

Heterogeneous Catalytic Hydrogenation

Platinum group metals as hydrogenation catalysts in a two-day course

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Introduction

Heterogeneous catalytic hydrogenations are important reactions that find wide industrial application in the production of pharmaceuticals, agrochemicals, fine chemicals, flavours, fragrances and dietary supplements. The reactions are generally highly selective and easy to work up, the catalyst can often be recovered and recycled, and the processes are atom efficient. It is therefore no surprise that somewhere between 10–20% of the reactions used to produce chemicals today are catalytic hydrogenations. Despite the importance of the technique, and mainly because of its multidisciplinary nature, development chemists and engineers have a hard time finding training on this highly specialised subject.

Scientific Update has filled this gap with a training course run for the first time on the 16th and 17th of April 2012, in Brussels, Belgium (1). Attended by 35 scientists from 10 European countries and the USA, representing 27 chemical companies and research institutions, the course was an extensive scientific overview of heterogeneous catalytic hydrogenation, but also touched on engineering, safety and economic topics.

The tutor was Felix Roessler, a catalysis expert who during his long career has worked at Roche and DSM, was honoured twice with the Sandmeyer Award granted by the Swiss Chemical Society (2), has authored 18 publications or monographs and holds 4 patents. He currently works as an independent consultant.

Herein I will provide a flavour of the topics that were presented at the course.

Surfaces

Many processes that involve the exchange of material, energy or even information happen through surfaces. Natural selection has helped living organisms to come up with efficient solutions to the problem of gathering energy and nutrients, systems often based on high surface areas, as for example broad leaves where photosynthesis takes place, or the wrinkled and folded tissue of the small intestine.

Technological applications also take advantage of the properties of surfaces, for instance solar cells, heat exchangers, microchips and of course heterogeneous catalysis whereby a chemical reaction takes place on the surface of a metal at the interface between a solid phase (the catalyst) and a liquid or gaseous phase (the reaction medium).

Most of the metals used in heterogeneous catalysis are organised in a face-centred cubic (fcc) tightly packed crystal structure in which each atom has a maximum of 12 nearest neighbours (Figure 1). The metal atoms at the surface are the only ones presenting vacancies where the reactants can bind. For this reason a catalyst made in such a way that the metal particles are highly dispersed on a porous support with high surface area generally has higher activity. As an example palladium on carbon support has higher activity than palladium supported on graphite. At the microscopic level the surface of a catalyst is an irregular and dynamic structure in which the metal particles can be rearranged by interaction with the reaction medium.

The adsorption of chemicals onto the catalyst surface takes place in two stages: physisorption characterised by weak forces (van der Waals) and chemisorption that involves the formation of chemical bonds. Chemisorption can be associative, meaning that the adsorbate maintains intact its chemical structure (for example, in the case of alkenes adsorbed onto platinum on carbon), or dissociative, when by binding to the metal the structure of the adsorbate is

fragmented (as in the case of hydrogen adsorbed onto platinum on carbon).

Types of Heterogeneous Catalysts

The properties required for a heterogeneous catalyst are:

- (a) high activity;
- (b) high selectivity;
- (c) fast filtration rate; and
- (d) recycle capability.

Activity and selectivity are greatly dependent on the choice of metal. This influences the strength of adsorption of reactants, the rate of desorption of reaction products and the rate of chemical transformations. The metals most frequently used in heterogeneous catalytic hydrogenation are palladium, platinum, rhodium, nickel, cobalt and ruthenium. More rarely iridium, copper and rhenium find applications. Figure 2 (3) illustrates how the product of a reaction can vary depending on the choice of metal catalyst.

Heterogeneous catalysts may be unsupported or supported. Examples of unsupported catalysts include Raney nickel or cobalt. These are made by chemically dissolving the aluminium out of nickel-aluminium or cobalt-aluminium alloys and they are used for the reduction of carbonyl functions, nitriles and oximes. In supported catalysts, the metal is deposited on an inert material such as carbon, graphite, alumina or inorganic salts. They find a vast range of applications according to the metal used. Supported palladium

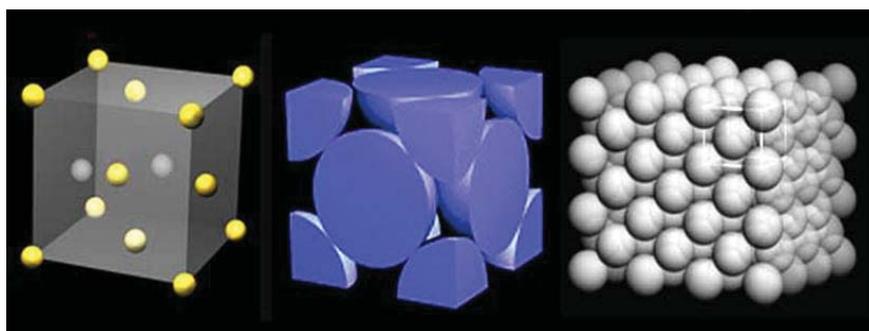


Fig. 1. The fcc unit cell. This structure is exhibited by platinum, palladium, rhodium and iridium

