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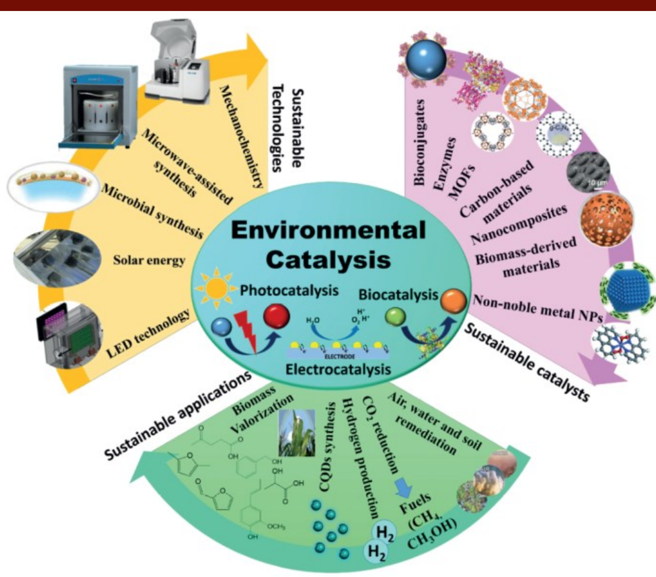
Environmental Catalysis

Name: Jana Roithova
Function: Prof
Website: https://www.ru.nl/science/spectroscopy-and-catalysis/

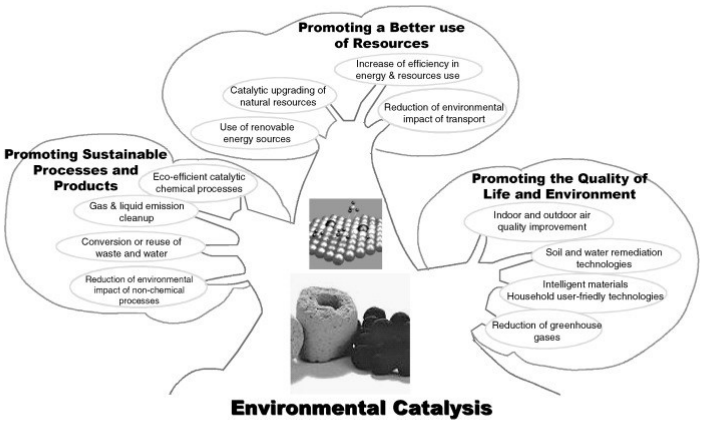
Environmental Catalysis



Rodrıguez-Padron et al. ChemCatChem **2019**, *11*, 18–38

Environmental Catalysis

- Catalytic technologies for reducing emissions of environmentally unacceptable compounds.



Catalysis Today
Volume 75, Issues 1–4, 3 July 2002, Pages 3-15

Features of environmental catalysis

Developing environmental catalysts:

- Conditions are often given (e.g., emissions in air, exhaust gases, waste water)
- Catalysts often operate at unfavorable conditions
  - low/high temperatures
  - in the presence of catalyst poisons
  - with ultra-low concentrations
  - under varying conditions

Catalysis Today
Volume 75, Issues 1–4, 3 July 2002, Pages 3-15

Examples in Environmental Catalysis

- Catalysis for clean air
- Catalysis for clean water

- Catalysis for use of renewables – production of H_2
- Catalysis for use of renewables – CO_2 reduction
- Catalysis for use of renewables – Biomass conversion
- Catalysis of plastic recycling

Catalysis for clean air

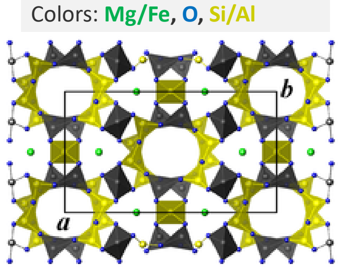
Catalytic removal of toxic substances

Toxic substance	Source	Removal
Hydrocarbons (VOCs)	Chemical / petroleum industry, Solvents, Car exhausts	Oxidative
Carbon monoxide	Car exhausts	Oxidative
Sulphur dioxide	Power plants, Heating	Reductive / Oxidative
Nitric oxides	Car exhausts, Power plants	Reductive

- catalysts: usually precious metals (Pt, Pd, Rh) dispersed on a porous support (e.g., honeycomb ceramics – synthetic cordierite)
- Reduction (Pt, Rh): $NO_x \rightarrow N_2 + O_2$
- Oxidation (Pt, Pd): $CO + O_2 \rightarrow ½\ CO_2$ and $C_nH_m + O_2 \rightarrow CO_2 + H_2O$

- See also a separate video clip!

