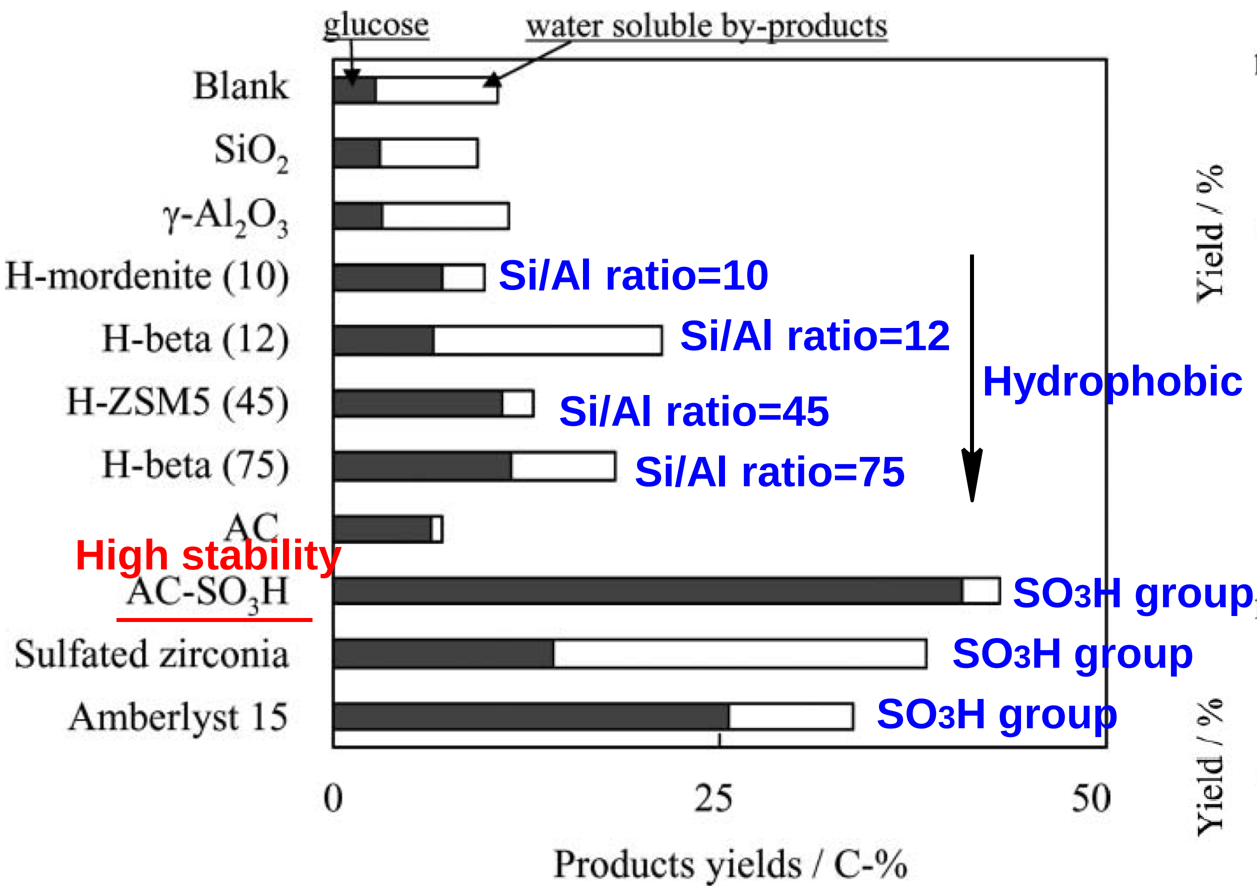


Hydrogen bonding in cellulose

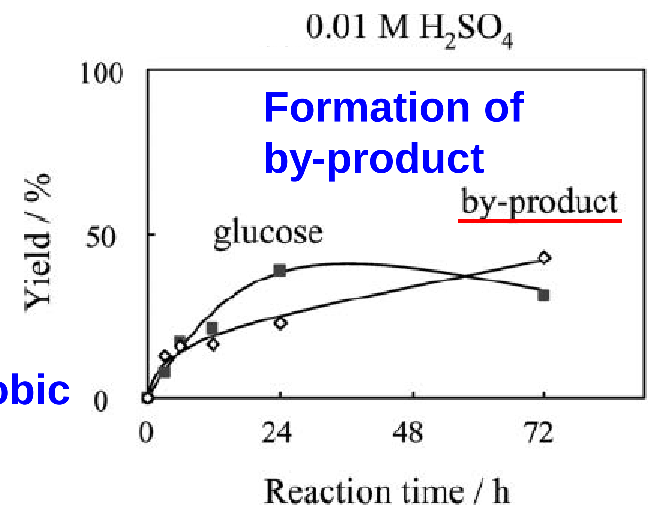


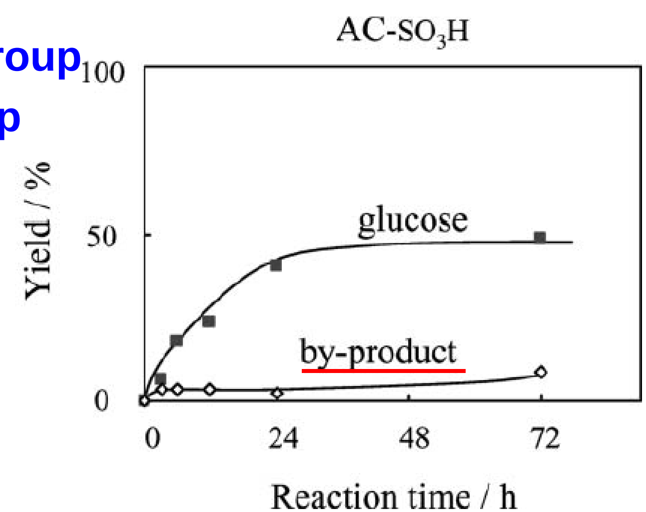
Glucose

2-1. Hydrolysis of cellulose with solid acids



Cellulose hydrolysis over various solid acid catalysts at 423 K. Reaction conditions: milled cellulose 45 mg, catalyst 50 mg, distilled water 5.0 mL, 24 h.

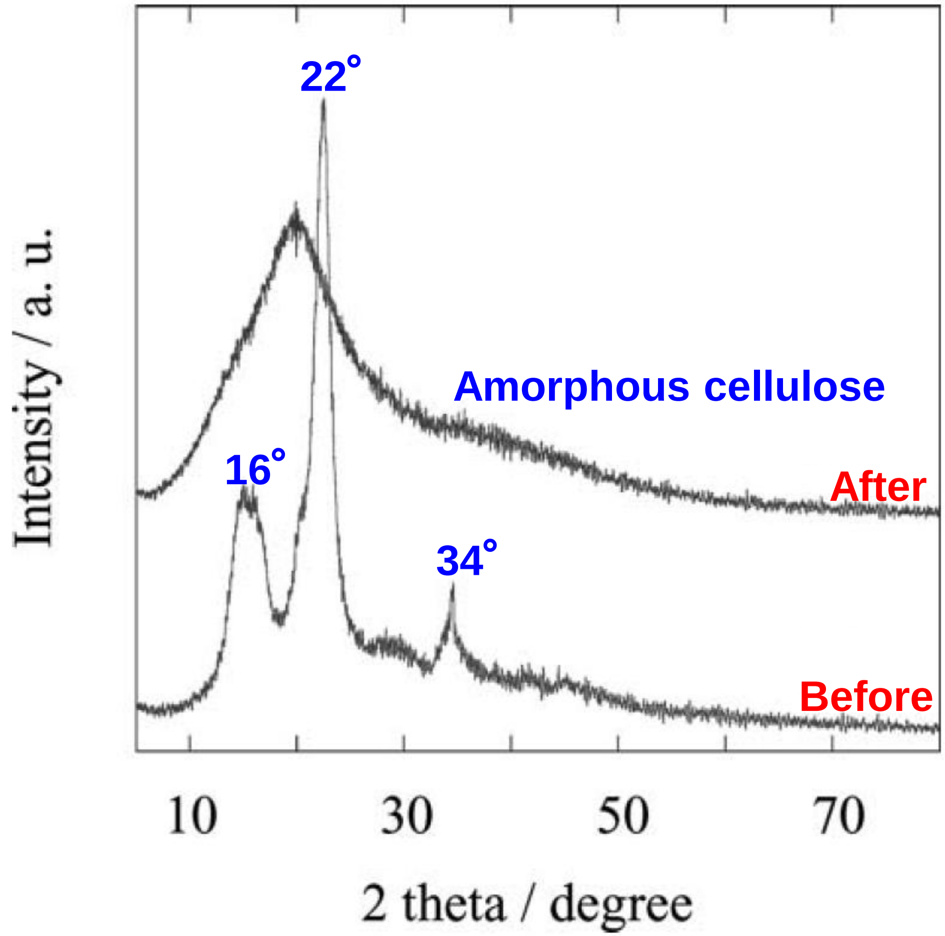




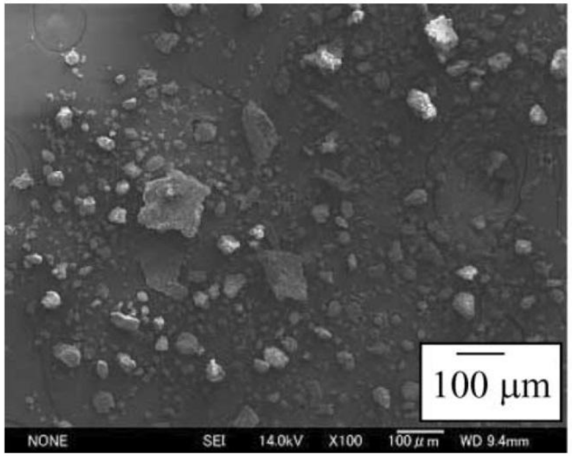
K. Yanagisawa et al. *Green Chem.* **2008**, *10*, 1033.

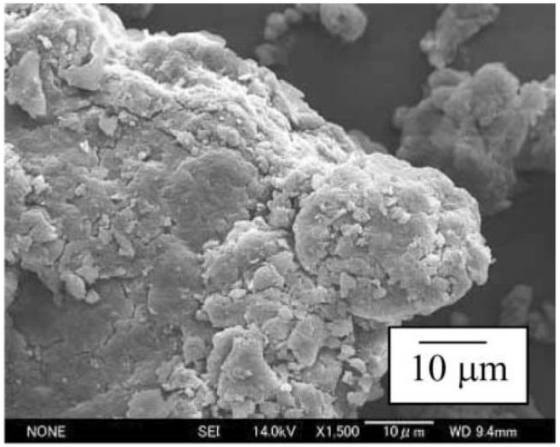
2-1. Hydrolysis of cellulose with solid acids

Ball-milling of cellulose



XRD pattern





SEM image

K. Yanagisawa et al. *Green Chem.* **2008**, *10*, 1033.

2-2. Hydrolysis of cellulose with amorphous carbon

Hydrolysis of Crystalline Cellulose by Various Acid Catalysts[a]

catalyst	functional groups	density mmolg^{-1}	maximum acidity H_0	surface area $m^2\ g^{-1}$	yields of hydrolysis products
H_2SO_4		20.4	−11	—	glucose: 10% β-1,4 glucan: 38%
niobic acid	acidic OH	0.4	−5.6	90	—
H-mordenite	acidic OH	1.4	−5.6	480	—
Nafion	SO_3H	0.9	−11 to −13	<1	—
Amberlyst-15	SO_3H	4.8	−2.2	50	—
carbon material ($CH_{0.62}O_{0.54}S_{0.05}$)	SO_3H	1.9	−8 to −11	2	glucose: 4%
High stability	COOH	0.4	—		β-1,4 glucan: 64%
	phenolic OH	2.0	—		

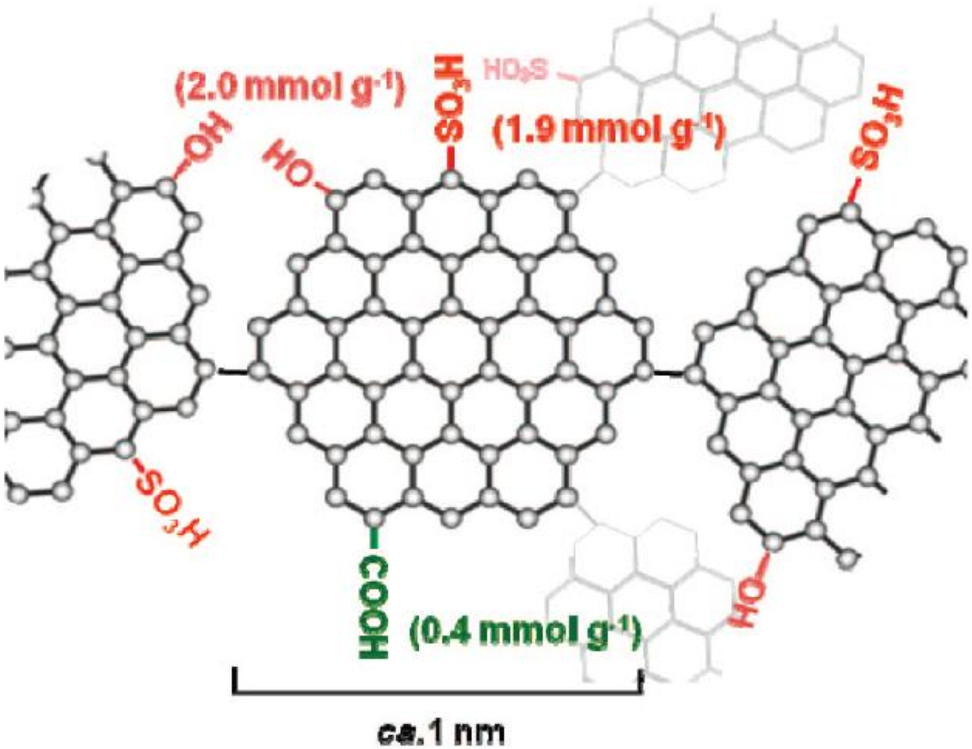
[a] Catalyst, 0.3 g; cellulose, 25 mg; water, 0.7 g; reaction time, 3 h.

Amorphous carbon gave high activity.

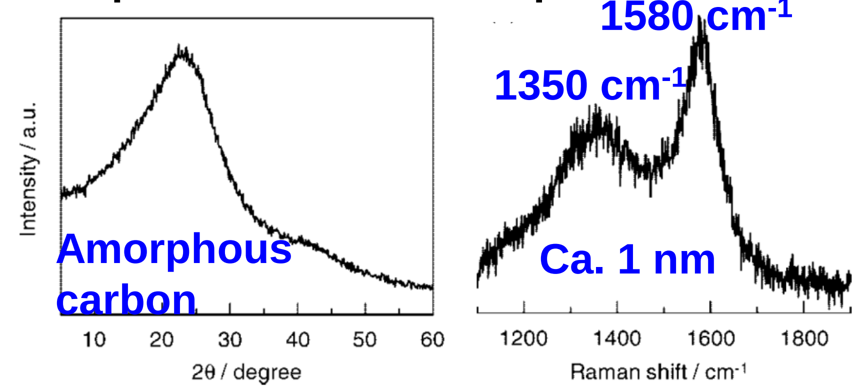
M. Hara et al. *J. Am. Chem. Soc.* **2008**, *130*, 12787.

