

H₂

Hydrogen

APPLICATION REPORT

High pressure reactor Hydrogenation



Hydrogenation by highpreactor Basics and Safety

The fields of application for Berghof highpreactor are chemical reactions proceeding at increased temperature and pressure demand with a maximum at 300°C/200bar which can be found in various sectors of chemical engineering. Ideal reaction conditions are realized due to the modern and diverse design of highpreactor. In the present series of highpreactor Application Reports an overview on selected research topics is given. The intention is not to provide exhausted scientific information but an introduction to various topics for our customers.

Introduction

Hydrogenation is a chemical process in which hydrogen is added to a chemical multiple bond. Modern applications of hydrogenation are diverse and are used in various industries. Here are some examples:

Food industry: Hydrogenation is used to convert unsaturated fats into saturated fats, which increases the shelf life of food. A well-known example is the partial hydrogenation of vegetable oils for the production of margarine.

Chemical synthesis: In organic chemistry, hydrogenation is often used to reduce double or triple bonds in organic molecules. This is important for the production of pharmaceuticals, agrochemicals and other chemical products.

Fuel production: Hydrogenation plays a role in the conversion of biomass into liquid fuels (e.g. by hydrothermal liquefaction) and in the production of synthetic fuels from hydrocarbons.

Catalytic processes: In the petrochemical industry, hydrogenation is often used in catalytic processes to refine crude oil fractions and produce high-value products such as petrol and diesel.

Hydrogen storage: Hydrogenation can also be used to store hydrogen in the form of chemical compounds.

Hydrogenations are therefore among the most important chemical reactions in organic synthesis. Unsaturated compounds with double or triple bonds are converted from alkenes or alkynes into C-C single bonds and thus alkanes in a single step. Similarly, C=O double bonds are converted from esters, aldehydes or ketones into C-O or amines with C-N bonds are obtained from imines or Nitrile.

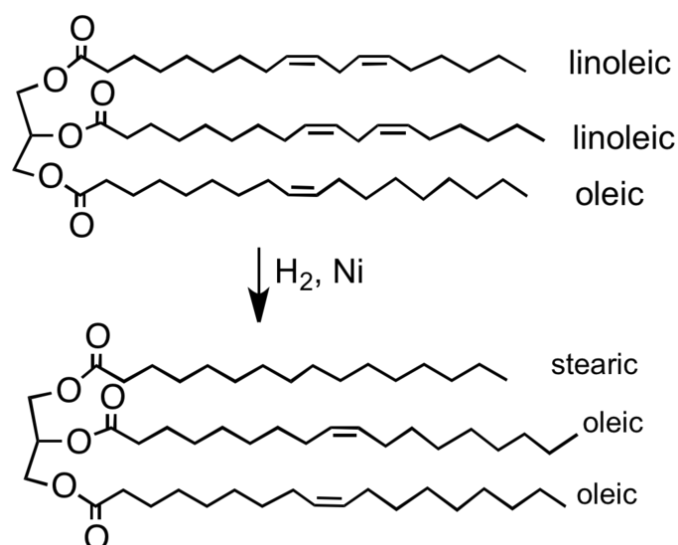
Hydrogenations usually require a catalyst for the reaction to occur at various temperatures and pressures, depending on the catalyst and substrate used. Most hydrogenation reactions use gaseous hydrogen as the hydrogen source, but alternative sources have been developed.

Hydrogen

Hydrogen is a colorless, odorless gas with a very low density (14 times less dense than air). It is an asphyxiant non-toxic gas, 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. The ignition temperature in air is 560 °C. During handling, the hydrogen must be kept away from ignition sources, including electrostatic discharges. The containers should be stored away from oxidising gases (oxygen, chlorine) and other oxidising substances.

Hydrogenation of Fats and Oils

In the food industry, hydrogenation is used to convert liquid vegetable oils into solid fats such as margarine. This improves the shelf life and texture of the products.

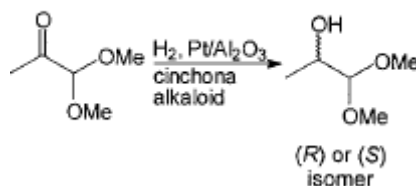


Example: Partial hydrogenation of margarine.

Margarine is a semi-solid butter substitute created from vegetable oil, which is typically unsaturated and therefore liquid at room temperature. The process of partial hydrogenation adds hydrogen atoms and reduces the double bonds in the fatty acids, creating a semi-solid vegetable oil at room temperature.