Crystal structure of Cordierite.
Colors: Mg/Fe, O, Si/Al



Waclawek et al. *Ecol. Chem. Eng.* **2018**, *25*, 9.

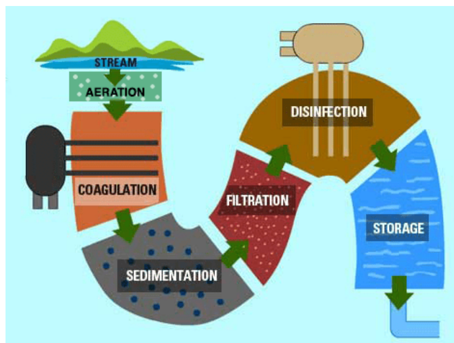
Catalysis for clean water

Contaminants of dirty (grey) water:

- **Physical**: particles of soil or organic matter from soil erosion
- **Chemical**: elements or compounds that are natural or human-made, such as pesticides, bleach, nitrogen, human and/or animal drugs, metals, or toxins produced by bacteria. Some chemical contaminants (such as cesium, plutonium and uranium) are also dangerous because they can emit radiation.
- **Biological (or Microbial)**: organisms that live in water, such as bacteria, viruses, protozoan, and parasites

For details see:

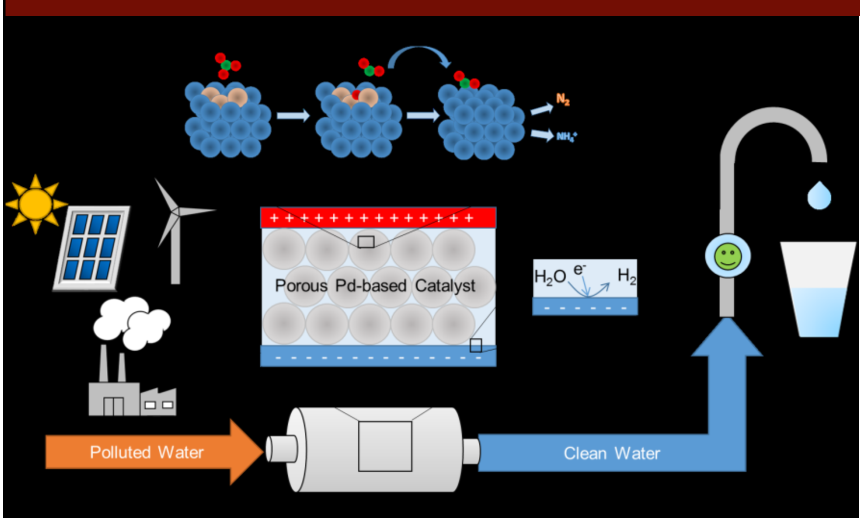
https://youtu.be/oaXth88i7rk



Source: http://www.eschooltoday.com/global-water-scarcity/how-water-is-treated-for-drinking.html

K. H. Heck et al. *Acc. Chem. Res.* **2019**, *52*, 906–915.

Catalysis for clean water



K. H. Heck et al. *Acc. Chem. Res.* **2019**, *52*, 906–915.

Catalysis for clean water

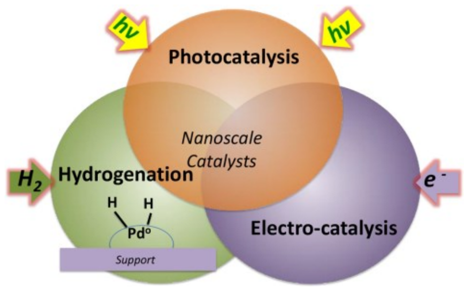
The common contaminants:

- **Chlorinated Volatile Organic Compounds**
  - low-molecular-weight organic chemicals such as perchloroethylene, trichloroethylene, trichloroethane, vinyl chloride, and chloroform
- **Nitrate and Nitrite Contamination**

How can we remove them?

