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HYDROGENATION | FACT SHEET

Background

Hydrogenation reactions are a mainstay of synthetic chemistry, used to reduce double and triple bonds and in the deprotection of certain functional groups. These reactions are, however, often intrinsically hazardous due to the necessity of hydrogen gas, which is highly flammable. These reactions often also require catalysts, particularly for syntheses that require selective reduction or aim for specific stereochemistry. Assessing the risks of such reactions is often complicated: while the hazards associated with hydrogen are well-documented, the hazards associated with the catalysts are less well known. In some cases, hazard classification of the same material can be different from manufacturer to manufacturer. This fact sheet will familiarize you with several of the most common hydrogenation catalysts, the hazards involved in their use, strategies for risk reduction, and resources for more in-depth information.

Reagents

Hydrogen

Hydrogen is a colorless, odorless gas with a very low density (>10 times less dense than air). It is an asphyxiant, but hydrogen's primary hazard comes from its extreme flammability. Hydrogen has a very wide range of flammability, with a lower explosive limit of 4% and an upper explosive limit of 76% in air. Hydrogen also has a very low energy of ignition, meaning that it catches fire very easily.

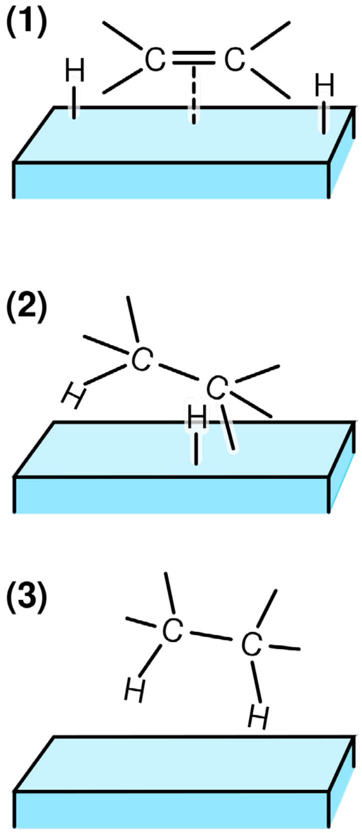

Figure 1. Simplified depiction of catalytic hydrogenation. (Schmid)

Catalysts

The three most common hydrogenation catalysts (Raney nickel, palladium on carbon, and platinum oxide) have shared properties. All are metals that have been prepared in such a way that they have a high surface area. They all work by roughly the same mechanism, adsorbing hydrogen to their surface, then adsorbing the substrate, and facilitating reaction by bringing the two into closer physical proximity. This adsorption means that even once the reaction is completed, there is often excess hydrogen on the catalyst surface, with no simple way of telling once it all has been driven off. Consequently, the catalyst can accelerate the reaction of hydrogen with oxygen in a highly exothermic process, igniting excess hydrogen. This means that once hydrogen is adsorbed (a state referred to by saying the catalyst is charged), these catalysts become pyrophoric.

Raney Nickel

Raney nickel is a form of nickel made by special treatment of a nickel-aluminum alloy, resulting in highly porous small grains. In addition to hydrogenation, Raney nickel is used in desulfurization reactions. Raney nickel is often sold as an air-stable slurry, with the particles suspended in water. If this slurry dries, the resultant powder is highly pyrophoric. Raney nickel sold as a loose powder will ignite almost instantly upon contact with air. Raney nickel's efficacy decreases with age, rendering it non-pyrophoric but also unusable for synthesis.

Palladium on Carbon

Palladium on carbon, often abbreviated as Pd/C, consists of palladium deposited onto activated carbon, forming a black powder. The percentage of palladium on the carbon (referred to as the "loading") varies, with 5% and 10% being common loadings. Before being charged with hydrogen, Pd/C is non-pyrophoric in air, though it becomes pyrophoric in the presence of flammable solvent and air. Once charged with hydrogen, Pd/C is pyrophoric when dried of water. Ignition is accelerated in the presence of flammable solvent and/or vapors.

Platinum Oxide

Platinum (IV) oxide, also known as Adams' Catalyst, is a dark brown powder. PtO2 is an oxidizing solid (category 2), meaning that it will moderately accelerate an ongoing combustion reaction and/or may cause spontaneous combustion when in contact with combustible material. Once charged with hydrogen, dry PtO2 is very pyrophoric in presence of air, igniting instantly.

Solvents

Solvents used in hydrogenation reactions vary. As a general rule, less flammable solvents are preferred for hydrogenation reactions.

Best Practices

The section below gives you many key notes on how to safely perform hydrogenation reactions, but is ultimately just an overview; there is a wealth of other resources. We strongly recommend you read "Hazards associated with laboratory scale hydrogenations" by Zebrowski and Chandra (see here), a short paper that provides more in-depth explanation of best practices and includes diagrams.