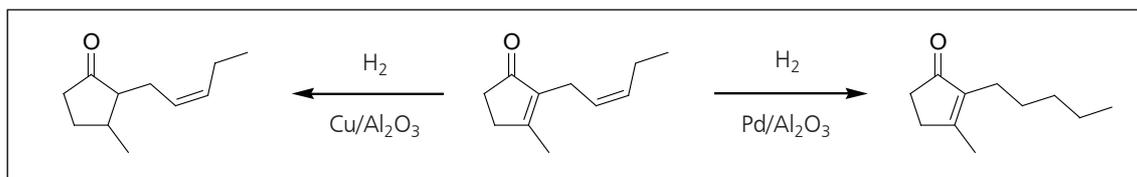


Fig. 2. Divergent outcomes in the hydrogenation of *cis*-jasmone when catalysed by copper or palladium (3)

catalysts are used for the reduction of carbon-carbon multiple bonds, multiple bond isomerisation and hydrogenolyses. Supported platinum is used for carbon-carbon and carbon-heteroatom double bonds; rhodium for the reduction of aromatic systems; and ruthenium for the reduction of aromatic, carbonyl and carboxylic acids.

Supported catalysts present advantages such as easy separation from the reaction medium and more effective use of the metal surface, as the metal is generally deposited as nanoparticles (between 1 to 10 nm in diameter). Its interaction with the support can also influence the properties of the catalyst, as well as providing stabilisation against particle conglomeration. The metal can just decorate the surface of the support or it can reach inside the micropores; depending on the mode of distribution, catalysts can thereby be classified as eggshell, uniform or intermediate. The rate of reaction with an 'eggshell' catalyst responds linearly to changes of hydrogen pressure, while uniform catalysts require higher pressure to overcome pore diffusion limitations (Figure 3), although they usually provide better selectivities.

The metal may be present in oxidic or reduced form, depending on the method of catalyst preparation. Oxidic type catalysts are reduced *in situ* and therefore frequently show an induction period. They are best suited for hydrogenolyses but they are also prone to metal leaching with consequent colloid formation.

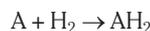
Kinetics and Thermodynamics

The observed rate of heterogeneous catalytic hydrogenations is affected by a combination of factors:

- (a) the mass transport of reactants through the gas/liquid interface;
- (b) the liquid bulk and liquid/solid interface;

- (c) adsorption or desorption of reactants on the catalyst surface; and
- (d) the intrinsic rate of the chemical reactions.

Given the catalysed hydrogenation of a generic substrate A:



A simple equation of the rate of the rate of reaction based on Langmuir model of adsorption (4) is the following (i):

$$r = m_{cat} k \frac{K_A p_A K_H p_H}{(1 + K_A p_A + K_H p_H + K_{AH_2} p_{AH_2})^2} \tag{i}$$

where r is the rate of reaction, m_{cat} is the mass of the catalyst, k is the reaction rate constant, K_i is the adsorption constant of component i and p is the concentration (or partial pressure) of the adsorbate.

Mass transport limitation (i.e. the transport of hydrogen from gas to liquid phase) can have a negative effect on reaction selectivity and can become an important factor when stirring is inefficient or when catalyst activity or loading are high. In such cases the observed rate will only depend on the concentration of hydrogen and can be described by Equation (ii):

$$r = k_1 a (p_{H_2g} - p_{H_2l}) \tag{ii}$$

where r is as defined above, and p_{H_2g} and p_{H_2l} are the concentration of hydrogen in the gas and liquid phase respectively. The constant $k_1 a$ (volumetric mass transfer coefficient) is an important parameter that is often calculated to estimate the efficiency of hydrogenation equipment. It varies hugely with reaction scale, ranging typically from 2.1 s⁻¹ for a 1 litre vessel to 0.05 s⁻¹ for a 24,000 litre reactor. As a consequence, the bigger the scale the harder it becomes to set up a process outside the boundaries of the mass transport limitation.