→ **catalytic reduction to**

- Cl^-, C_nH_m
- N_2



K. H. Heck et al. *Acc. Chem. Res.* **2019**, *52*, 906–915.

Catalysis for clean water

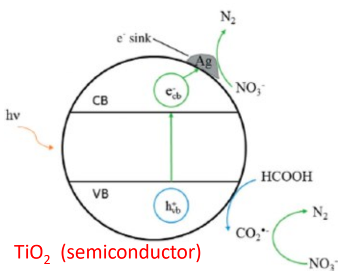
- **Heterogeneous Hydrogenation Catalysis**
  - Metal nanoparticles (e.g., Pd) on a support (e.g., SiO_2, Al_2O_3, C)
  - Pd NPs can reduce NO_2^- to N_2
  - Pd alone cannot reduce NO_3^- → mixed NPs
  - In-on-Pd NPs
    - In catalyzes NO_3^- → NO_2^-
    - Pd catalyzes NO_2^- → N_2 and generated H adatoms
    - H adatoms reduce the oxidized In atoms

- **Alternatively – catalytic production of H_2O_2**
  - $H_2 + O_2 \rightarrow H_2O_2$ with the selectivity of >95%
  - Catalyst: Palladium-tin
    - Tin oxide surface layer encapsulates small Pd-rich particles
    - Larger Pd-Sn alloy particles exposed

K. H. Heck et al. *Acc. Chem. Res.* **2019**, *52*, 906–915.
S. J. Freakley et al., *Science*, **2016**; *351* (6276): 965.

Catalysis for clean water

- **Photocatalytic Nitrate Reduction**
  - UV light to generate the electrons required for reduction
  - the best (composite) catalyst: silver-loaded TiO_2



TiO_2 (semiconductor)

organic "hole" scavenger

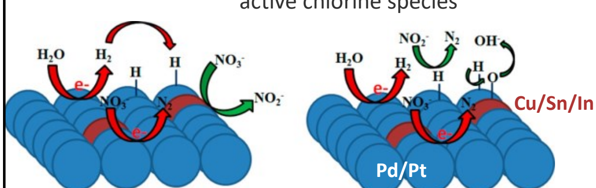
Composite photocatalysts
- modify the charged region near the surface
- the work function of the metal is lower than that common photocatalysts (e.g., TiO_2)

→ The metal behaves as an electron sink and enables nitrate reduction.

K. H. Heck et al. *Acc. Chem. Res.* **2019**, *52*, 906–915.

Catalysis for clean water

- **Electrochemical Nitrate Reduction**
  - Electrolytic reactors at least two electrodes
    - **cathode** → e.g., nitrate reduction
      - Pt/Pd reduce nitrate and protons → highly reductive H adatoms ($H_{(ad)}$) → reduction involves both direct charge transfer via electrocatalysis and catalytic reduction by $H_{(ad)}$.
    - **anode** → oxidation reactions occur
      - with a high overpotential→ in situ hydroxyl radicals or active chlorine species



K. H. Heck et al. *Acc. Chem. Res.* **2019**, *52*, 906–915.

Use of renewables: H_2 production

- Electrochemical water splitting
  - HER catalysts: transition metals, metal carbides, C-based materials
  - OER catalyst: Co-, Ni-based
- Also photocatalytic water splitting
  - less efficient
  - TiO_2, ZnO, MOF
  - noble-metals as co-catalysts
  - sacrificial reagents produced from biomass

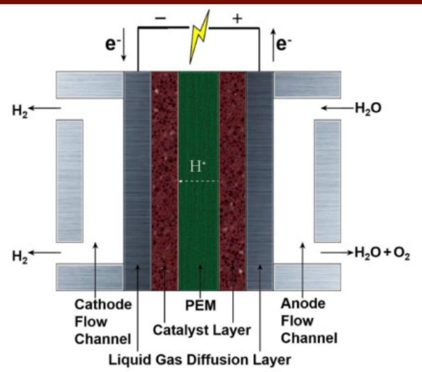


Figure 15. Schematic representation of a PEMEC. Reproduced with permission of ref.[144] Copyright, 2016 Royal Chemical Society.

