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CATALYSTS USED IN THE HYDROGENATION PROCESS

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Abstract: Catalysts used in hydrogenation:Ph3P)3,RhCl, Pt, Ni, Ru,Os, Rh and compounds containing rhodium.
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Hydrogenation (hydrogen - hydrogen) is a reaction of attaching hydrogen to simple substances (chemical elements) or complex compounds in the presence of catalysts. Separation of hydrogen from chemical compounds - dehydrogenation is the reverse reaction of hydrogenation. Hydrogenation and dehydrogenation are important methods of synthesis of organic substances in the presence of catalysts, based on oxidation-reduction reactions. These reactions are carried out in industry in giant reactors. These include hydrogenation of oils and fats. In other series of reactions, hydrogenation and dehydrogenation reactions are carried out in combination. An example of this is the reaction of turning ethyl alcohol into acetaldehyde in the presence of catalysts.

Despite the fact that the hydrogenation of ethylene and other alkenes to alkanes occurs with the release of heat, this reaction occurs at a significant rate only in the presence of certain catalysts. The catalyst, by definition, does not affect the heat of the reaction, and its role is reduced to reducing the activation energy. It is necessary to distinguish between heterogeneous and homogeneous catalytic hydrogenation of alkenes.

In heterogeneous hydrogenation, finely ground metal catalysts - platinum, palladium, ruthenium, rhodium, osmium and nickel, are supported in their pure form or on inert carriers - BaSO4, CaCO3, activated carbon, Al2O3. All of them are insoluble in organic media and act as heterogeneous catalysts. Among them, the most active are ruthenium and rhodium, but platinum and nickel are the most common. Platinum is usually used in the form of black dioxide PtO2, known as Adams catalyst. Platinum dioxide is obtained by dissolving chloroplatinic acid H2PtCl6. 6H2O or ammonium hexachloroplatinate (NH 4)2PtCl6 with sodium nitrate. Hydrogenation of alkenes with Adams catalyst is usually carried out in alcohol, acetic acid, ethyl acetate at normal pressure and temperature of 20-500C. When passed through hydrogen, platinum dioxide is directly reduced to platinum black in the reaction vessel, which catalyzes hydrogenation. Other more active platinum group metals are used on inert supports, for example, Pd / C or Pd / BaSO4, Ru /Al2O3; Rh/C and others. Charcoal-supported palladium catalyzes the hydrogenation of alkenes to alkanes in alcoholic solution at 0-200C and normal pressure. Nickel is commonly used in a form called "Raney nickel". To obtain this catalyst, the nickel-aluminum alloy is treated with hot aqueous hydroxide to remove almost all the aluminum and treated with water until the reaction is neutral. The catalyst has a porous structure and is therefore also called a skeletal nickel catalyst.

Since both hydrogen atoms are attached to the carbon atoms of the double bond from the catalyst metal surface, the addition usually occurs on one side of the double bond. This type of connection is called syn- joining. Anti-coupling occurs when two reagent moieties are added to different sides of a multiple bond (double or triple).

The double bond in alkenes is hydrogenated at a high rate compared to many other functional groups (C=O, COOR, CN), and therefore the hydrogenation of the C=C double bond is often a selective process, if the hydrogenation is under mild conditions (0-20 0C and atmospheric pressure).
An important advantage of homogeneous catalysts is their ability to selectively reduce mono- or di-substituted double bonds in the presence of tri- and tetra-substituted double bonds due to large differences in hydrogenation rates.
In the same catalysts, hydrogen addition also occurs syn- addition. Thus, reduction of cis-butene-2 under these conditions leads to deuterium meso-2,3-dideuterobutane.
To simple and complex chemical bodies. Only a few elements react directly with hydrogen gas. Most of the complex chemical bodies that organic compounds are of great interest from the point of view of hydrogenation can bind hydrogen only in the presence of catalysts. Thus, hydrogenation is often understood as the catalytic bonding of hydrogen with organic compounds. In addition to hydrogenation, it is recommended to consider catalytic reduction (deoxidation), since both processes are equally related to activation events and are achieved by practically the same methods

