

Catalytic dehydration of alcohols

Theoretical introduction

Instructor dr Hanna Wilczura-Wachnik

University of Warsaw
Faculty of Chemistry

Organic Chemistry and Chemical Technology Division

Introduction – Theoretical Background

Nearly all biological reactions and most industrial synthesis require catalyst. Presently, catalysis is the most important technology in environmental protection, i.e., the prevention of emissions different toxic chemicals. A well-known example is the catalytic converter for automobiles.

The term “catalysis” was introduced by Berzelius in 1836. Describing various reactions he found that catalysts possess special powers that can influence the affinity of chemical compounds. After many years in 1895 Ostwald proposed the following definition of catalysts: “a catalyst accelerates a chemical reaction without affecting the position of the equilibrium”. Additionally it was assumed that the catalyst remained unchanged in the course of the reaction. This definition is still valid today. Now it is known that during the catalytic process between reactants and catalyst the chemical bondings are formed. The catalysis is realized as a cyclic process with the following steps:

1. the reactants are bound to one form of the catalyst,
2. the intermediate catalysts-reactant complexes are formed (usually the intermediate catalyst complexes are highly reactive and difficult to detect),
3. the reaction performs,
4. the products are released from another form of catalyst, regenerating its initial state.

The simple catalytic cycle is shown in Figure 1.

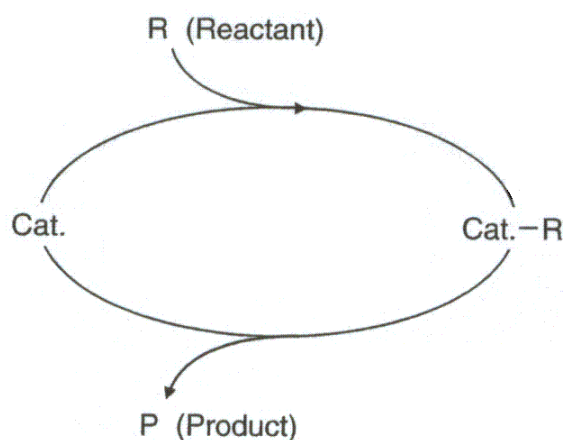


Figure 1. Catalytic cycle scheme

The suitability of a catalyst for an industrial process depends mainly on the following properties:

- activity
- selectivity
- stability.

Depending on industrial priority mentioned above properties can be ordered as follows:

selectivity>stability>activity.

Such order is a consequence of today's preference according to which optimizing of existing processes is more preferable than developing new ones.

The catalyst definition assumes that, an ideal one would not be consumed during reaction, but this is not the case in practice. Usual the catalyst undergoes chemical changes, and its activity as a function of time becomes lower. Such activity decreasing is called catalyst deactivation. Deactivated catalyst must be regenerated or if it is necessary replaced.

Activity of given catalyst is a measure of how fast reaction (or reactions) proceeds in the presence of the catalyst. The reaction rate v is calculated according the following equation:

$$v = \frac{m_s}{c * t} \text{ [mol L}^{-1} \text{ h}^{-1} \text{ or mol kg}^{-1} \text{ h}^{-1}]$$

where:

m_s - a converted amount of substance of a reactant [mol]

c - a catalyst volume or mass [L] or [kg]

t - a time [h].

Another important property of catalysts apart from accelerating reaction is the influencing on the selectivity of chemical reactions. The catalyst selectivity involves obtained different products from a given starting compound by using different catalyst system. It means that employing two different catalysts is possible obtaining completely different products from the same starting material. In Figure 2 are given samples of different products obtaining from the same material – synthesis gas using different catalysts.