PEMEC= proton exchange membrane electrolyzer cell

Rodrıguez-Padron et al., *ChemCatChem* **2019**, *11*, 18–38.

Use of renewables: CO_2 reduction

- Electrochemical reduction of CO_2 → see also the separate video clips on
  - CO_2 reduction
  - Fischer-Tropsch synthesis
- Photochemical reduction of CO_2
  - semiconductors
    - active field of research, new 2D materials with improved efficiencies and selectivities
  - competition with H_2 evolution

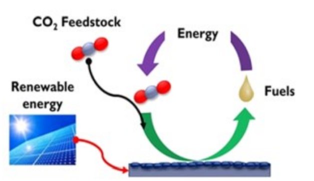


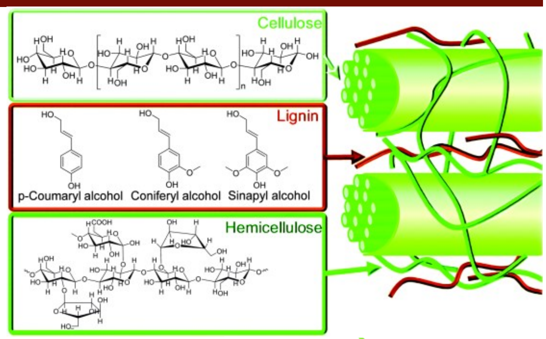
Figure 16. Overview of an electrochemical CO_2 conversion system powered by renewable energy. Reproduced with permission of ref.[145] Copyright, 2016 Elsevier.

Rodrıguez-Padron et al., *ChemCatChem* **2019**, *11*, 18–38.

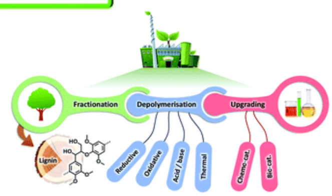
Use of renewables: Biomass conversion

Main composite:

- Lignocellulose (>170 billion tons ann.)
- Currently: pyrolysis or gasification → syngas

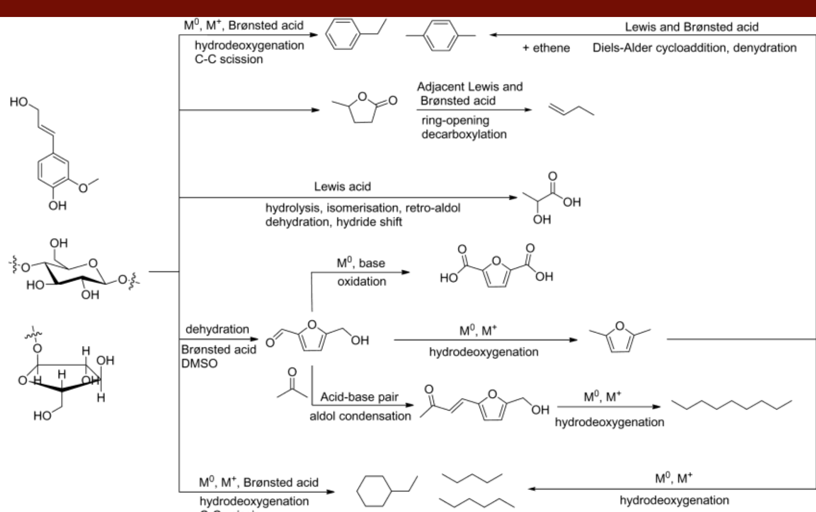


- Alternatively – catalysis
  - need for a pre-treatment to isolate pure components (separation based on different properties)