2-2. Hydrolysis of cellulose with amorphous carbon

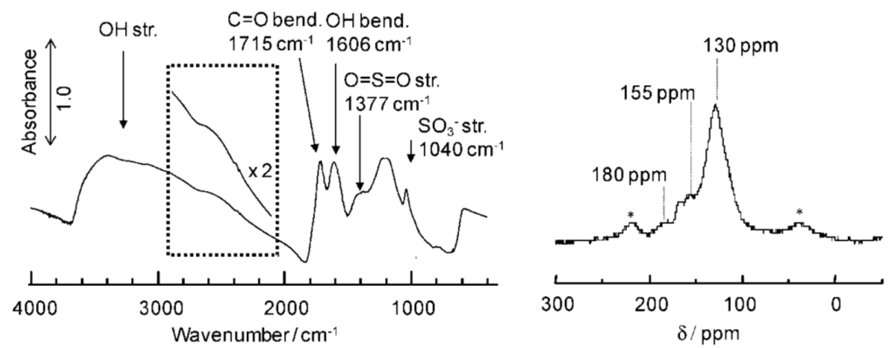
Amorphous carbon



XRD pattern and Raman spectrum



FTIR spectrum and ¹³C MAS NMR spectrum



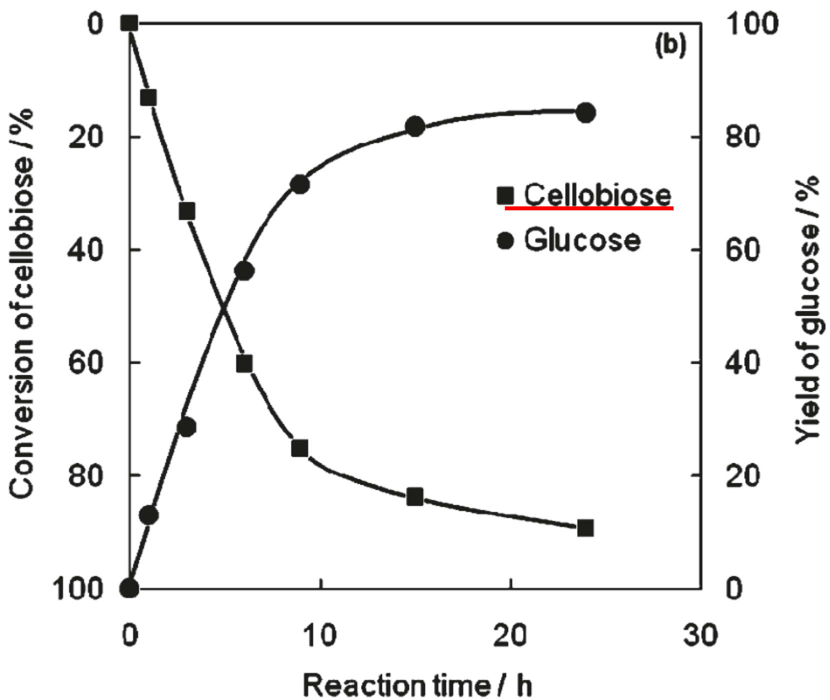
SO_3H group, polycyclic aromatic carbon atoms, phenolic OH, COOH group

Elemental analysis and cation-exchange experiment ($CH_{0.622}O_{0.540}S_{0.048}$)

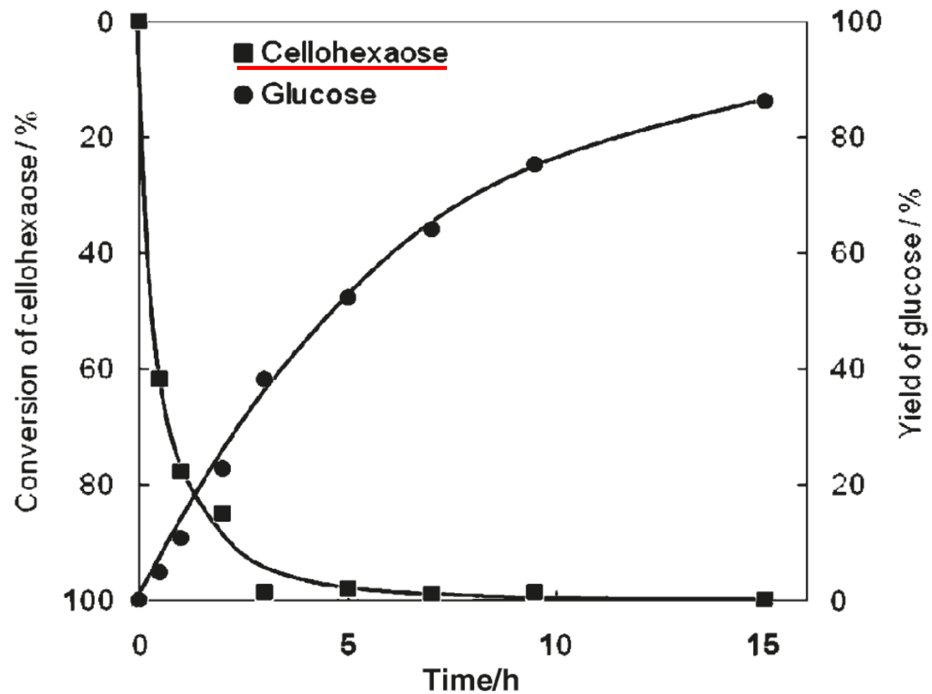
M. Hara et al. Nature **2005**, *438*, 178.

M. Hara et al. *Angew. Chem. Int. Ed.* **2004**, *43*, 2955. M. Hara et al. *J. Am. Chem. Soc.* **2008**, *130*, 12787.

2-2. Hydrolysis of cellulose with amorphous carbon



Hydrolysis of cellobiose with the carbon-based solid catalyst (catalyst 0.1 g, cellobiose0.12 g, water 0.7 g, 363 K)



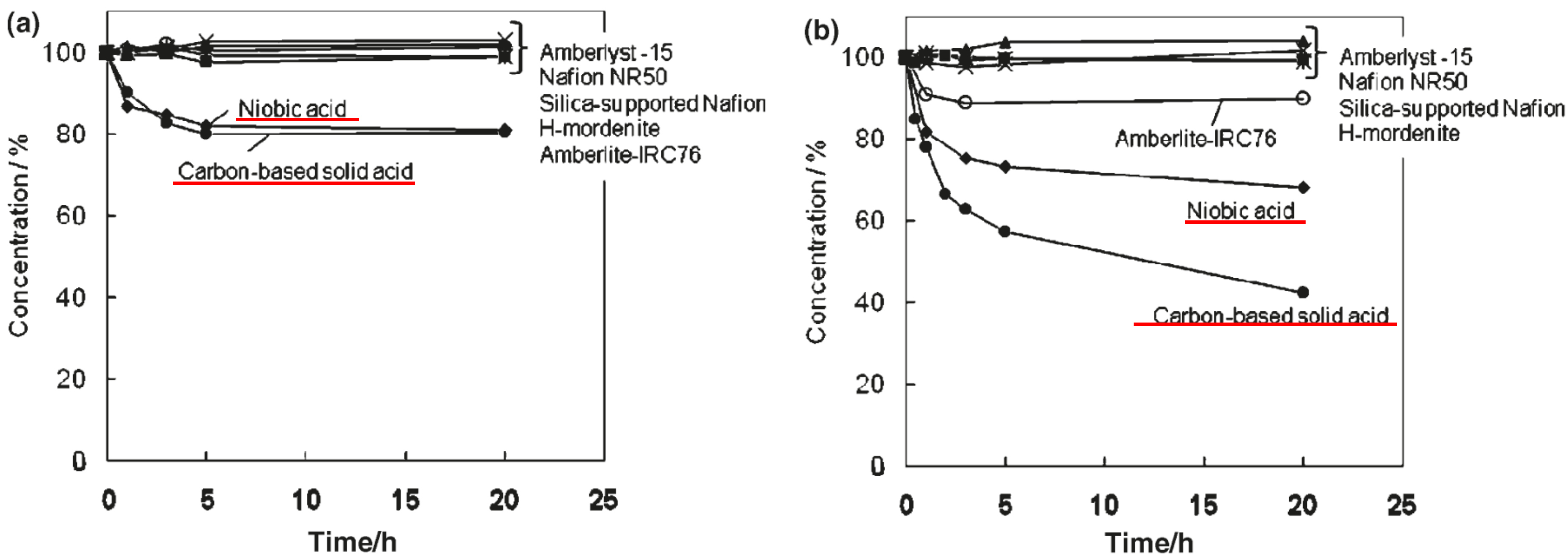
Hydrolysis of cellohexaose with the carbon-based solid catalyst (catalyst 0.3 g, cellohexaose 5.25 mg, water 0.7 g, 363 K)

With amorphous carbon glucose was obtained in good yields.

M. Hara et al. *Langmuir*. **2009**, *25*, 5068.

2-2. Hydrolysis of cellulose with amorphous carbon

Adsorption of cellobiose and cellohexaose



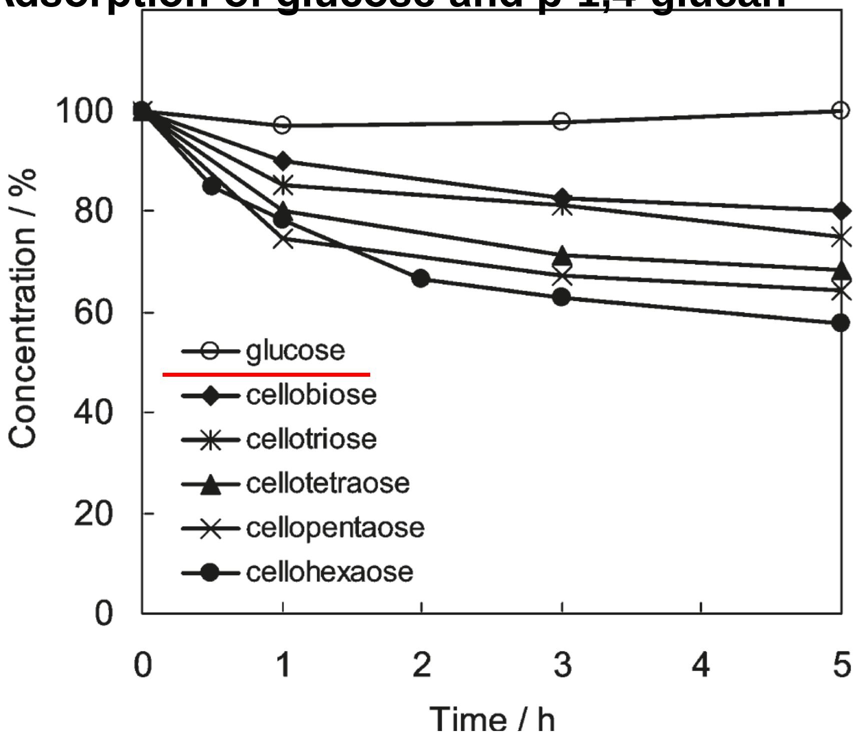
Concentrations of (a) cellobiose and (b) cellohexaose in cellobiose and cellohexaose solutions in the presence of various solid acids at room temperature (298 K).

The carbon-based materials were capable of incorporating cellobiose and cellohexaose. And, niobic acid which has a high density of OH groups was also capable of it.

M. Hara et al. *Langmuir*. **2009**, *25*, 5068.

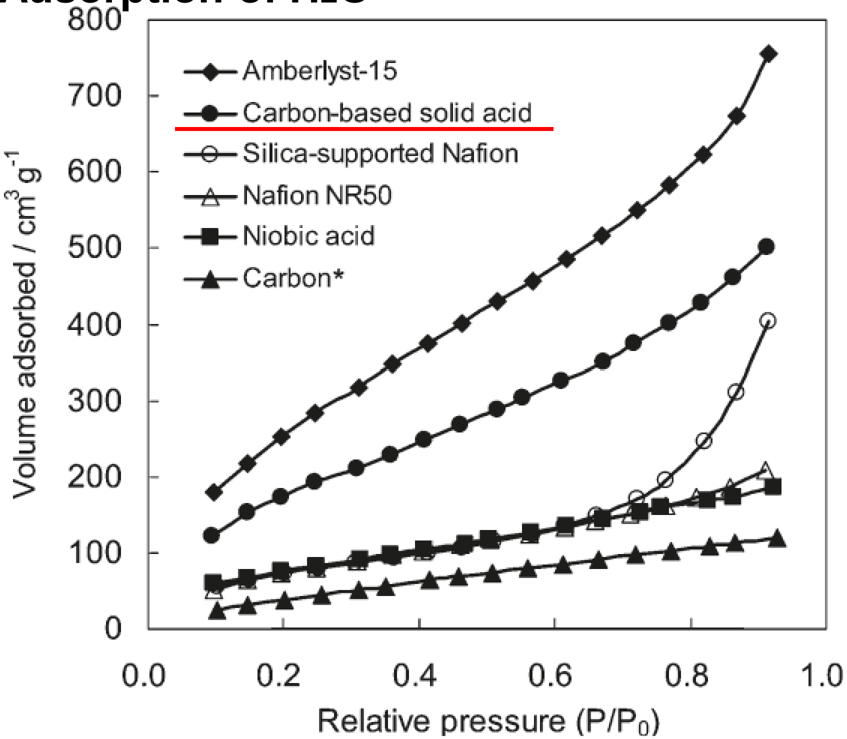
2-2. Hydrolysis of cellulose with amorphous carbon

Adsorption of glucose and β-1,4-glucan



Concentration of β-1,4-glucan and glucose in each aqueous solutions in the presence of the carbon-based solid acid at room temperature (298 K).

Adsorption of H_2O



Water vapor adsorption isotherms (293 K) for various solid acid catalysts. *Carbon is partially carbonized cellulose (precursor for the present carbon-based material) before sulfonation.

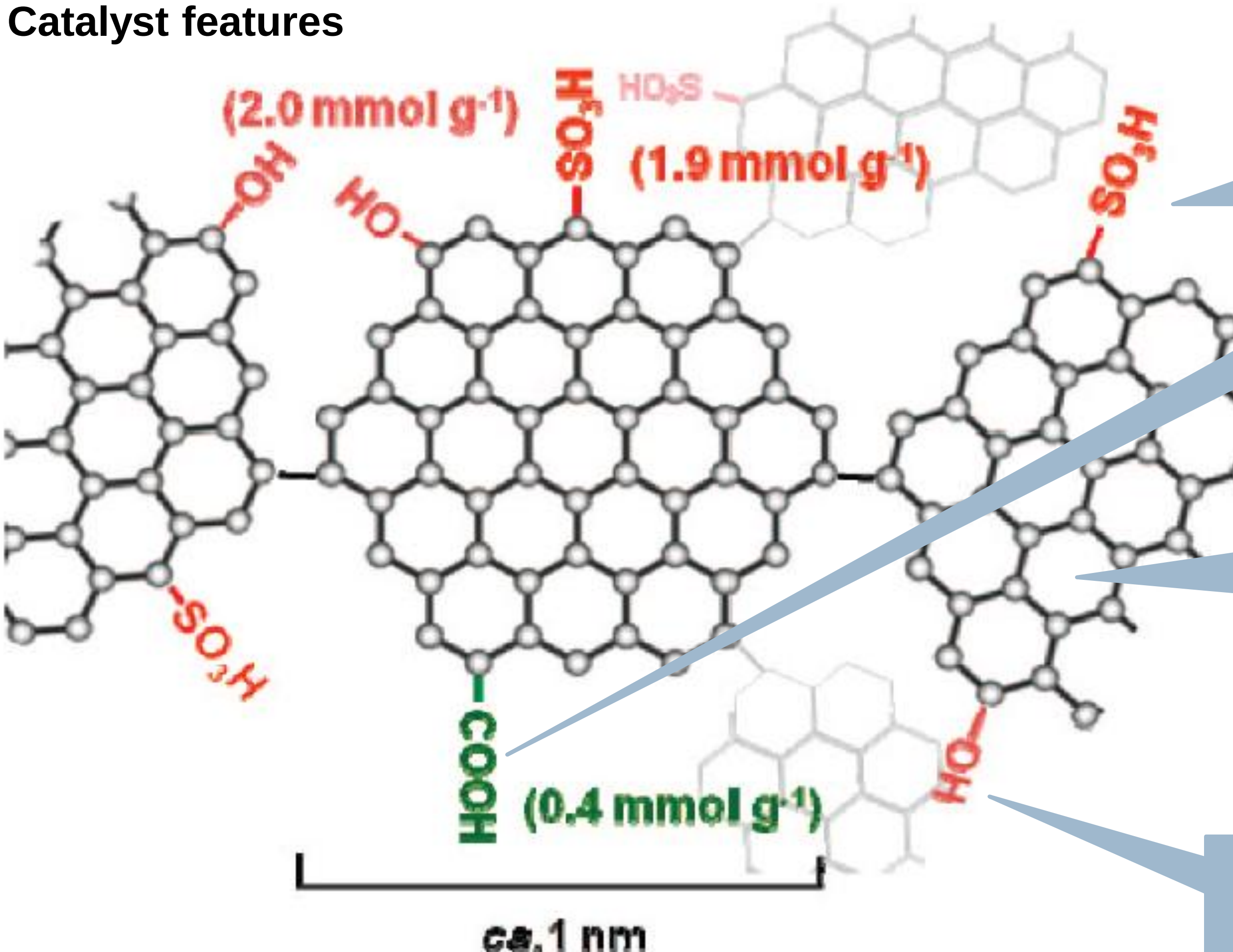
Although glucose was not adsorbed on the carbon materials, the amount of β-1,4-glucan adsorbed on the carbon material increased with increasing chain length of β-1,4-glucan.