Hydrogenation of unsaturated alcohols, ketones or aldehydes

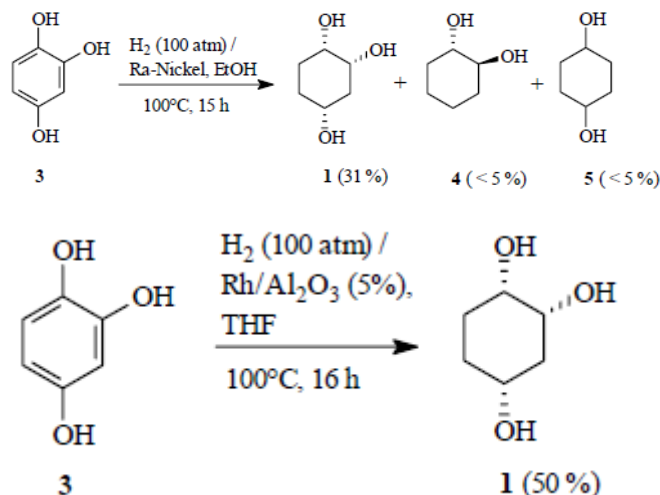
The hydrogenation of unsaturated alcohols can lead to the production of saturated alcohols, which are used in various chemical processes. Enantioselective syntheses are of particular interest. In the example below, depending on the catalyst used, either 93% of the R-isomer or 88% of the S-isomer is obtained. [Török et al].



Hydrogenation of Aromatics

Aromatic compounds such as benzene can be converted into saturated hydrocarbons by hydrogenation, which is important in the petrochemical industry.

The hydrogenation of 1,2,4-trihydroxybenzene to all-cis-cyclohexane-1,2,4-triol by De Kimpe et al. is shown as an example. The choice of catalyst determines the yield and by-products.



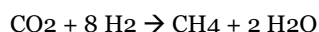
Fuel Production

Hydrogenation plays a role in the conversion of biomass into liquid fuels (e.g. through hydrothermal liquefaction) and in the production of synthetic fuels from hydrocarbons.

Methanisation

The conversion of carbon dioxide (CO₂) into methane (CH₄) can take place through various chemical processes, the most well-known methods being the following:

Hydrogenation of CO₂: This is the process by which CO₂ reacts with hydrogen (H₂) to produce methane and water. The reaction is often depicted as follows



This reaction requires a catalyst, typically nickel or ruthenium, and takes place at elevated temperatures and pressures. The hydrogen can come from various sources, including the electrolysis of water or from fossil fuels

Biological methanisation: In this process, microorganisms are used to convert CO₂ into methane. This typically occurs in anaerobic fermentation processes, where certain bacteria utilise CO₂ together with organic substances to produce methane

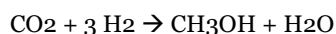
Catalytic reduction: There are also chemical processes based on the catalytic reduction of CO₂, in which CO₂ reacts with other chemicals to produce methane. However, these methods are less common than those mentioned above.

Carbon dioxide reduction reactions: Recent research has focused on the development of catalysts and processes to directly reduce CO₂ using renewable energy or electrical energy (e.g. through electrochemistry) to produce methane

Converting CO₂ into methane is a promising approach to reducing greenhouse gas emissions and creating sustainable energy sources, especially if the hydrogen and energy required comes from renewable sources.

Similarly the conversion of carbon dioxide (CO₂) into methanol (CH₃OH) can also take place using various chemical processes. The best known methods are:

Catalytic hydrogenation: In this process, CO₂ reacts directly with hydrogen (H₂) using a catalyst, typically copper or zinc oxide, at elevated temperatures and pressures. The reaction can be summed up as follows:



This method requires specific conditions to maximise the formation of methanol and minimise by-products.

Direct CO₂ reduction: Recent research has focussed on the direct electrochemical reduction of CO₂ to methanol. This involves reducing CO₂ in an electrochemical cell using renewable electricity. This method has the potential to be more efficient and environmentally friendly, as it generates electricity directly from CO₂ and water.

The conversion of CO₂ into methanol is particularly interesting as a sustainable route to low carbon methanol, as methanol serves as a chemical raw material for many industrial applications and can also be used as a potential fuel or energy source.

Catalysis

Most hydrogenation reactions require metallic catalysts to reduce the high activation energies and/or to achieve special stereochemical selectivity. Both heterogeneous and homogeneous catalysts are used. Nickel, platinum, rhodium, iridium or palladium catalysts are often used for the

hydrogenation of alkynes and alkenes. In each case, the choice of catalyst, its concentration, the solvent, the temperature and the pressure has a significant influence on the reaction.

Catalysts are responsible for binding the H₂ molecule and facilitating the reaction between the hydrogen and the substrate. Platinum, palladium, rhodium, and ruthenium are known to be active catalysts which can operate at lower temperatures and pressures. Research is ongoing to procure non-precious metal catalysts which can produce similar activity at lower temperatures and pressures. Nickel-based catalysts, such as Raney nickel, have been developed, but still require high temperatures and pressures.