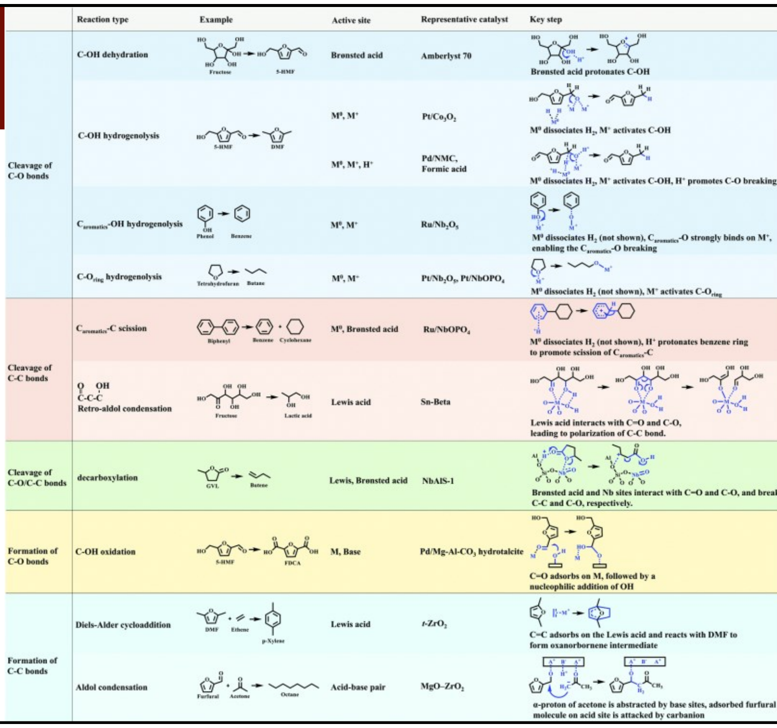


L. Lin et al., *Chem. Soc. Rev,* **2021**, *50*, 11270.
Limayem A. et al., *Prog. Energy Combust. Sci.* **2012**, *38* , 449 —467.
Schutyser W. et al., *Chem. Soc. Rev.* **2018**, 47, 852-908.

Use of renewables: Biomass conversion



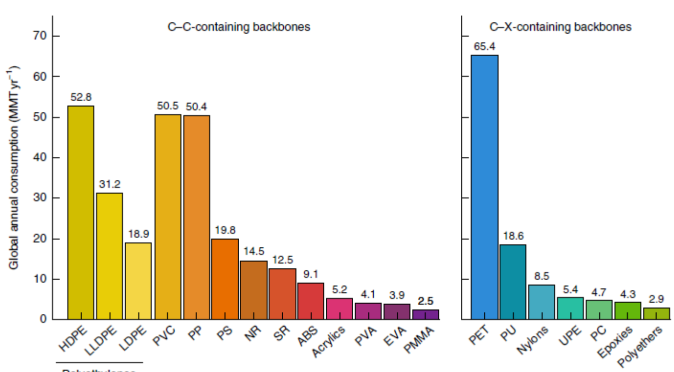
L. Lin et al., *Chem. Soc. Rev,* **2021**, *50*, 11270.
Schutyser W. et al., *Chem. Soc. Rev.* **2018**, 47, 852-908.



	Reaction type	Example	Active site	Representative catalyst	Key step
Cleavage of C-O bonds	C-OH dehydration	Fructose → 5-HMF	Brønsted acid	Amberlyst 70	Brønsted acid protonates C-OH
	C-OH hydrogenolysis	5-HMF → DMF	M^0, M^+	Pt/Co_3O_4	M^0 dissociates H_2, M^+ activates C-OH
			M^0, M^+, H^+	Pd/NMC, Formic acid	M^0 dissociates H_2, M^+ activates C-OH, H^+ promotes C-O breaking
	$C_{aromatics}$-OH hydrogenolysis	Phenol → Benzene	M^0, M^+	Ru/Nb_2O_5	M^0 dissociates H_2 (not shown), $C_{aromatics}$-O strongly binds on M^+, enabling the $C_{aromatics}$-O breaking
	$C-O_{ring}$ hydrogenolysis	Tetrahydrofuran → Butane	M^0, M^+	Pt/Nb_2O_5, $Pt/NbOPO_4$	M^0 dissociates H_2 (not shown), M^+ activates $C-O_{ring}$
Cleavage of C-C bonds	$C_{aromatics}$-C scission	Biphenyl → Benzene + Cyclohexane	M^0, Brønsted acid	$Ru/NbOPO_4$	M^0 dissociates H_2 (not shown), H^+ protonates benzene ring to promote scission of $C_{aromatics}$-C
	Retro-aldol condensation	Fructose → Lactic acid	Lewis acid	Sn-Beta	Lewis acid interacts with C=O and C-O, leading to polarization of C-C bond.
Cleavage of C-O/C-C bonds	decarboxylation	GVL → Butene	Lewis, Brønsted acid	NbAlS-1	Brønsted acid and Nb sites interact with C=O and C-O, and break C-C and C-O, respectively.
Formation of C-O bonds	C-OH oxidation	5-HMF → FDCA	M, Base	$Pd/Mg\text{-}Al\text{-}CO_3$ hydrotalcite	C=O adsorbs on M, followed by a nucleophilic addition of OH
Formation of C-C bonds	Diels-Alder cycloaddition	DMF + Ethene → p-Xylene	Lewis acid	$t\text{-}ZrO_2$	C=C adsorbs on the Lewis acid and reacts with DMF to form oxanorbornene intermediate
	Aldol condensation	Furfural + Acetone → Octane	Acid-base pair	$MgO–ZrO_2$	α-proton of acetone is abstracted by base sites, adsorbed furfural molecule on acid site is attacked by carbanion