The carbon-based materials were capable of incorporating a large amount of water into the carbon bulk.

M. Hara et al. *Langmuir*. **2009**, *25*, 5068.

2-2. Hydrolysis of cellulose with amorphous carbon

Catalyst features



Decomposition of the hydrogen bond and β-1,4-glycosidic bond

Good access of reactants in solution to SO_3H groups

Adsorption of β-1,4-glucan

M. Hara et al. *Langmuir*. **2009**, *25*, 5068.

2-3. Hydrolysis of cellulose with carbon-supported ruthenium

Entry	Catalyst	Yield based on carbon (%)		Total yield (%)	Conv. (%)[b]
		Glucose	Oligomers		
1	Blank	4.6 (19)	14.1 (58)	22.6	24.2
2[h]	Blank	4.9 (22)	4.9 (22)	17.3	22.5
3	CMK-3	15.9 (30)	22.1 (41)	47.3	53.6
4	2 wt% Ru/CMK-3	23.8 (43)	16.2 (29)	48.0	55.9
5[h]	2 wt% Ru/CMK-3	20.4 (43)	3.0 (6)	35.1	47.5
6	5 wt% Ru/CMK-3	25.9 (42)	10.3 (17)	43.7	62.2
7	10 wt% Ru/CMK-3	31.2 (47)	5.1 (8)	41.8	67.6

High stability

Milled

Cellulose 324 mg (2 mmol, 50 mM based on glucose unit), catalyst 50 mg, water 40 mL, 503 K, <1 min.
[h] 463 K, 2 h.

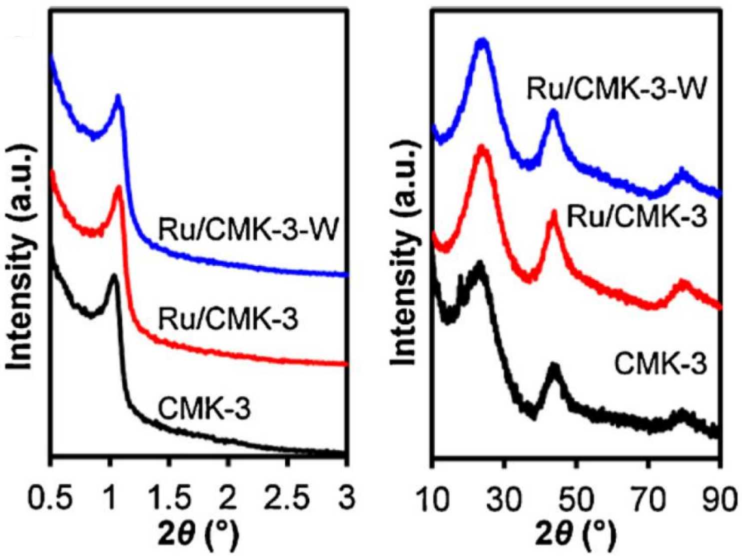
2.8 MPa, Hot compressed water

CMK-3 converted cellulose to oligomers and glucose along with hot compressed water.
Ru was more effective to increase the glucose yield than CMK-3.
Ru species on CMK-3 worked as an acid catalyst to hydrolyze β-1,4-glycosidic bonds of oligomers to yield glucose from the result of hydrolysis of cellobiose at 393K.

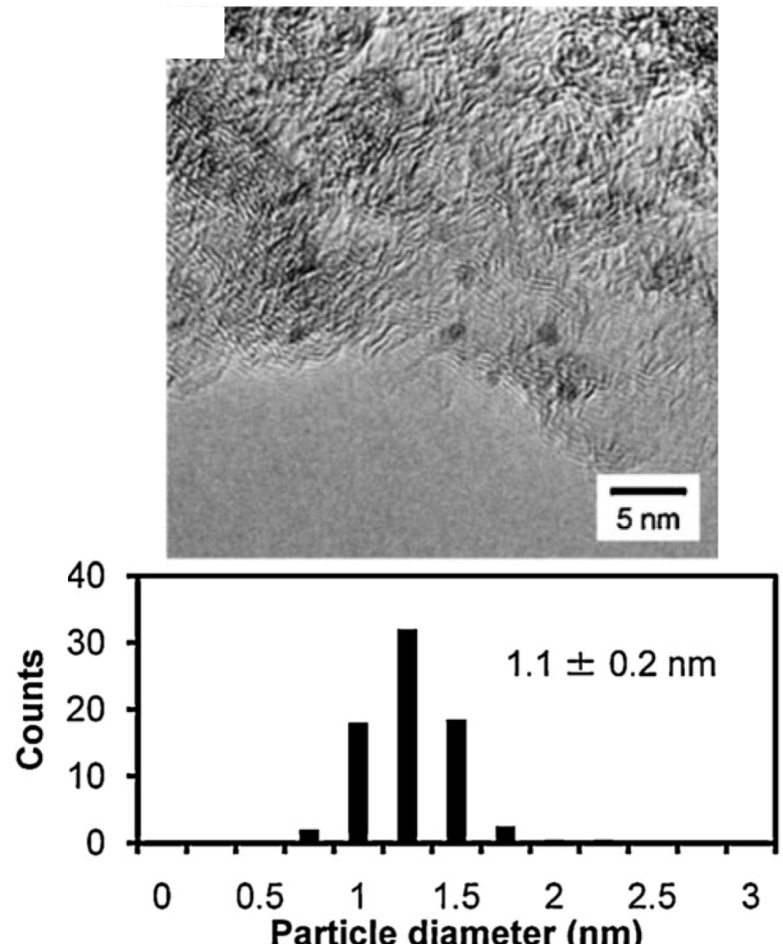
A. Fukuoka et al. *Applied Catalysis A: General.* **2011**, *407*, 188.

2-3. Hydrolysis of cellulose with carbon-supported ruthenium

SAXS pattern and XRD pattern



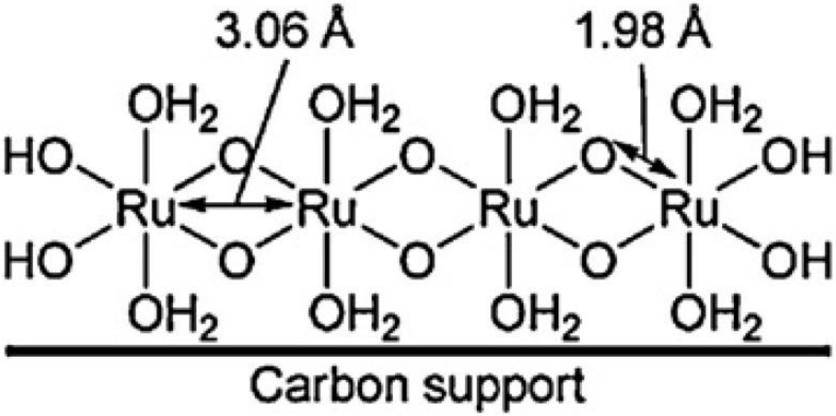
TEM image of 2 wt% Ru/CMK-3, and particle size distribution



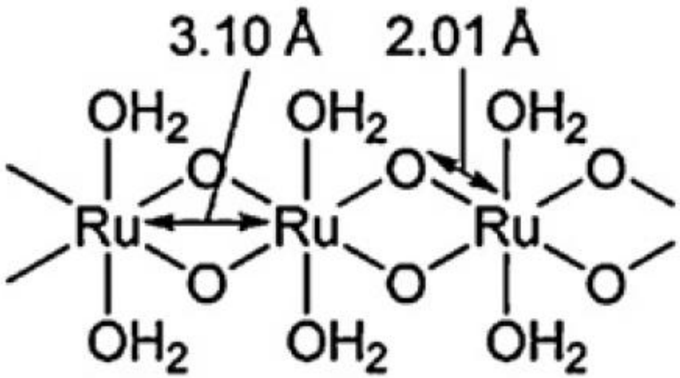
A certain type of Ru nanoparticles

A. Fukuoka et al. *Applied Catalysis A: General.* **2011**, *407*, 188.

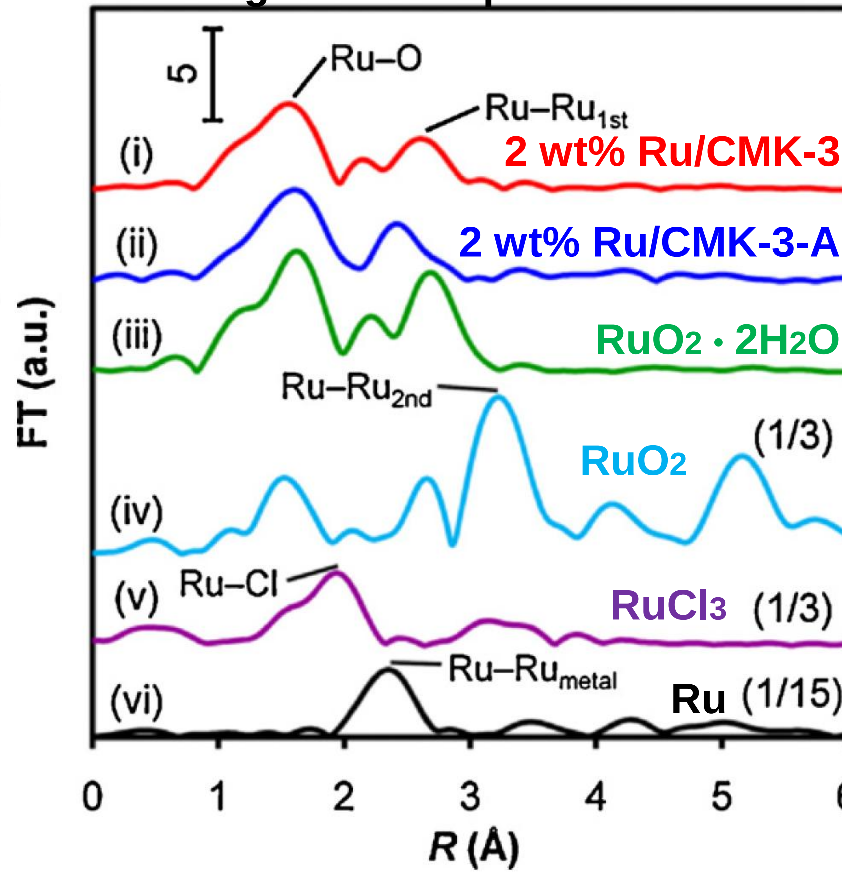
2-3. Hydrolysis of cellulose with carbon-supported ruthenium



Reported structure of $RuO_2 \cdot 2H_2O$



Fourier transforms of k^3 –weighted Ru K-edge EXAFS spectra

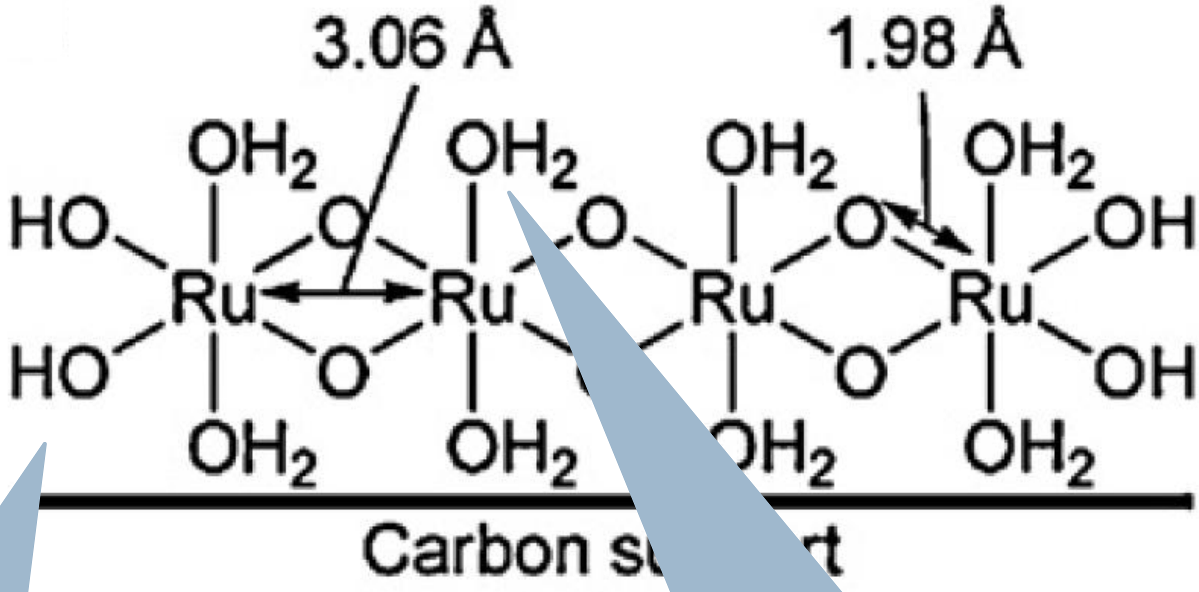


Ru/CMK-3 was similar to $RuO_2 \cdot 2H_2O$.

A. Fukuoka et al. *Applied Catalysis A: General.* **2011**, *407*, 188.

2-3. Hydrolysis of cellulose with carbon-supported ruthenium

Catalyst features

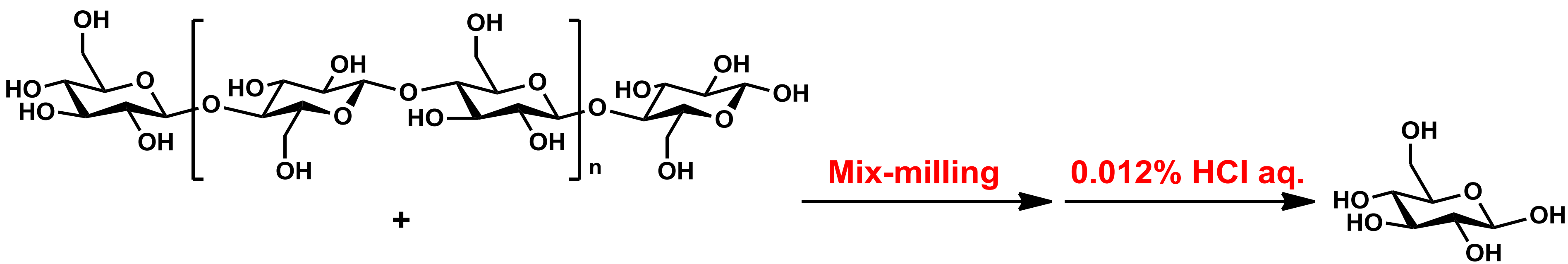


One-dimensional chain structure

$RuO_2 \cdot 2H_2O$ may give a Brønsted acid. The dissociation of a water molecule coordinated on Ru could give a vacant site with Lewis acidity.