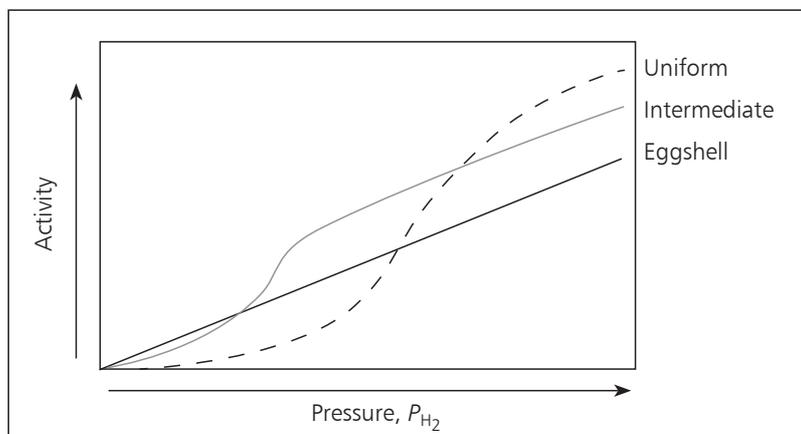


Fig. 3. Influence of hydrogen pressure on the hydrogenation rate for eggshell, intermediate and uniform catalysts

Hydrogenation reactions have enthalpies of 100–500 kJ mol⁻¹ and are in most cases reversible, nevertheless a steady pressure of hydrogen is usually all that is needed to drive them to completion.

Reaction Conditions, Solvents and Additives

In real-world industrial applications, almost every time a hydrogenation is carried out a problem of selectivity arises. The desired transformation is often only one among several possible outcomes, since if multiple reaction pathways are involved their relative rate will depend on parameters such as temperature, pressure, concentration of reagents, amount of catalyst and so on. Therefore optimisation of the reaction conditions is required.

In the rhodium-catalysed hydrogenation of nitrochlorobenzenes, higher pressure favours the selective reduction of the nitro group, while at low pressure the hydrogenolysis of the carbon-chlorine bond prevails (5). Hydrogenations form preferentially *cis* products (6), although the selectivity can be influenced by the reaction conditions. Low hydrogen pressure and high temperature usually bring an increase of *trans* products (7, 8), as demonstrated in the case of a rhodium-catalysed hydrogenation carried out on disubstituted aromatic compounds (Figure 4).

Solvents are an important but not indispensable component of heterogeneous catalytic hydrogenation. A liquid substrate can in fact be hydrogenated without a solvent, although solvents are useful as they strongly affect the reaction rate and selectivity and act as heat sinks. Hydrogenation can be carried out in a variety of solvents, from water to non-polar organic solvents. The latter are about four times better

at dissolving hydrogen. Hydrogenation reactions catalysed by platinum group metals may be carried out in water, alcohols, tetrahydrofuran (THF), ethyl acetate or more rarely dimethylformamide (DMF), acetone, ethers or hexane.

Often hydrogenations are carried out in the presence of additives, such as bases or acids, to promote a certain outcome. Acids are used to stop product inhibition in reductions that produce amines and to minimise dimer formation in nitrile reduction. Basic additives accelerate the palladium on carbon catalysed hydrogenolysis of carbon-halogen bonds and enable the partial hydrogenation of phenols to cyclohexanones (9). The hydrogenolysis of benzylic alcohols by palladium on carbon catalysts is accelerated by acids and suppressed by bases.

Reaction Engineering and Safety

Chemical reaction engineering is a multidisciplinary subject involving concepts of chemistry, chemical engineering and physics. The establishment of a viable production process requires careful thinking from the molecular level up to the scale of the production plant.

Operations can be carried out in three possible modes:

- batch (all the reagents added at once);
- semi-batch (one reactant continuously fed to the reactor); or
- continuous (all reagents and products continuously fed in or out of the reactor).

The different modes of operation are implemented using alternative types of reactor. Each has its advantages and disadvantages. The stirred tank

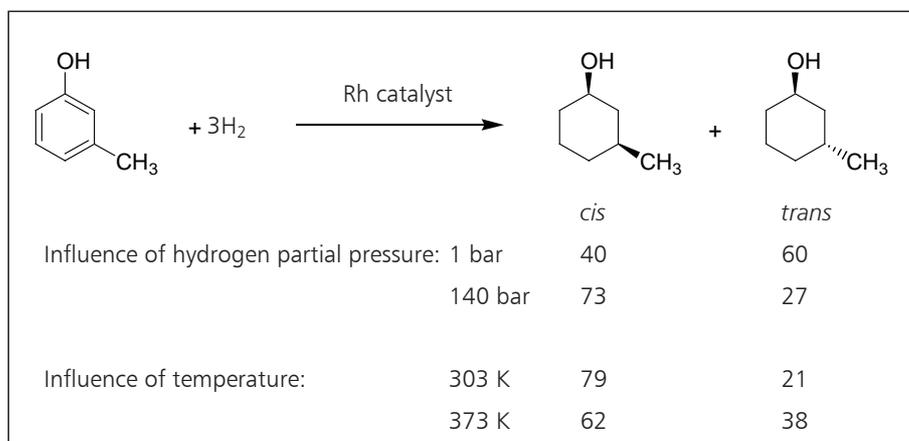


Fig. 4. Influence of hydrogen pressure and temperature on the rhodium-catalysed hydrogenation of disubstituted aromatic compounds