L. Lin et al., *Chem. Soc. Rev,* **2021**, *50*, 11270.

Catalysis for plastic recycling



L. D. Ellis et al., *Nat. Cat.* **2021**, *4*, 539.

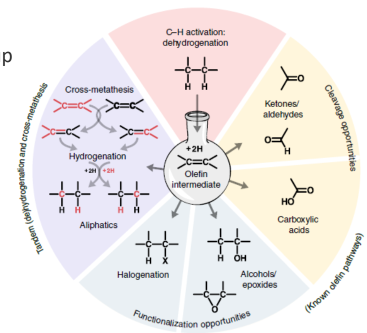
Catalysis for plastic recycling

Processes of depolymerization

- C-C bonds (PE, PP, polystyrene, …)
  - Non-catalyzed pyrolysis (C-C hemolysis, radical mechanism)
  - Catalytic cracking (usually with acidic zeolites, carbocation-based chemistry)
  - Catalytic processes (initiated by C-H activation reactions)

Olefin-intermediate process

- Cracking can be coupled with follow-up reactions leading to valuable feedstocks
  - hydrogenation
  - oxidative C=C cleavage
  - hydration
  - halogenation

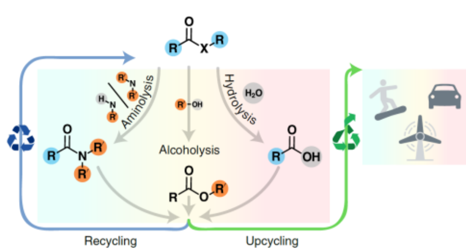


L. D. Ellis et al., *Nat. Cat.* **2021**, *4*, 539.

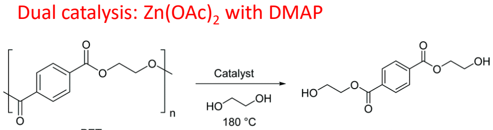
Catalysis for plastic recycling

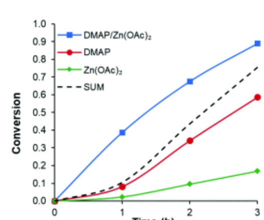
Processes of depolymerization

- C-O and C-N bonds (PET, nylon, polycarbonate, …)
  - much easier than C-C bond, require less energy, ~thermo-neutral
  - nucleophilic reactions (reaction with carbonyls)
  - **solvolysis**



Glycolysis of PET
Dual catalysis: $Zn(OAc)_2$ with DMAP





L. D. Ellis et al., *Nat. Cat.* **2021**, *4*, 539.
k. R. Delle Chiaie et al., *Polym. Chem.* **2020**, *11*, 1450.

Learning objectives

You should be able to explain and understand

- what catalytic processes you can encounter at everyday life
- how is the catalysis used to make air cleaner
- how is the catalysis used to clean water
- how is the catalysis used to convert biomass to useful chemicals
- what would be greener ways to produce H_2
- how the exhaust catalysts for car work (see the extra video clip)
- how does CO_2 reduction work (see the extra video clip)
- how we can recycle plastics and
  what would be a role of catalysis in it.

Do the quiz and see you in the class!