A. Fukuoka et al. *Applied Catalysis A: General.* **2011**, *407*, 188.

2-4. Hydrolysis of cellulose with simple activated carbons and trace hydrochloric acid



Activated carbon
(K26)

88%

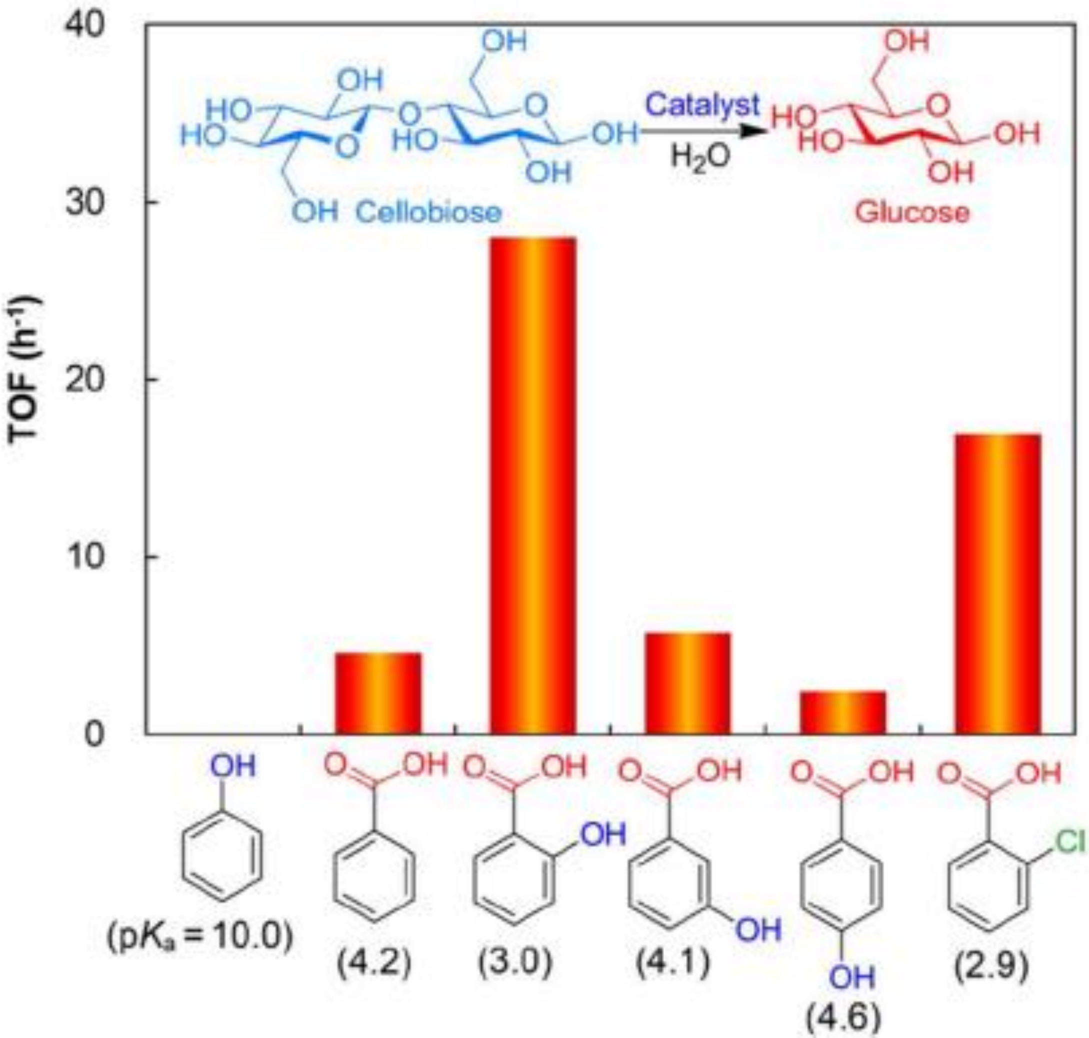
High stability

Carboxylic acid, phenolic groups from TPD measurement

(catalyst 50 mg, cellulose 324 mg, water 40 mL, 453 K, 20 min)

A. Fukuoka et al. *ACS Catal.* **2013**, *3*, 581.

2-4. Hydrolysis of cellulose with simple activated carbons and trace hydrochloric acid



Salicylic acid gave a high TOF.

The catalytic activities can be explained by two factors.
One is pKa.
The other is the structure of acids.

(TOF = mol of glucose produced in the catalytic reaction – blank/2 mol of catalyst • reaction time)

(catalyst 0.5 mM, cellulobiose 25 mM , 443 K)

A. Fukuoka et al. *ACS Catal.* **2013**, *3*, 581.

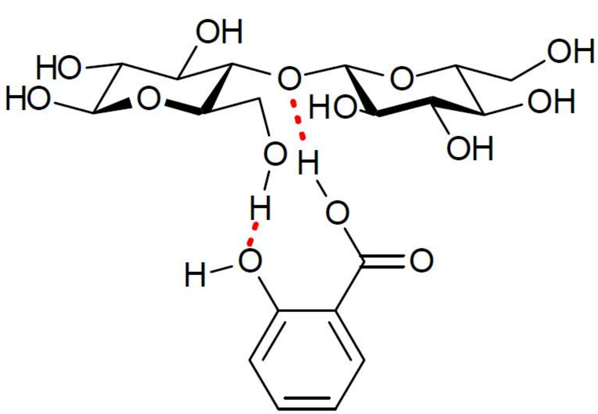
2-4. Hydrolysis of cellulose with simple activated carbons and trace hydrochloric acid

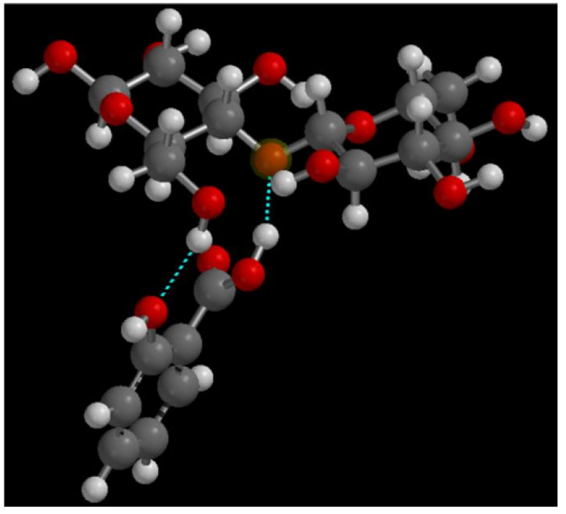
Catalyst features

Activated carbon (26)

Phenolic groups form hydrogen bonds with hydroxyl groups of a cellulose chain, and that adjacent carboxylic acids have an opportunity to hydrolyze glycosidic bonds.

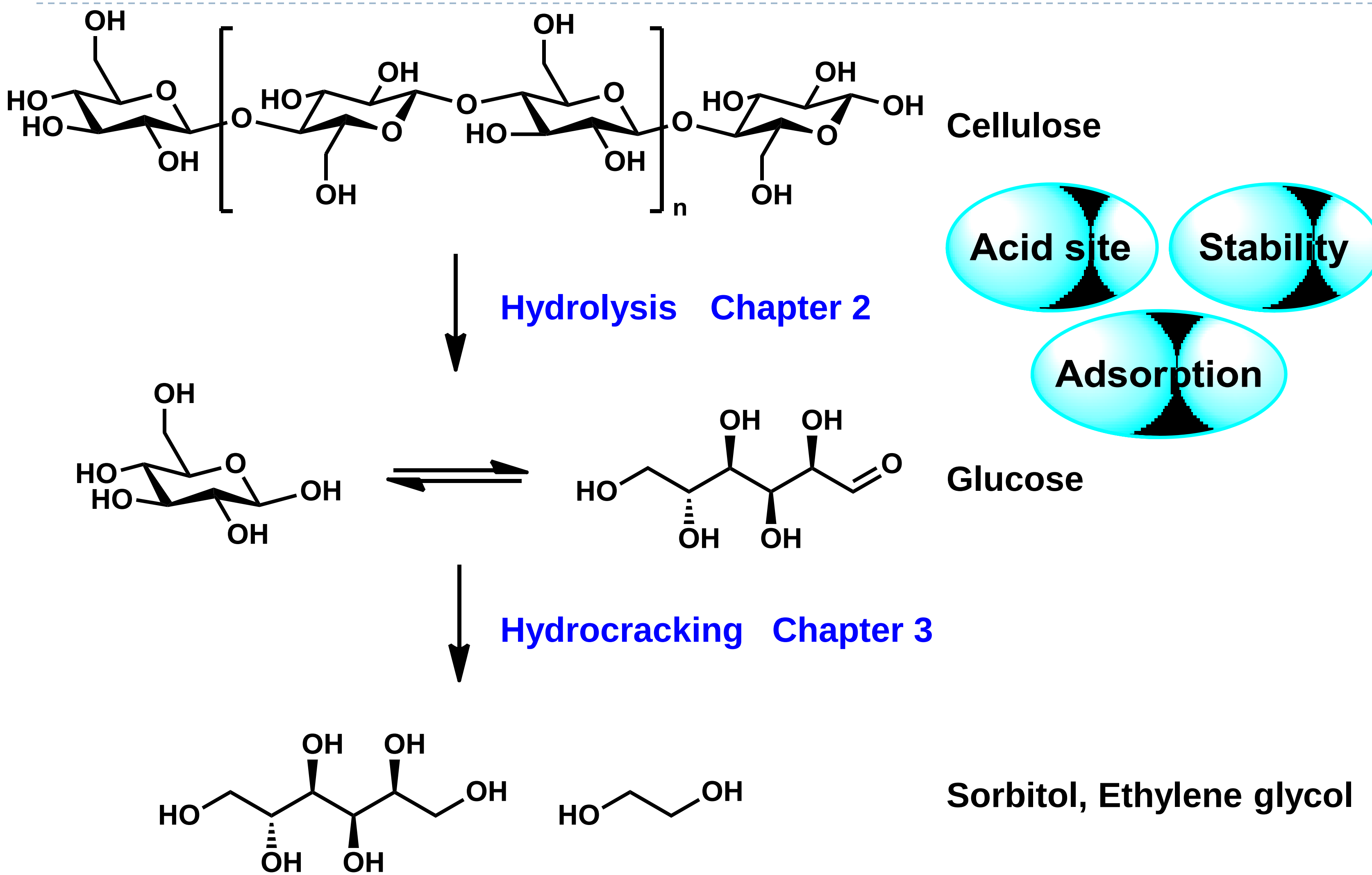
Interaction predicted by spartan'08





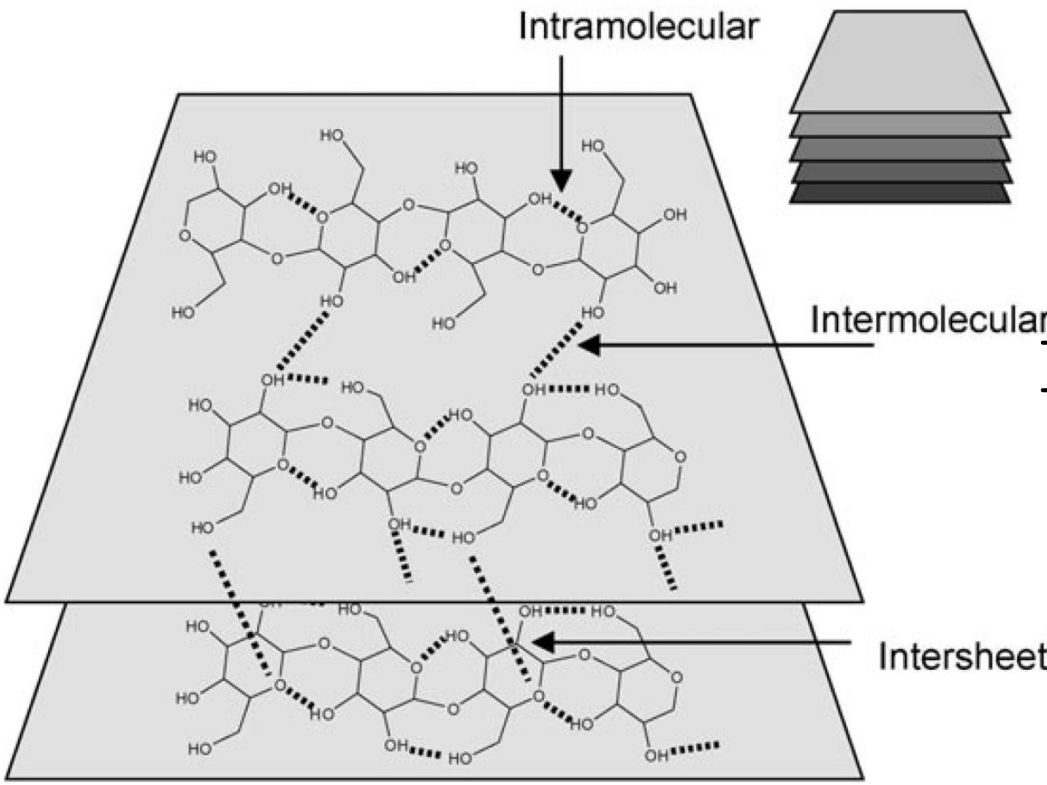
A. Fukuoka et al. *ACS Catal.* **2013**, *3*, 581.