- Before beginning your experiment, meet with your PI to discuss your plans. If during the course of the experiment it seems like you may have to deviate from your plan, clear any changes with your PI.
- EH&S strongly recommends conducting a risk assessment and/or writing an SOP before conducting the experiment. EH&S is always available for consultation on SOPs, and we particularly recommend reaching out if hydrogenation reactions are a new process for your laboratory.
- Hydrogenations at elevated pressures can pose unique challenges that fall outside the scope of this sheet. If you would like to pursue these reactions, please contact EH&S.
- Perform your experiments at the smallest feasible scale.
- Be highly cautious of scaling up your reaction or making any other changes. Scaling up and/or altering existing procedures without reassessing risk is a common cause of incidents. Do not scale greater than three times for each iteration.
- Clear your work area of combustible materials before you begin.
- Make sure you have an ABC fire extinguisher accessible.
  - A Class D metal fire extinguisher is not necessary because the catalyst is not burning, the hydrogen is.
- Thoroughly review proper work practices for all materials involved before beginning. For example, Raney nickel often cannot be weighed out easily because it is a slurry.
- Perform the hydrogenation reaction behind a blast shield.
- Ensure that air is kept out of the reaction vessel at all times.
- Never allow your catalyst to dry out, especially once charged with hydrogen. This can be particularly challenging during filtration.

- Be sure that all free hydrogen has been removed from the reaction vessel by purging with inert gas for 3-5 minutes before allowing air to enter the reaction for any reason, including opening the reactor to take an aliquot for monitoring conversion, to add more catalyst, or to begin working up the reaction. It is critical to remove the hydrogen atmosphere before opening the reactor for any reason.
- If your hydrogenation was carried out at elevated temperature, allow the reaction mixture to return to room temperature before handling.
- If practical, provide an inert atmosphere over the filtration apparatus per Figure 2. If this is not practical, consider using a Schlenk frit.
- During filtration do not allow the solvent level in the fritted funnel to go below the top of the celite pad, this is what we call letting the catalyst become dry, to maintain this solvent level, apply only a low vacuum to the filter flask and have additional solvent and water on hand.
- Do not pour solvent for this process from a 4-liter solvent bottle, first pour the amount of solvent you will need into a separate flask or beaker and then pour from this.

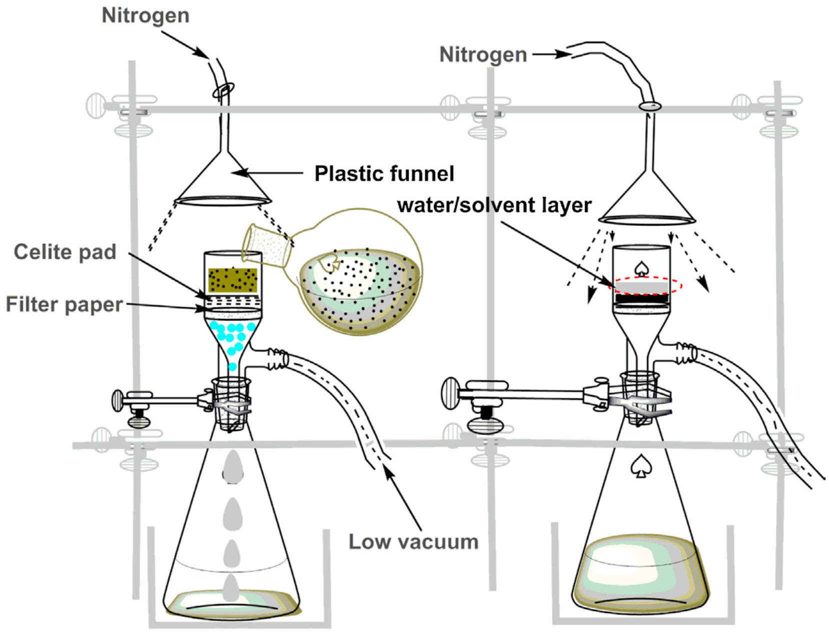

Figure 2. A diagram of how to create an inert atmosphere over filtration apparatus. (Chandra et al.)

- Do not allow the filter cake to dry; following the filtration it is best to wet the filter cake (containing catalyst) with water.
- Never leave filtration of the catalyst unattended.

Waste Disposal

- Once your experiment is complete, remove any waste catalyst to its own waste container and immediately submerge it in copious water. Be sure to affix a waste tag to the container.

Incident Response

- For small spills of moist catalyst, use wetted paper towel to wipe up the catalyst. Place the paper towel in a waste container and submerge it in water.
    - If the catalyst ignites during the clean-up process, follow fire guidance below.
- For spills of dry catalyst, widely dispersed spills, and other spills that you cannot address before the catalyst ignites, evacuate the area and call 911.
- If a fire starts, call 911 and evacuate the area immediately.

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