reactor (used for batch processes) is flexible and allows for variation of conditions such as pressure and temperature during the cycle, but the set up time decreases productivity. The continuous stirred tank reactor (used for semi-batch processes) is good for isothermic conditions, but backmixing leads to lower productivity and in some cases influences selectivity. Lastly the tubular flow reactor (used for continuous production) gives potentially the highest productivity, but produces temperature gradients and may allow the development of high pressures.

Heterogeneous catalytic hydrogenations are inherently dangerous processes. Hydrogen forms an explosive mixture if allowed to come into contact with air; the catalyst is pyrophoric especially when spent and can be a potent ignition source; and the reactions themselves are often highly exothermic. Some of the measures that allow the chemistry to be performed in a safe way are:

- to perform a kinetic and thermodynamic study of the reaction and all possible side-reactions, assess mass and heat-transport limitation and put in place efficient means of heat removal;
- to isolate ignition sources;
- to give consideration to semi-batch or continuous flow working modes to avoid the accumulation of reagents that could cause runaway reactions;
- to inert the reactor before loading the hydrogen;
- to work at higher than atmospheric pressure; and
- to unload spent catalyst using closed filtration systems.

Economic Aspects

Heterogeneous catalytic hydrogenations are generally economically viable processes. Catalyst can be sent back to the manufacturer after use for refining and re-manufacturing, allowing the intrinsic value of the metal to be recovered. This can be particularly important for precious metal-catalysed processes where the value of the metal catalyst is high, and recovery can aid the overall cost effectiveness of the process. The efficiency of metal recovery during refining varies (Table I) and some metal losses are inevitable. Manufacturing and pre-treatment costs are approximately the same for both base and precious metals.

Table I

Typical Losses at Refining for Platinum Group Metals Used as Hydrogenation Catalysts

Metal	Metal losses, %
Pd	2–5
Pt	2–5
Rh	5–10
Ru	10–15

When comparing the cost of heterogeneous catalytic hydrogenations *versus* alternative reduction methods, another consideration is that hydrogen gas is currently considerably cheaper than hydrogen deriving from other sources such as hydrides.

Conclusions

The first Heterogeneous Catalytic Hydrogenation course provided a great deal of information during the two days of the programme. The course material can additionally be used at a later time by the attendee as a starting point to expand on the subjects of interest. This course will appeal to development scientists and engineers engaged in heterogeneous catalytic hydrogenation, and especially to those involved with plant scale processes. In my opinion it is a greatly welcomed addition to the training panorama available and I hope it will continue to be successful in the future. The course will be held again on 18th–19th March 2013 at The Radisson Blu Hotel in Nice, France (1).

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The Reviewer



Fabrizio Nerozzi is a Team Leader at Johnson Matthey, Catalysis and Chiral Technologies based in Royston, UK, since 2009. Previously he worked at GlaxoWellcome (later GlaxoSmithKline) in Stevenage, UK, as a Medicinal Chemist, and later as a Team Leader. He graduated in Chemistry at the University of Bologna, Italy, in 1998.

The Course Tutor



Dr Felix Roessler studied chemistry at the University of Zürich (UZH), Switzerland. After obtaining his PhD at UZH, he moved to Cambridge, UK, to work with Professor Ian Fleming. He started his industrial career with Roche in Basel in 1980, first with central research where his focus was heterogeneous catalysis for the production of pharmaceuticals and fine chemicals and then in process research and development within Roche's pharma division.

In 2000 Felix joined the vitamins division of Roche, where he initiated, developed and introduced highly economic and ecological heterogeneous catalytic processes for the production of nutraceuticals. Following the takeover of Roche vitamins division by DSM in 2004, Felix worked as a catalysis expert for DSM where he supported catalysis for the nutraceutical, pharma and base chemical divisions. Felix was honoured twice with the Sandmeyer award in 1997 and 2008, granted by the Swiss Chemical Society.

Since his retirement in 2007, Felix is active as an independent consultant for all aspects of heterogeneous catalytic processes, including selection of the proper equipment and appropriate chemical systems; determination of basic reaction data; troubleshooting and analysis of production processes; the development of highly economic processes; and scale-up from laboratory to plant.

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