2-5. Short summary of 2 chapter



Contents

3-0. Hydrocracking of cellulose

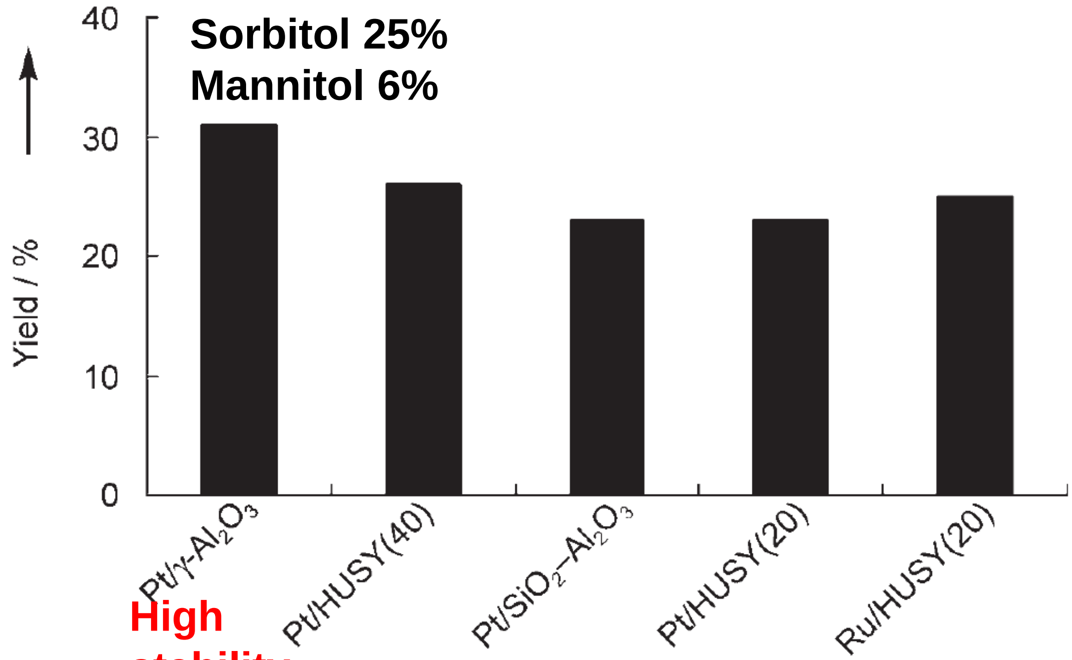


H_2O, H^+ ⟹ **Glucose**

Hydrogenation ⟹ **Sorbitol**, **Ethylene glycol**

Hydrogen bonding in cellulose

3-1. Hydrocracking of cellulose with supported metal



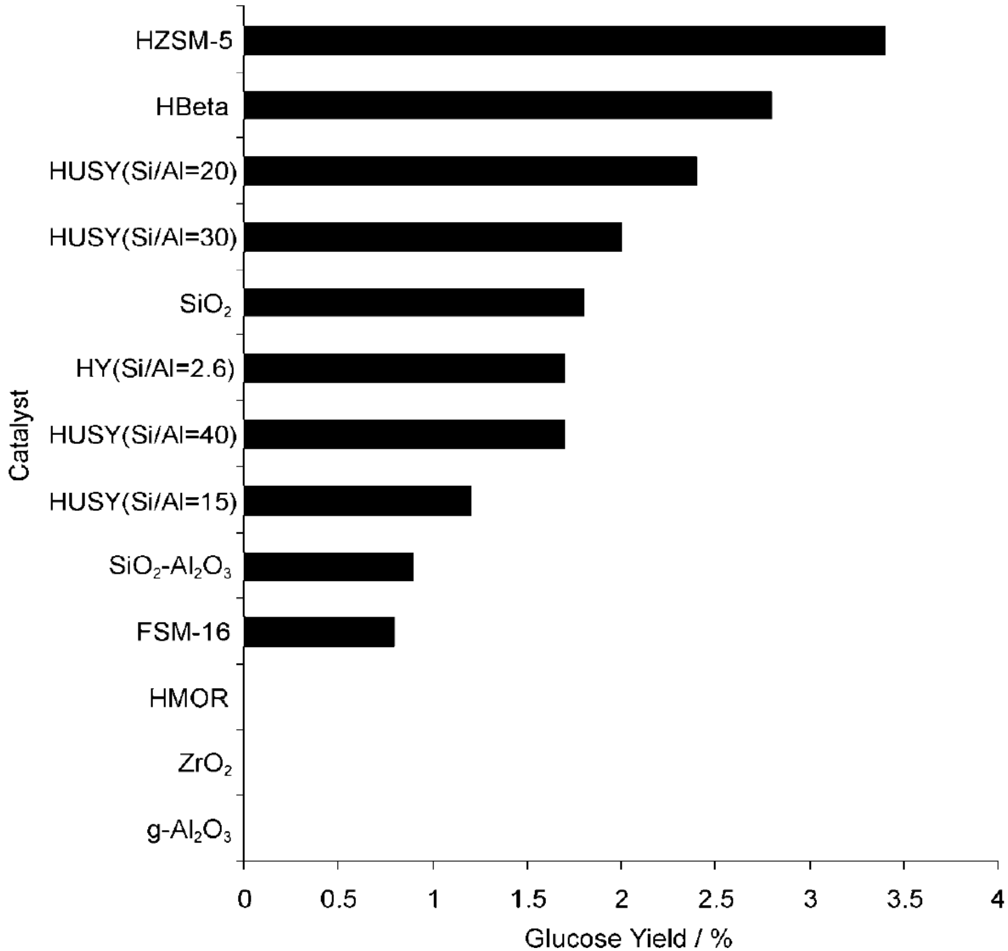
Conversion of cellulose into sugar alcohols by supported metal catalysts. Reaction conditions: cellulose (0.48 g), Pt catalyst (0.21 g), Ru catalyst (0.11 g; Pt, Ru 2.5 wt%), water (60 mL), initial H_2 pressure at RT = 5 MPa, 463 K, 24 h.

Supported metal gave good results and led to the formation of sugar alcohols from cellulose.

Hydrogen gas was pressurized in the autoclave with a supported metal catalyst.

A. Fukuoka et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 5161.
A. Fukuoka et al. *ChemSusChem* **2008**, *1*, 969.

3-1. Hydrocracking of cellulose with solid acids



Solid acid catalyzed conversion of cellulose into glucose. Conditions: cellulose (0.16 g), catalyst (0.068 g), water (20 mL), hydrogen pressure (5 MPa at RT), 190 °C, 24 h.

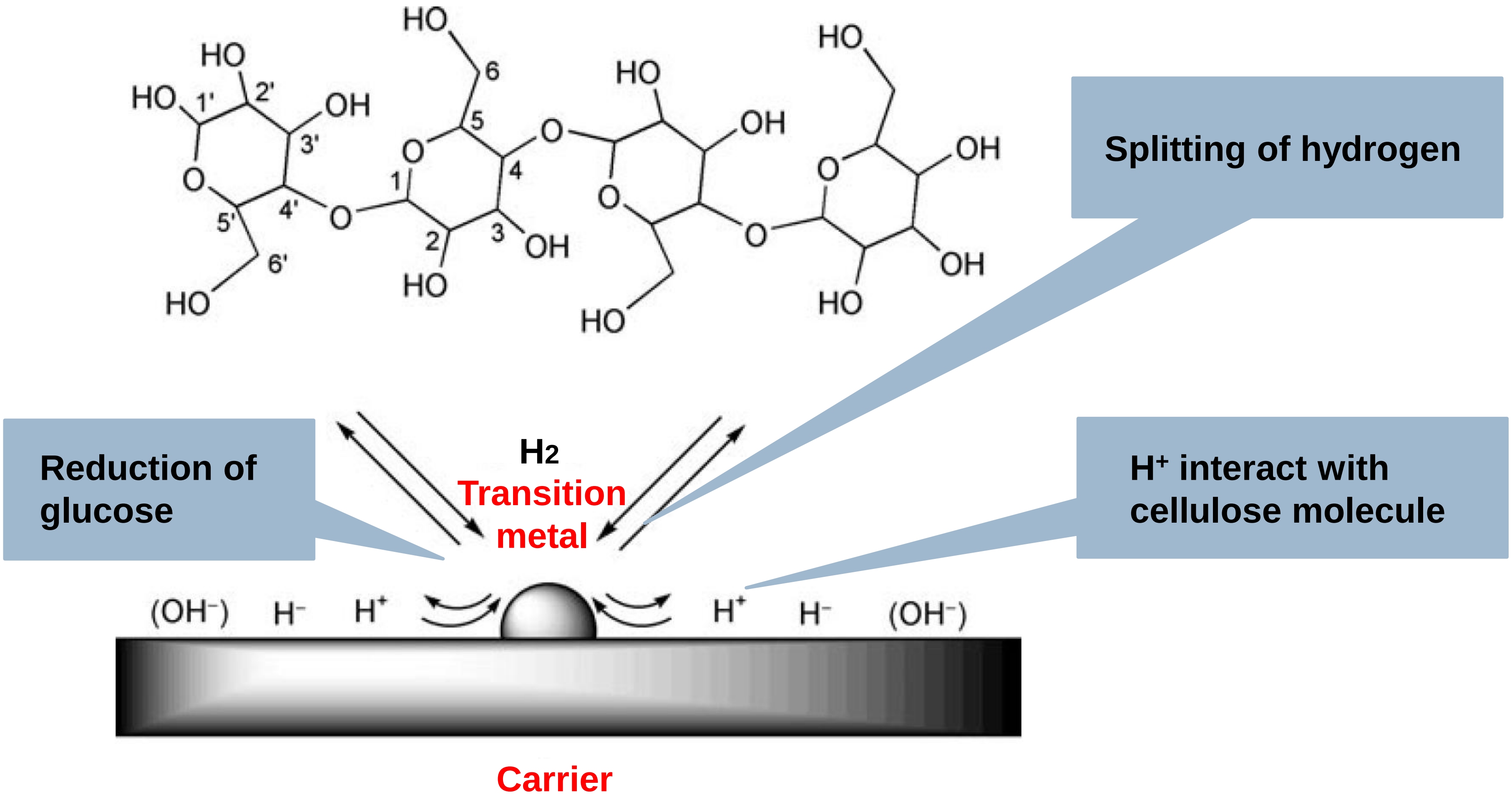
Various solid acids gave only low activity.
No sugar alcohol was observed.

The metal promoted the hydrolysis of cellulose.

A. Fukuoka et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 5161.
A. Fukuoka et al. *ChemSusChem* **2008**, *1*, 969.

3-1. Hydrocracking of cellulose with supported metal

Catalyst features



A. Fukuoka et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 5161.
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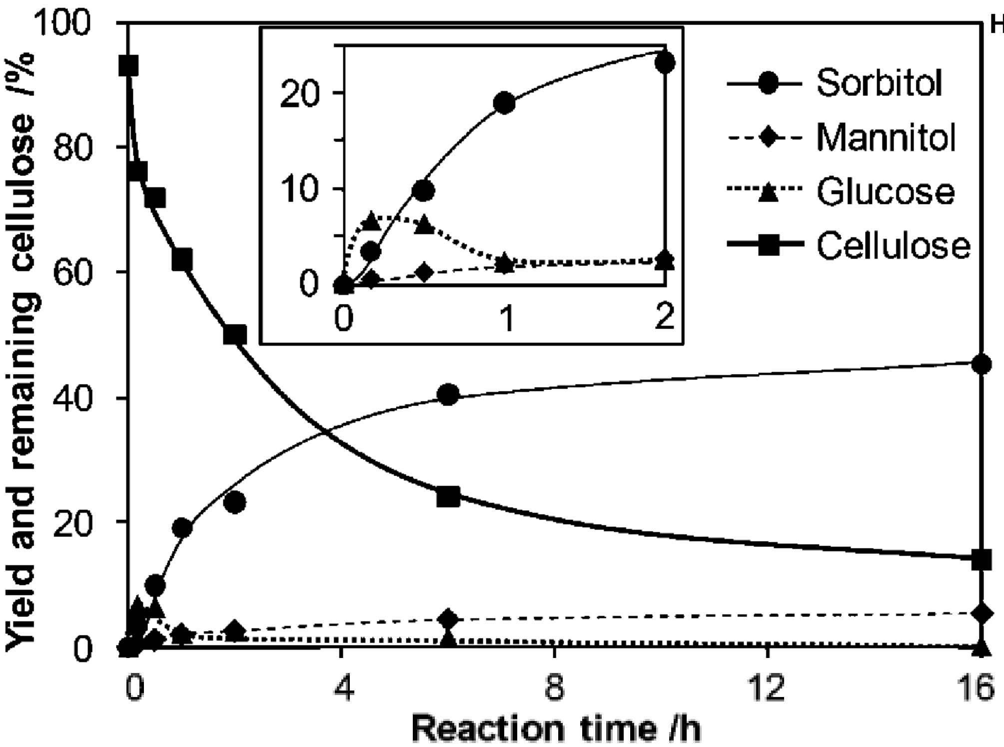
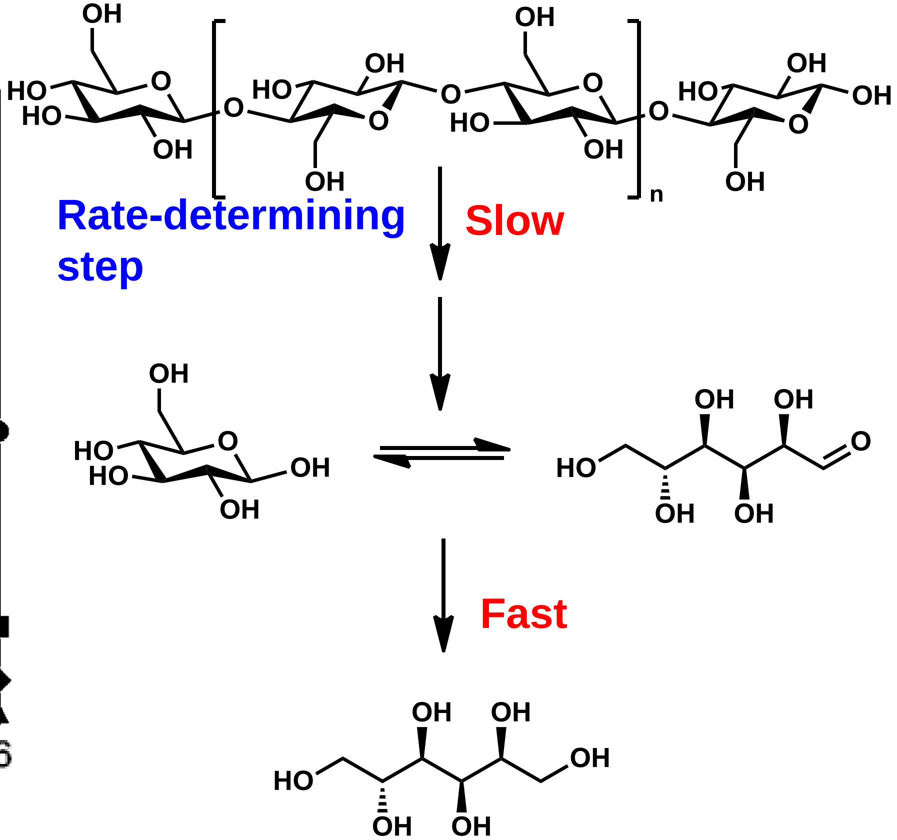
3-1. Hydrocracking of cellulose with supported metal

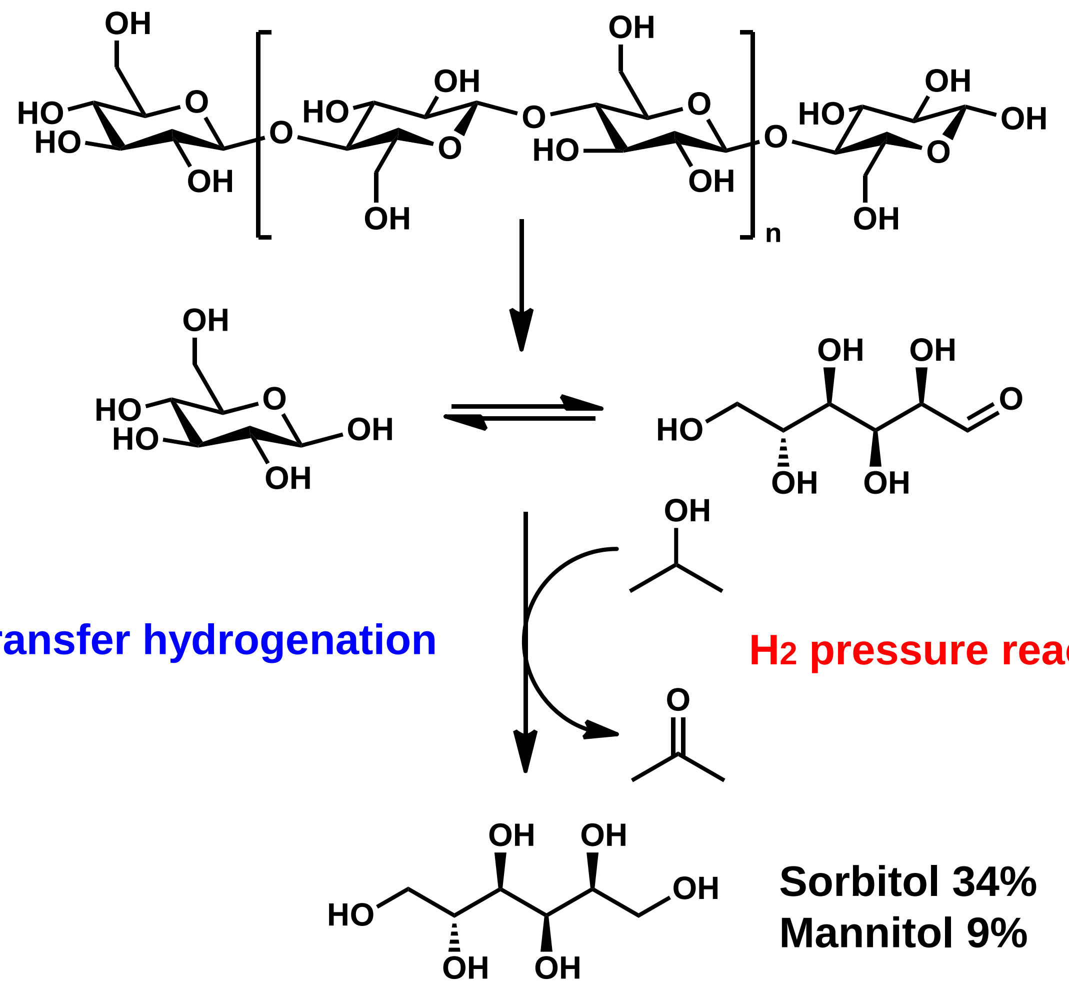
Time course of the hydrogenation of cellulose





A. Fukuoka et al. *Green Chem.* **2011**, *13*, 326.

3-1. Hydrocracking of cellulose with supported metal



Ru/AC gave good results.