Hydrogenation phenomena belong to the field of heterogeneous catalysis, and the solution of the question about the mechanism of hydrogenation is inextricably linked with the clarification of general catalytic issues. In the history of catalysis, the so-called intermediate theory. As applied to hydrogenation, the theory was developed most fully by the French chemist Sabatier. According to him, low-stable, but stoichiometrically responsible compounds capable of donating hydrogen to unsaturated or oxygen-containing substances in an active (probably atomic) form when interacting with hydrogen on the surface of a catalytic metal is formed. Thus, according to Sabatier, catalytic activity depends on two important points: the ability of a given metal to form hydrides with hydrogen and the degree of stability of the latter, that is, the greater or lesser degree of ease with which atomic hydrogen can be released by them. For example, the hydrogenation of ethylene can be represented by the following equations:
2 Ni + H2 = Ni2H2;
Ni2H2 + C2H4 = C2H6 + 2Ni.
In fact, some metals that act as catalysts in hydrogenation processes (for example, palladium) have the property of absorbing hydrogen in a finely divided state. However, in this case, it is still not completely clear whether systems such as chemical compounds or solid solutions are formed.

X-ray studies of hydrogen-charged metals and measurements of heats of adsorption did not give absolutely clear results. In some cases, however, the formation of a hydride-like substance could be proved chemically, with greater or lesser certainty. metal connections. For example, Schlenk obtained a compound from hydrogen and nickel that corresponds to the formula NiH -2 and has a hydrogenating effect. In connection with the deepening and extension of the fields of catalysis which can be studied in detail, many new points of partly physical and partly chemical order have arisen, which show that hydrogenation phenomena are much more complicated than theorized. Sabatier of intermediate compounds of the given form. For hydrogenation, adsorption phenomena and the orientation of adsorbed molecules, their deformation and other phenomena occurring in the surface layer are of great importance.
The hydrogenated substance is hydrogenated in the form of vapor (gas) or liquid (solution), depending on the state of aggregation used.
The steam (gas) method consists in passing the vapors of the hydrogen substance together with

the hydrogens through the catalyst layer, which can be metals: nickel, cobalt, iron, copper and platinum. Nickel has the greatest activity, in practice, nickel is almost always used, and copper is rarely used (for example, the reduction of nitro compounds is)

The method of preparation of nickel catalyst for hydrogenation is of great importance. It is usually obtained by reducing nickel oxide, hydroxide, or basic nickel carbonate in a stream of hydrogen. The activity of the catalyst largely depends on the reduction temperature: the lower it is, the greater the activity. For example, at temperatures above 350 °C, reduced nickel is no longer suitable for the hydrogenation of aromatic compounds, and above 450 °C, it has almost no significant catalytic effect. Along with the catalytic activity, the ability of the catalyst to cause side reactions (decomposition, rearrangement, elimination of water) also increases. For example, when phenol is hydrogenated in the presence of reduced nickel at 250°C, it becomes cyclohexane (abundant), cyclohexene, and cyclohexanol; Hydrogenation with nickel prepared at 310°C produces virtually no cyclohexane. The addition of hydrogen to different unsaturated groups occurs at different rates, and therefore partial hydrogenation can be achieved by choosing a certain temperature for reducing nickel oxide, that is, by obtaining a catalyst of different levels of activity. To increase the active surface of the catalyst, nickel is sometimes deposited on various substances (supports). For this purpose, the following are used: pumice, kieselguhr, clay, various types of aluminum and magnesium hydrosilicates, animal or bone coal, linden, sugar coal, as well as barium sulfate, aluminum oxide, etc., which can withstand high temperatures. inert substances. temperatures. Chlorine, bromine, iodine, phosphorus, arsenic, sulfur and sulfur compounds even minimal amounts strongly decrease the activity of the catalyst. The absence of sulfur compounds is especially important in the hydrogenation of aromatic substances. Therefore, the hydrogen used in hydrogenation operations first undergoes the most thorough purification.

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