Hydrogenation is an exothermic reaction. About 25 kcal/mol are released in the hydrogenation of fatty acids or vegetable oils. The Horiuti-Polanyi mechanism explains how heterogeneous catalysis works: First, the unsaturated bond binds to the catalyst, then H₂ dissociates into atomic hydrogen binding the catalyst, too. One hydrogen atom attaches first to the unsaturated bond in a reversible step, before the second hydrogen atom is added thus rendering the hydrogenation process irreversible. For homogeneous catalysis, the metal and hydrogen form a dihydride complex via oxidative addition. The metal also binds the substrate and then transfers one of the hydrogen atoms from the metal to the substrate by migratory insertion. Finally, the second atom of hydrogen is transferred to the substrate with simultaneous dissociation of the newly formed alkane by reductive elimination.

Technology and Safety

Hydrogenations are usually carried out at high hydrogen pressures and temperatures. These reaction conditions must first be established, monitored and maintained during the reaction. Pressure safety of the reaction system has to be assured therefore and applicable national pressure vessel directives been respected (e.g. 2014/68/EU). Beside this, as hydrogen forms explosive mixtures with oxygen, safe reaction control is particularly important.

Berghof high-pressure reactors are designed, built, and tested following the Pressure Equipment Directive DGR 2014/68/EU and the AD-2000 regulations. Berghof reactors thus ensure safest possible working conditions. For Hydrogenations some additional precautions during the installation of the reactor and during usage should be respected:

- The reactors should be installed in a well-ventilated area, that can be separated from the user. This can be realized by a fume hood, glass walls or by a separate room for example. In case of uncontrolled reactions during opening, emptying, or filling of the reactor the user is able to separate the reactor from himself and other persons.

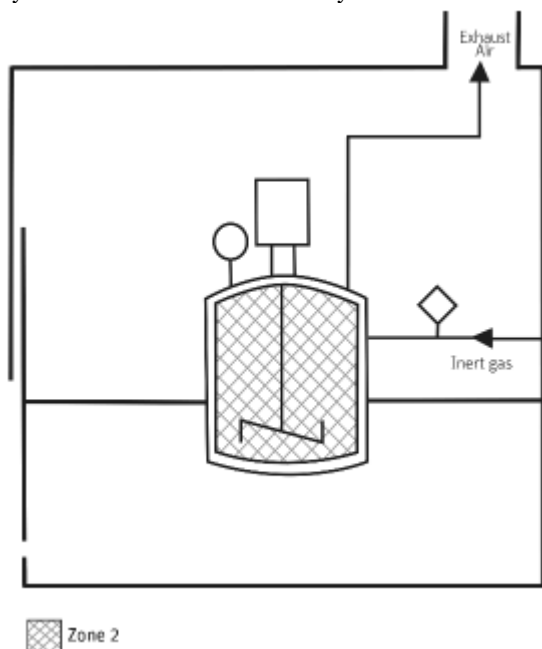
- Before starting an application, the reactor and all accessories (including O-rings) have to be checked for damage. In case any damages are observed the application should not be started.

- After closing the reactor and before starting the heating process the user should check the tightness of the reactor. This can be done by pressurizing the reactor with pressured air, nitrogen or other harmless gases. Tightness or the leakage rate of the reactor is determined by the pressure drop during a certain period of time.

- During the time the reactor is under pressure a sufficient tube should connect the rupture disc holder with an exhaust system. In case the rupture disc brakes, this tube can safely remove pressurized, hot and potentially dangerous content to the exhaust system.

- Before opening a reactor, the content should reach room temperature and the pressure has to be fully removed. Although a safe opening key is installed on reactors BR-100 or larger, it is highly recommended to use the vent valve with sufficient tubing to remove the pressure in a safe manner.

Prevention of potentially explosive atmospheres is most important. Inside the reactor this can be realized easiest by replacing oxygen and air by inert gases like nitrogen, argon. Thus, below the limiting oxygen concentration the system is not able to form explosive atmospheres. These concentration limits can be reached in reactor systems either by sufficient flushing of the system or by multiple cycles of pressurization with inert gas and emptying or even evacuation. To prevent explosive atmospheres in surroundings of the reactor, sufficient air circulation is recommended. This ensures that the area around stays under the lower flammability limit.



Schematic installation of a reactor inside a fume hood.

If the formation of explosive atmospheres cannot be prevented at any time additional explosion protection measures have to be taken. ATEX guidelines (for example 2014/34/EU) regulates the use of devices and protection systems in potentially explosive areas. It applies to devices that may function as a source of ignition and to protection systems. Potential sources of ignition are electrical and mechanical sparks, electrostatic discharges, electromagnetic radiation, hot surfaces and flames. Therefore, electrical devices like pressure sensors, motors or electrical heaters need to be ATEX certified. Non-electrical devices with fast moving parts, for example a magnetic clutch also need to be certified. Other non-electrical devices like pressure vessels, hand operated valves and tubes aren't ignition sources. Thus, these devices cannot and do not need to be ATEX certified.



Unique PTFE-lining in Berghof highpressure reactors avoids catalytic effects of metal surfaces – neither enhancement nor poisoning effects of catalyst by the metal surfaces of the reactor itself can occur.

Literature Overview

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