Transfer hydrogenation

H_2 pressure reached 0.8 MPa.

Sorbitol 34%
Mannitol 9%

(catalyst 50 mg, milled cellulose 324 mg, water 30 mL, 2-propanol 10 mL, 463 K, 18 h)

A. Fukuoka et al. *Chem. Comm.* **2011**, *47*, 2366.

3-2. Hydrocracking of cellulose with supported metal

Entry	Catalyst	EG	
1	0.6% Ru/AC (0.1508 g) + H_2WO_4 (0.0508 g)	33.8	
2	1.2% Ru/AC (0.1503 g) + H_2WO_4 (0.0500 g)	54.4	
3	1.6% Ru/AC (0.1509 g) + H_2WO_4 (0.0500 g)	52.5	
4	2.4% Ru/AC (0.1507 g) + H_2WO_4 (0.0506 g)	36.0	
5	4.0% Ru/AC (0.1506 g) + H_2WO_4 (0.0506 g)	19.4	
6	1.2% Ru/MC (0.1010 g) + H_2WO_4 (0.0524 g)	58.5	High stability
7	1.2% Ru/AC (0.1502 g) + H_2WO_4 (0.0154 g)	22.2	
8	1.2% Ru/AC (0.1507 g) + H_2WO_4 (0.0304 g)	40.6	
9	1.2% Ru/AC (0.1500 g) + H_2WO_4 (0.0413 g)	48.7	
10	1.2% Ru/AC (0.1504 g) + H_2WO_4 (0.1037 g)	43.8	

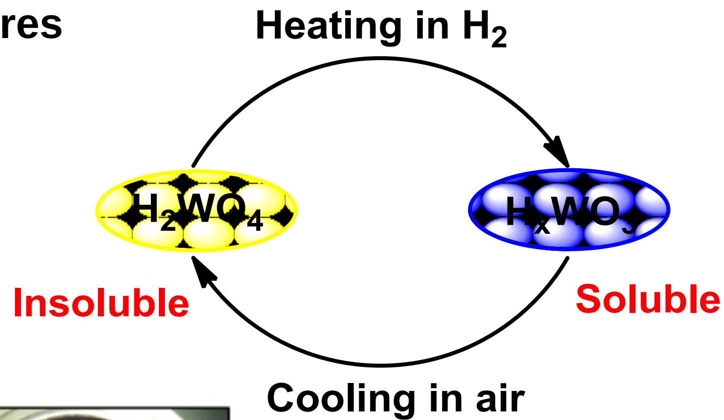
Hydrolysis of cellulose (cellulose 0.5 g, water 50 g, 518 K, 6 Mpa H_2, 30 min)

In the presence of a tungsten-based catalyst, ethylene glycol became the major product.

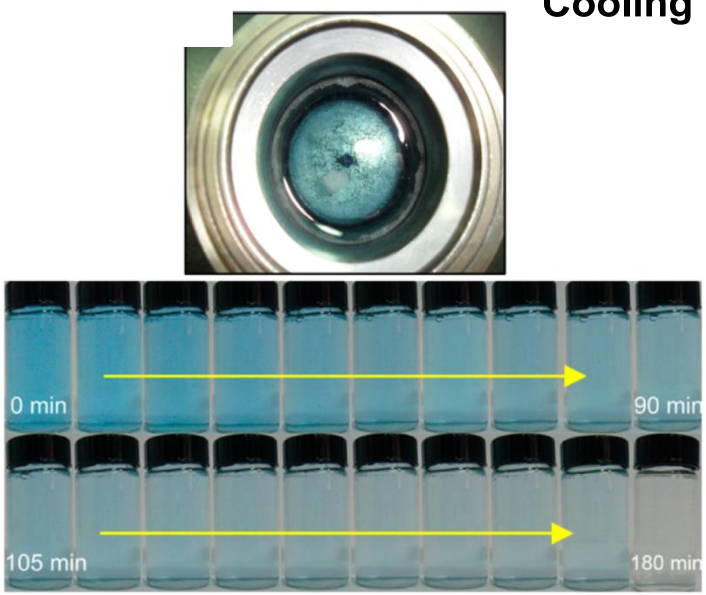
T. Zhang et al. *Chem. Commun.* **2012**, *48*, 7052.
T. Zhang et al. *Acc. Chem. Res.* **2013**, *46*, 1377.

3-2. Hydrocracking of cellulose with supported metal

Catalyst features

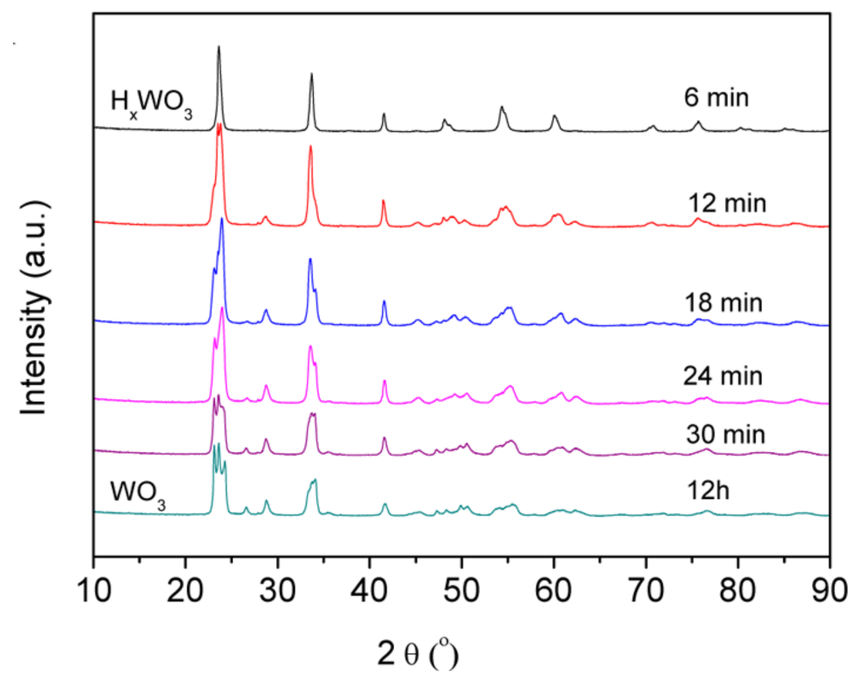


Temperature-controlled phase-transfer catalyst



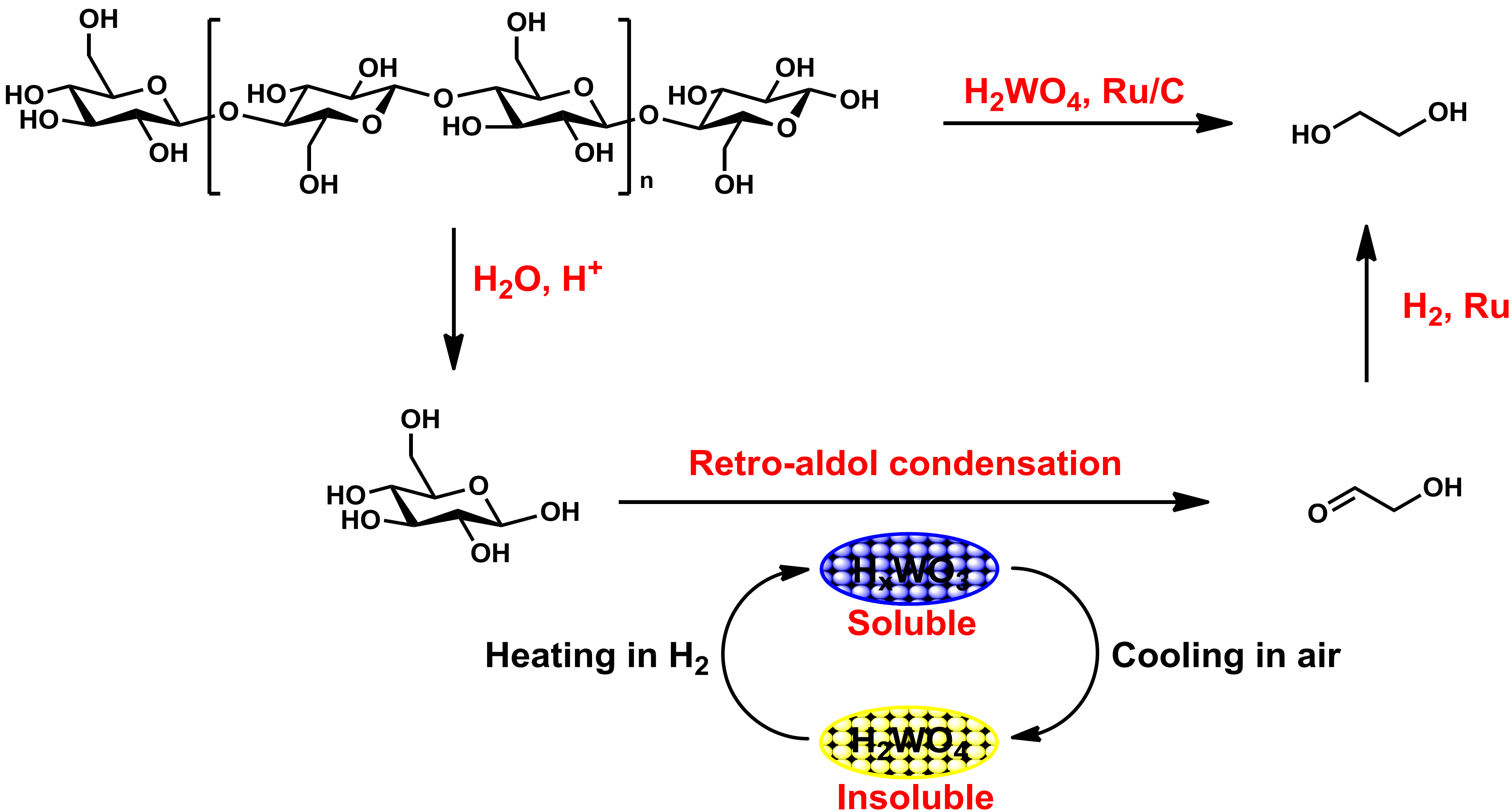
Blue to yellow

XRD pattern



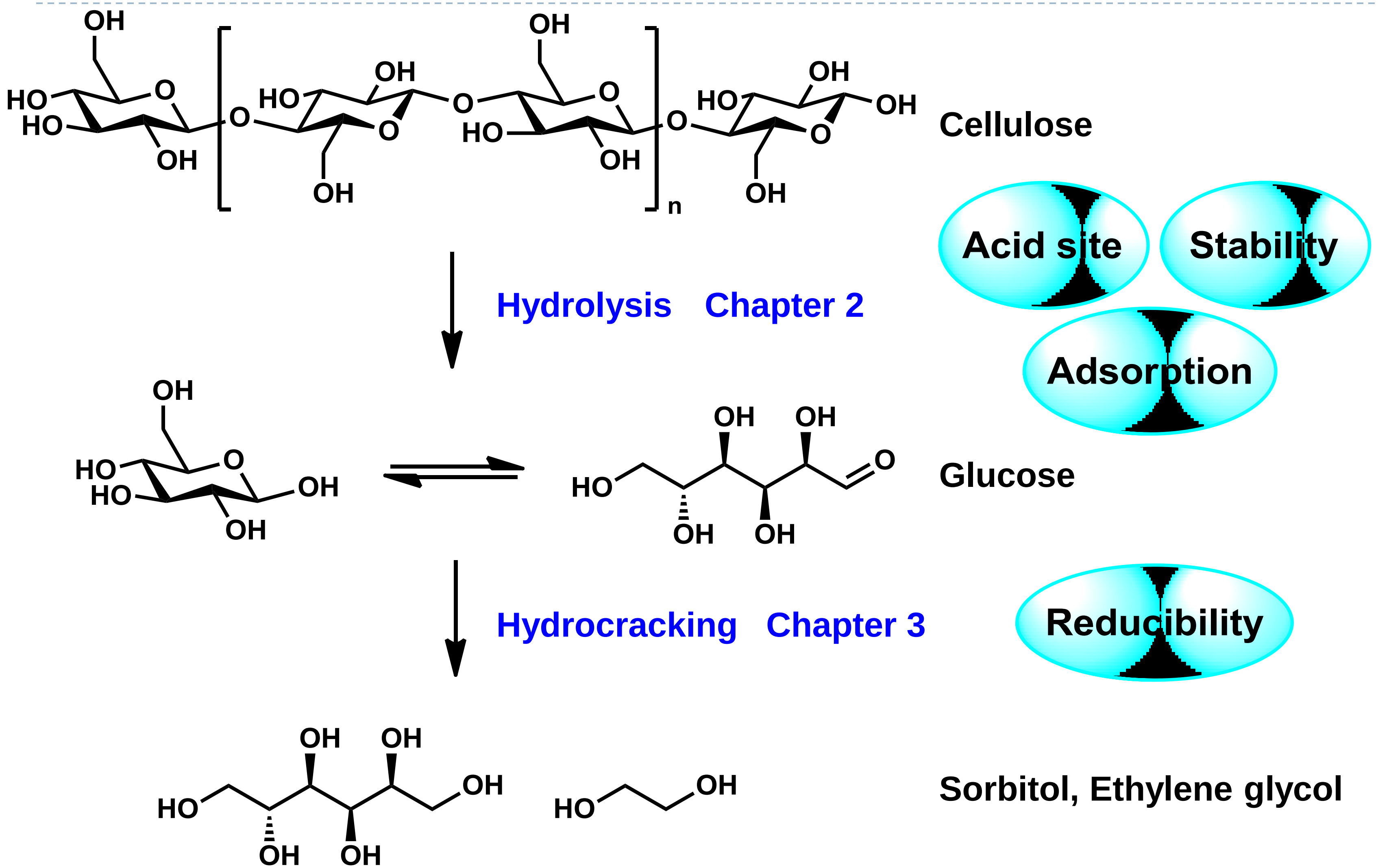
T. Zhang et al. *Chem. Commun.* **2012**, *48*, 7052.
X. Zuwei et al. *Science* **2001**, *292*, 1139. T. Zhang et al. *Acc. Chem. Res.* **2013**, *46*, 1377.

