Water as a Solvent in Heterogeneous Catalysis

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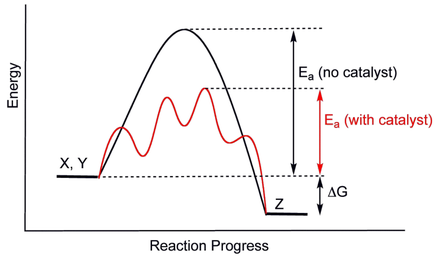
Heterogeneous catalysts[1]

Catalyst: a material that is able to increase the rate of a reaction

Heterogeneous catalyst: catalysts that differ in state compared to the reaction medium



Previous applications of heterogeneous catalysts in aqueous media[2]

CH_4 Activation

- High ionization energy, weak acidity, and low electron/proton affinity make CH_4 activation difficult
- Activation proceeds via a partial oxidation and oxidative carbonylation
- Catalyst system is typically iron or copper-doped Zeolite

Hydrogenation

- CO is a common pollutant in the Earth's atmosphere
- Water and CO act as reducing agents in the reaction in the presence of metal complexes
- Gold and ceric oxide (CeO_2) are common catalysts for the conversion of carbonyls to alcohols

Scheme 1: Reactions showing (i) CH_4 activation (ii) Hydrogenation

How/why does the tool relate to Green and Sustainable Chemistry?

Environmentally friendly solvent: Water is non-toxic, non-flammable, and readily available, eliminating the need for hazardous organic solvents often used in traditional catalysis.

Improved safety: Eliminating flammable organic solvents significantly improves safety during reaction setup, handling, and disposal.

Catalyst reusability: Catalyst can be easily separated from the aqueous reaction mixture after the reaction. This allows for the catalyst to be washed, dried, and reused in subsequent reactions, minimizing catalyst waste, and reducing production costs.

Reduced waste and pollution: Heterogeneous catalysis in water often leads to cleaner reactions with minimal byproducts compared to organic solvent systems. This minimizes waste generation and reduces the environmental impact of the process.

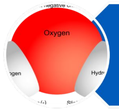
Water as a green solvent in heterogeneous catalysis

Water, covering 71% of the planet, is abundant, cheap, and readily available. Unlike many commonly used solvents such as acetone, toluene, ethanol, ethyl acetate, and hexane, which are derived from fossil fuels and have significant environmental impacts, water is seen as a green alternative.

Advantages of using water as a solvent

Environmentally benign

- Safe and none toxic



Chemical properties

- Hydrogen bonds, polarity, low viscosity, high specific heat capacity and others

Establish use a solvent

- Diels-Alder reactions, aldol condensation and Esterification reactions.

When water is used in heterogeneous catalysis is not only used regarding its ability as a solvent but instead also:

Promoter: The addition of water into a system can improve the ability of the catalyst in hydrogenation reactions and selectivity.

Green source of hydrogen: the use of heterogeneous catalysts in electrocatalysis and photocatalysis to preform water splitting.

Challenges with using water as a solvent

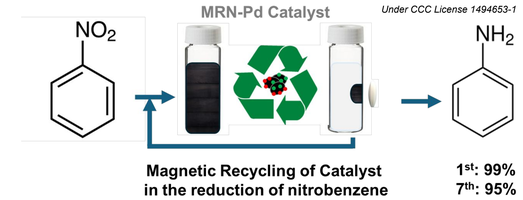
Reactivity and Solubility Issues: Water can also cause unwanted side reactions and has limited solubility for many compounds.

Operational Limitations: High freezing/boiling points, pressure requirements, and potential corrosion of equipment.

Environmental and Purity Concerns: Contaminated wastewater with heavy metals and chemicals leads to pollution of fresh water sources and the desalination of seawater to acquire fresh water uses fossil fuels derived energies which also has environmental impacts.

Examples of successful applications

***Magnetic nanocatalysis* for the reduction of nitroaromatics in aqueous media[4]**

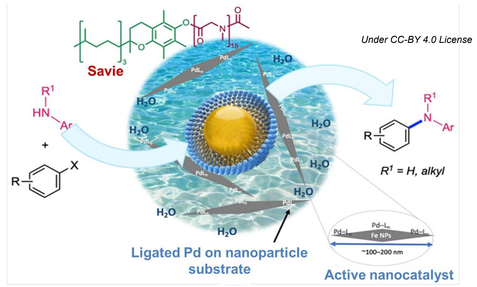


Environmental Metrics: Mild reaction conditions, no reducing agent.

Sustainability Metrics: Magnetic retrievability, efficiency across seven cycles, high yield over multiple cycles.

Range of applications: Reduction of nitroaromatics, Suzuki and Heck cross-coupling reactions for pharmaceuticals, polymers, pesticides, and cosmetics.

***Micellar catalysis* for aminations in water[5]**



Broad substrate scope | Use of a biodegradable surfactant
Complex pharmaceutical derivatization

Metal Economy: Low levels of Pd and use of Fe NPs.

Sustainability Metrics: Recyclable catalyst, recyclable aqueous reaction medium, use of ocean water.

Range of Applications: Pharmaceutical APIs and complex targets.

References

1. Lancaster, M. *Green Chemistry: An Introductory Text*; The Royal Society of Chemistry, 2016. https://doi.org/10.1039/9781839168888 (accessed June 9, 2024); **2.** Lin, L. *et al. JACS Au,* **2021**, *1* (11), 1834–1848; **3.** Lajoie et al., *Pharmaceuticals (Basel)* **2022**, 15 (12); **4.** Shokouhimehr *et al., Green Chem.*, **2018**,20, 3809-381; **5.** Iyer *et al., ACS Sustainable Chem. Eng.* **2024**, 12, 5, 1997–2008; **6.** Andrushkevich *et al., Molecular Catalysis.* **2020**, 484, 110734.

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