3-2. Hydrocracking of cellulose with supported metal



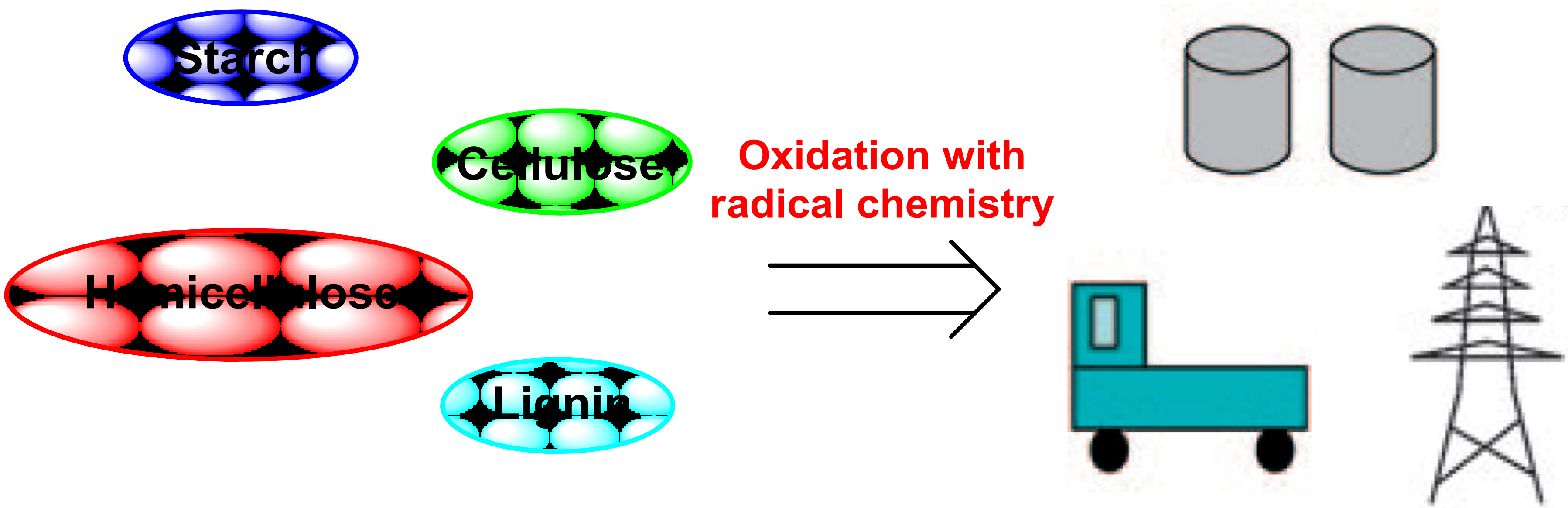
T. Zhang et al. *Chem. Commun.* **2012**, *48*, 7052.
T. Zhang et al. *Acc. Chem. Res.* **2013**, *46*, 1377.

3-3. Short summary of 3 chapter



Contents

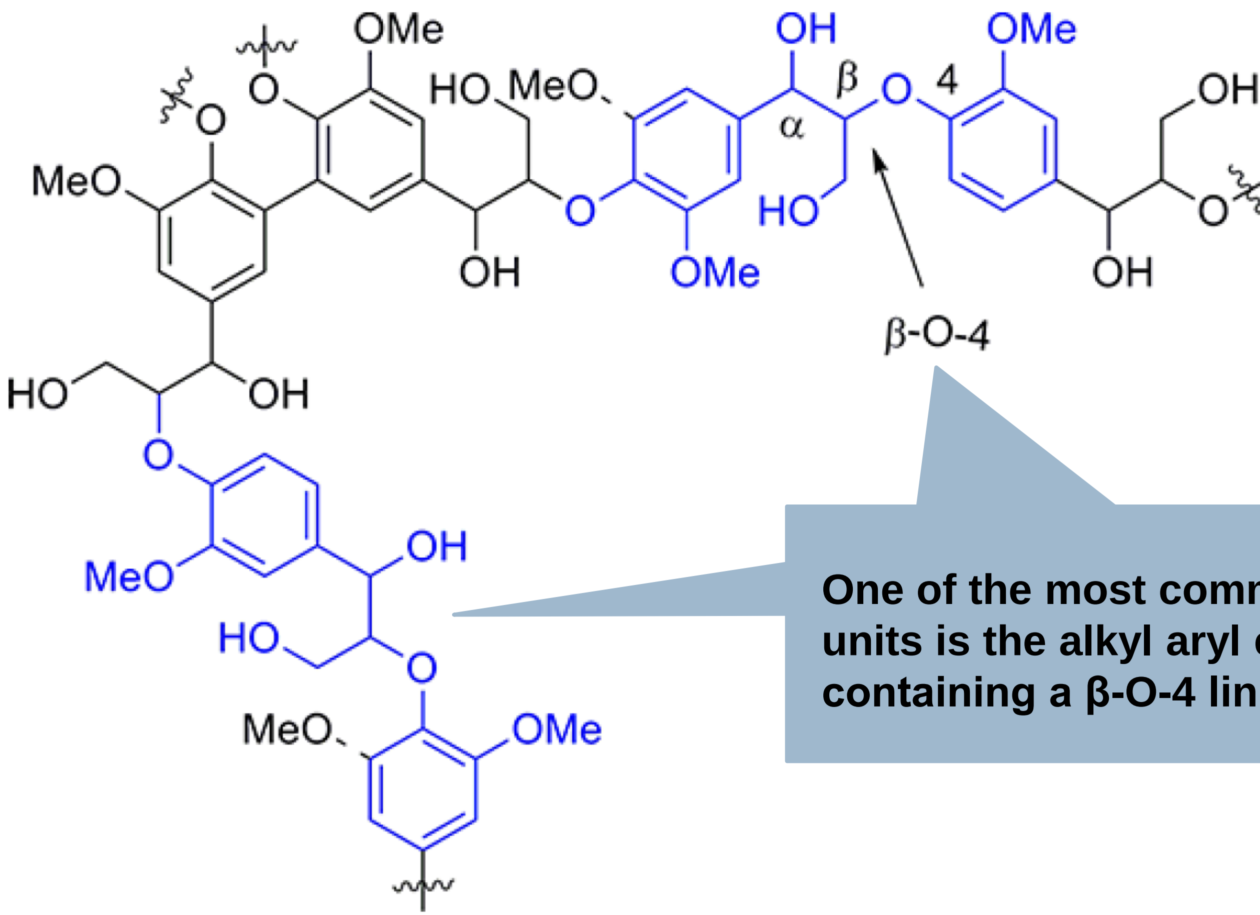
4-0. Future outlook



Lignocellulose

Chemicals, fuels, energy etc.

4-1. Chemoselective metal-free aerobic alcohol oxidation in lignin



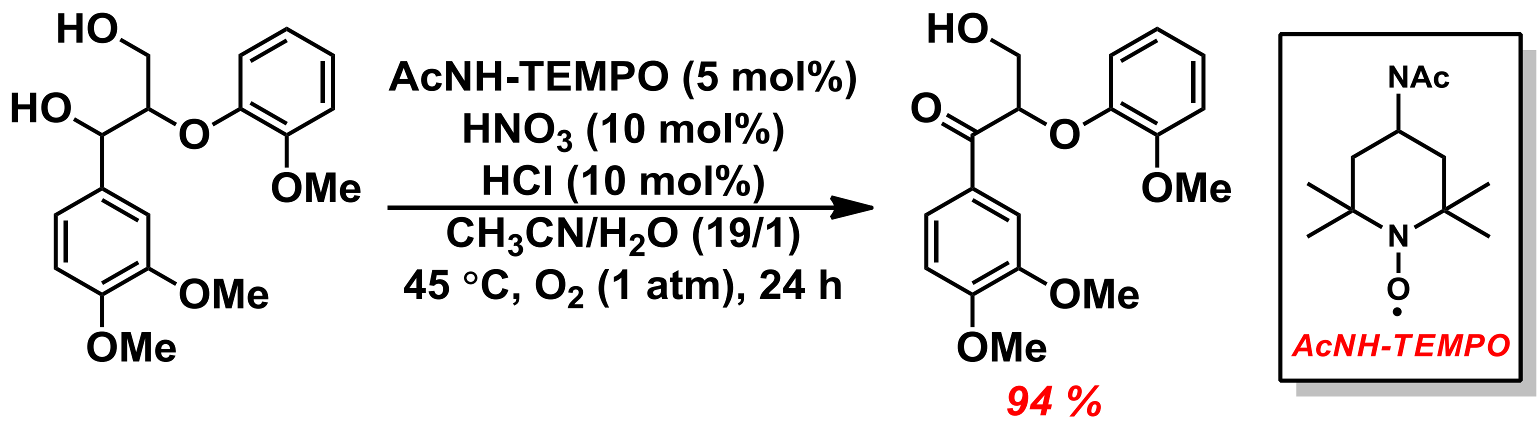
One of the most common structural units is the alkyl aryl ether unit containing a β-O-4 linkage

Fragment of lignin

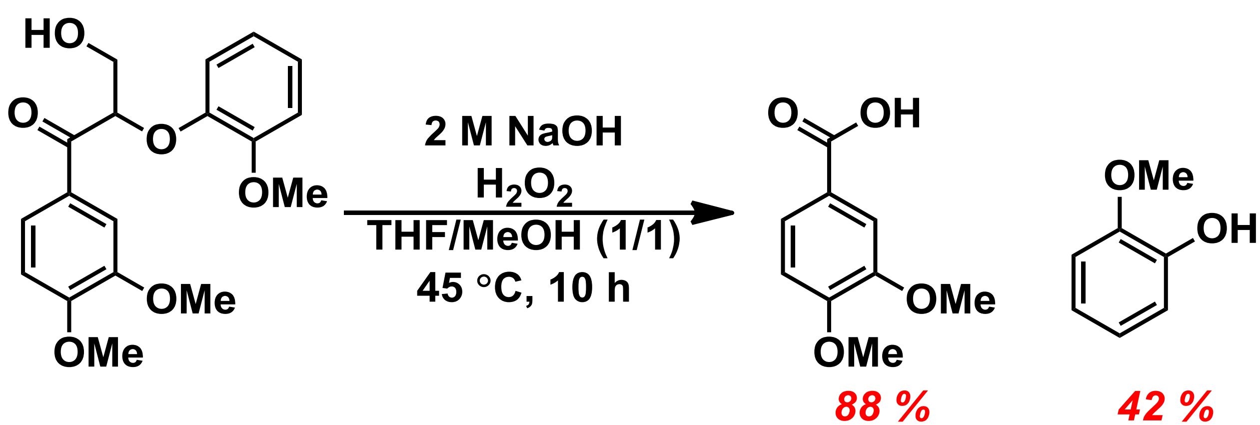
J. F. Hartwig et al. *Science* **2011**, *332*, 439.
S. S. Stahl et al. *J. Am. Chem. Soc.* **2013**, *135*, 6415.

4-1. Chemoselective metal-free aerobic alcohol oxidation in lignin

Chemoselective alcohol oxidation

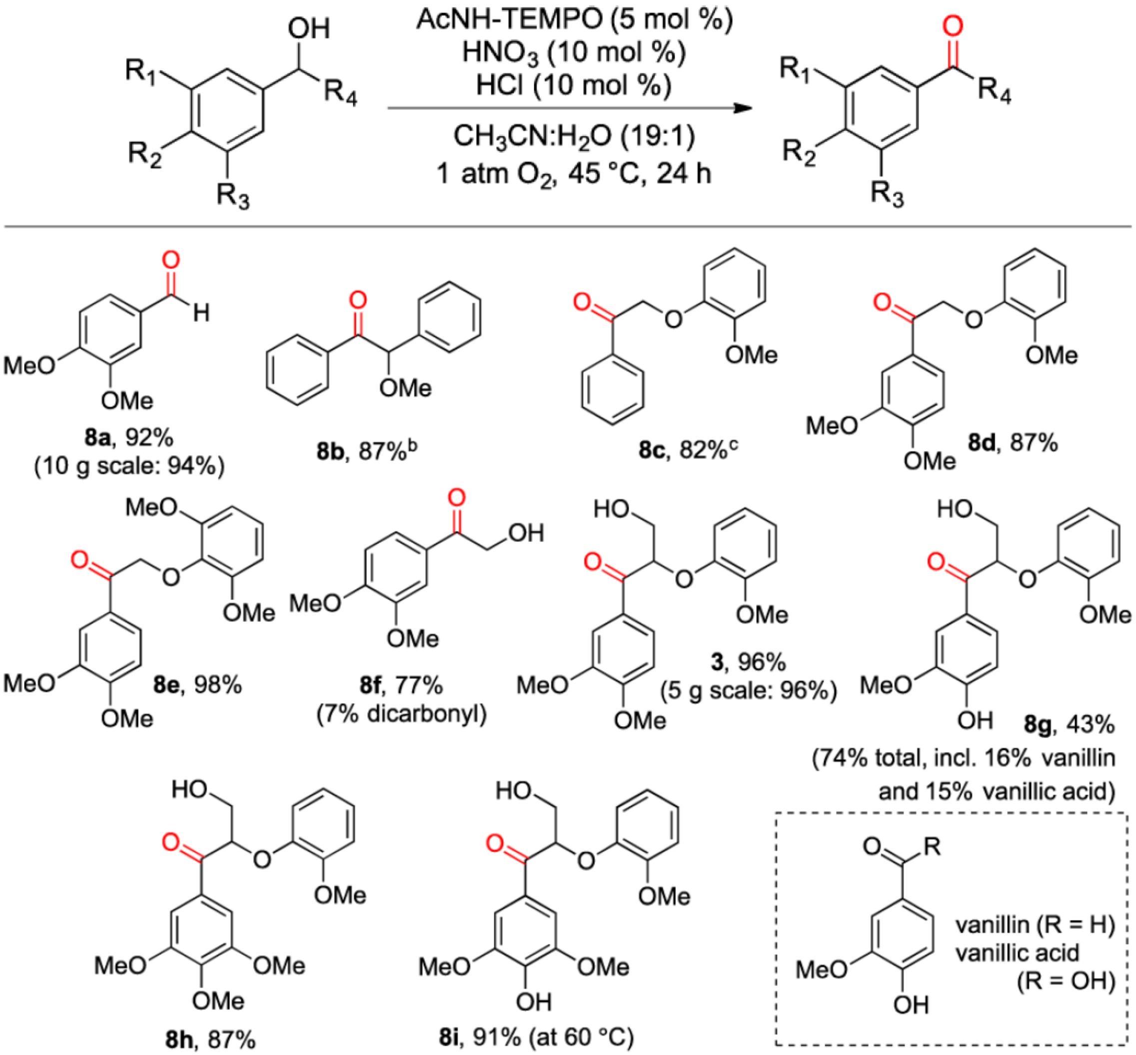


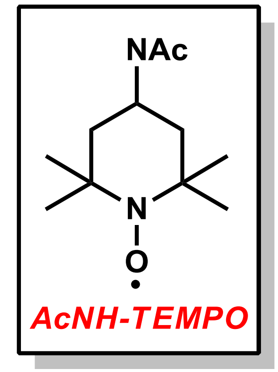
C-C bond cleavage



S. S. Stahl et al. *J. Am. Chem. Soc.* **2013**, *135*, 6415.

4-1. Chemoselective metal-free aerobic alcohol oxidation in lignin





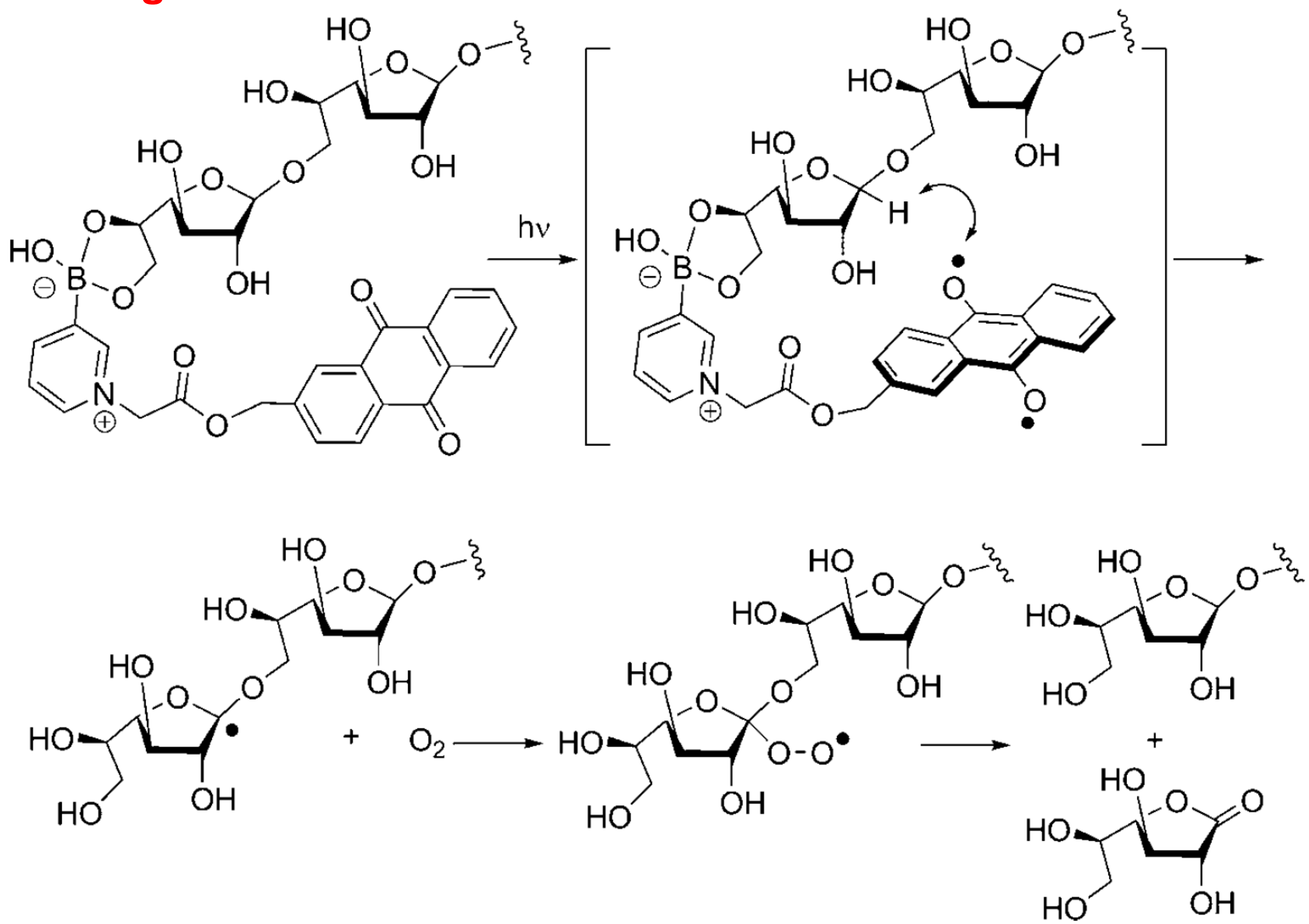
This reaction was applied to many lignin model compounds.

Moreover, it was also applied to real lignin.

S. S. Stahl et al. *J. Am. Chem. Soc.* **2013**, *135*, 6415.

4-2. Photodegradation of target oligosaccharides

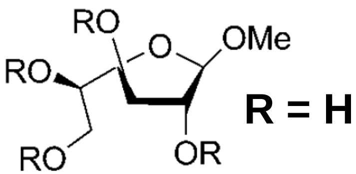
Oxidative cleavage



K. Toshima et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 10096.

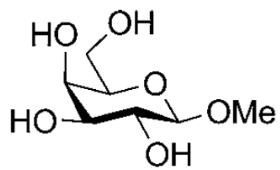
4-2. Photodegradation of target oligosaccharides

Association constant (K_a) for anthraquinone derivative with different diols

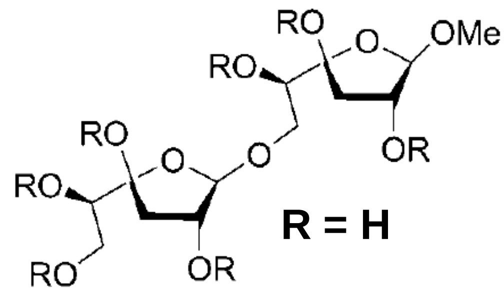


K_a = 170

Degradation y.32%

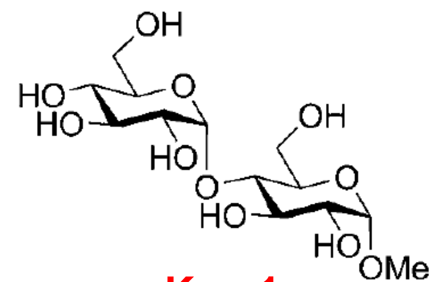


K_a = 7

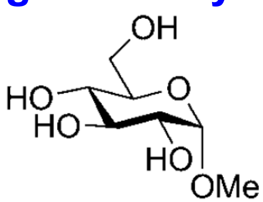


K_a = 174

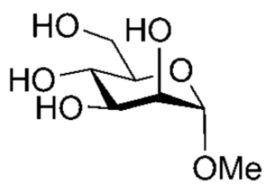
Degradation y.79%



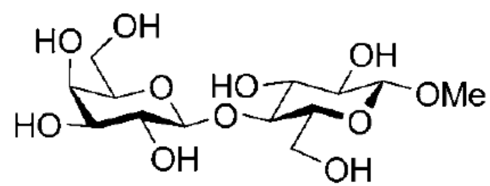
K_a = 1



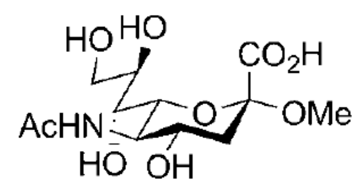
K_a = 6



K_a = 8



K_a = 1



K_a = 5

(glycoside 1.0 nM, catalyst 1.0 nM, 10% MeCN/0.1% phosphate buffer, 298 K, 10 min, UV lamp 365 nm 100 W)

K. Toshima et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 10096.

Contents

5. Summary

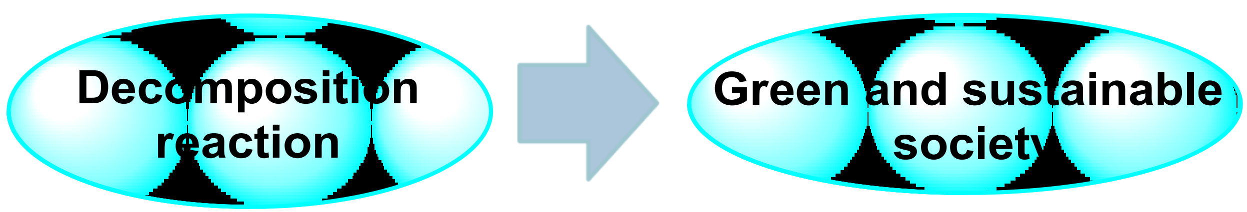
Although great progress has been made in conversion of cellulose, the efficient transformation of real biomass to important bulk chemicals is still in its infancy.

1. Development of cheaper but more efficient and robust catalyst

2. Development of powerful in situ characterization techniques

3. Achievement of industry-academia-government collaboration

are essential for green and sustainable society.



References

A. Fukuoka et al. *ChemSusChem* **2008**, *1*, 969.

T. Zhang et al. *Acc. Chem. Res.* **2013**, *46*, 1377.

A. Fukuoka et al. *Green Chem.* **2013**, *15*, 1740.

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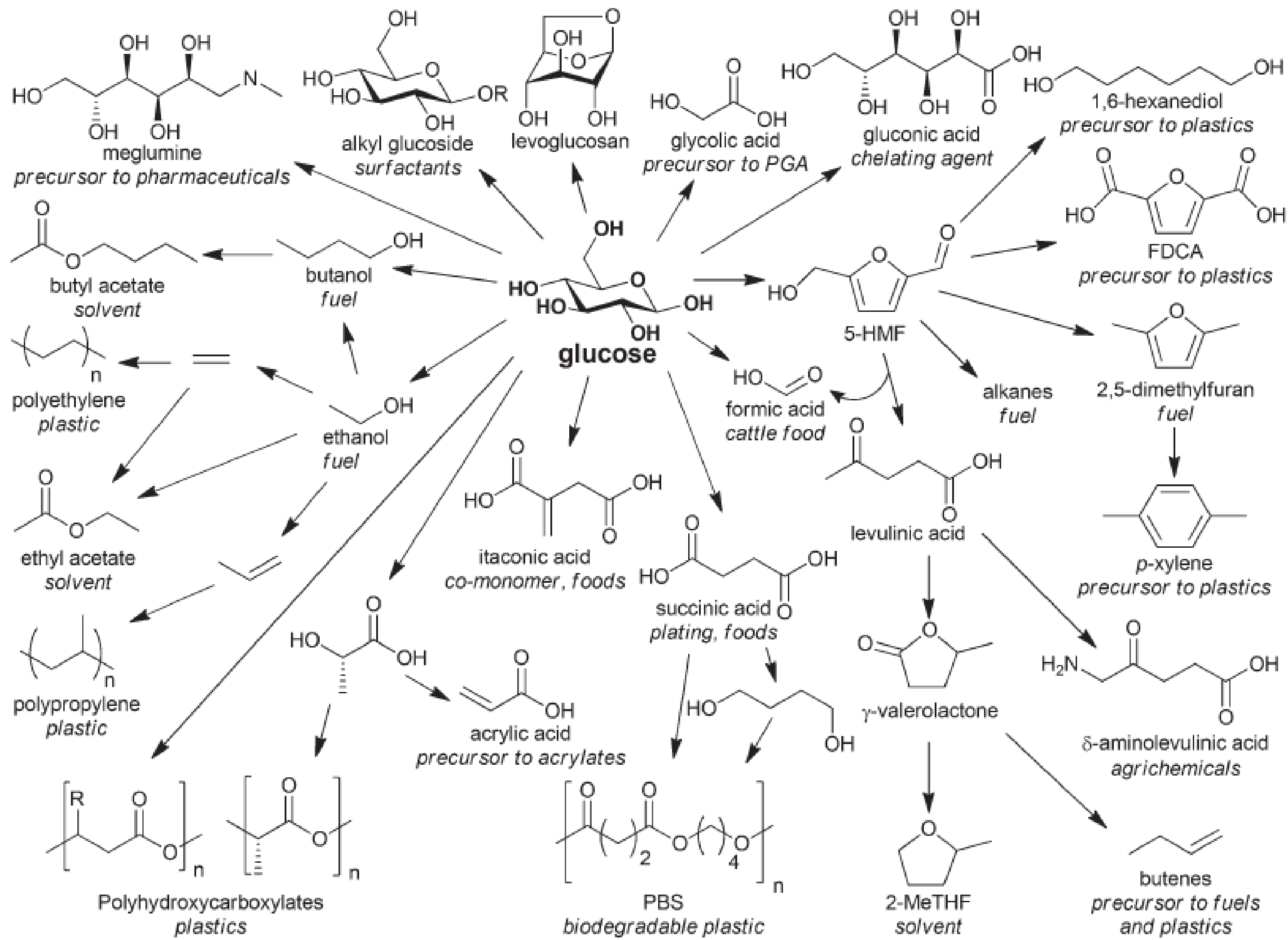
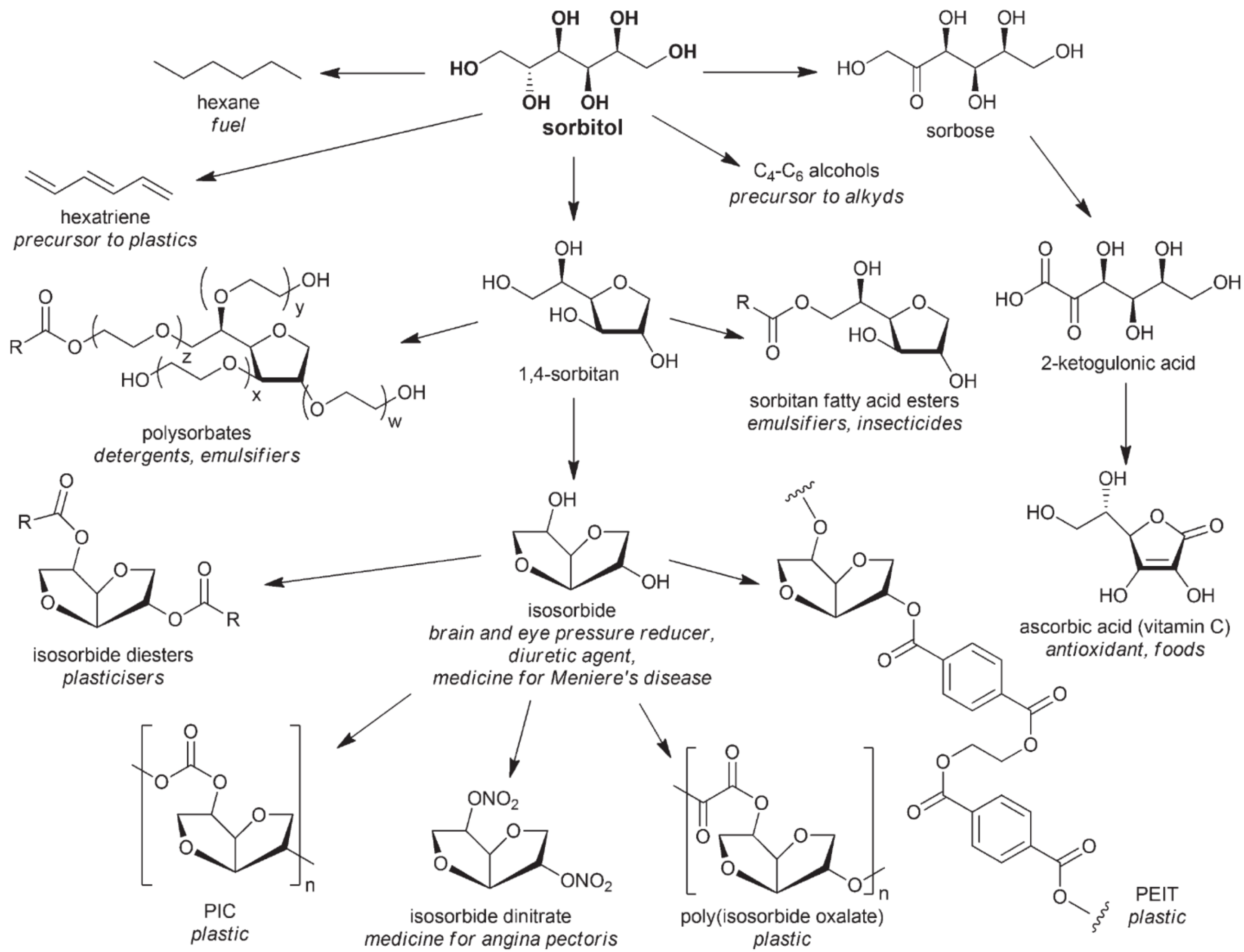
Appendix Derivatives of glucose and applications



A. Fukuoka et al. *Green Chem.* **2013**, *15*, 1740.

Appendix Derivatives of sorbitol and applications



A. Fukuoka et al. *Green Chem.* **2013**, *15*, 1740.