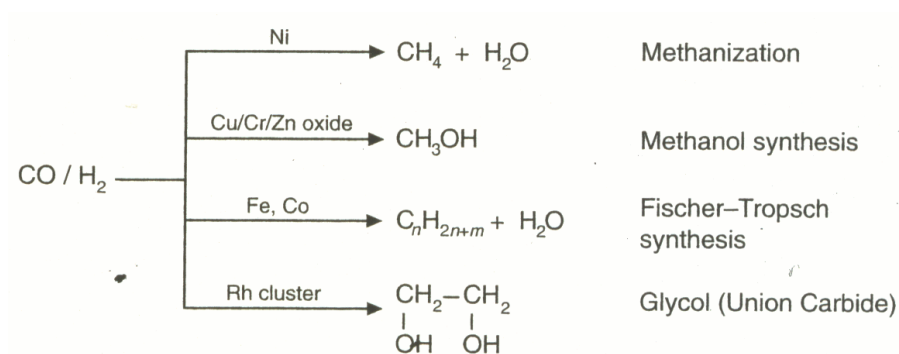


Figure 2. Synthesis gas products depending on used catalyst

In industrial practice this possibility reaction control sometimes is more important than the catalytic activity.

The selectivity S of a reaction is calculated as a fraction of starting material A that is converted to the product B . Selectivity S can be calculated according to the equation:

$$S = \frac{[m_{A(b)} - m_{A(end)}]}{[m_{A(b)} - m_{A(end)}]}$$

↗

in reaction $A \rightarrow B$

↘

totally in whole process

Catalyst stability is a third property important from industrial point of view because the chemical, thermal and mechanical stability of catalyst determines its lifetime in industrial reactors. The total catalyst lifetime is of crucial importance for the economics of a technological process.

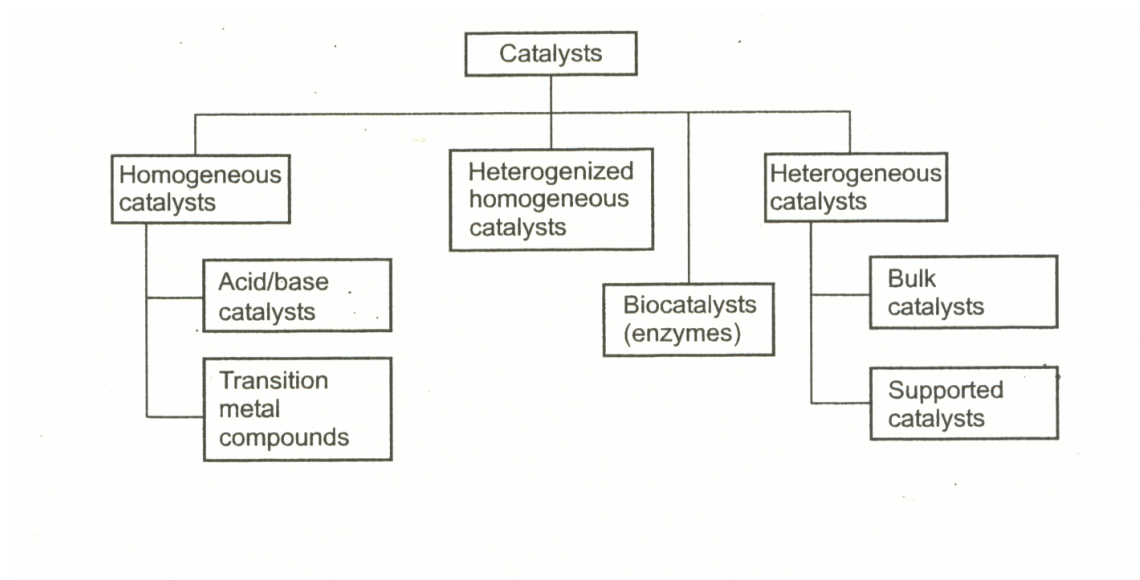
There are numerous factors influencing on catalyst stability. Among many there are: decompositions, coking and poisoning. Catalyst time stability depends on reaction conditions including reactants purity. Usually decreasing of catalyst stability is determined by measuring activity or/and selectivity as a function of time.

Catalyst deactivation can be reversible or not depending. Reversibly deactivated catalyst can be regenerated. Usually it is done in a separate process.

Catalyst classification

There is not general catalyst classification because variant criteria can be taken into account. Usually there are: aggregation state, structure, composition and

area of application. The most popular classification is according to the state of aggregation in which catalysts act. There are: heterogeneous, homogeneous and enzymatic catalysts (Scheme 1).



Scheme 1. Catalysts classification

Heterogeneous and homogeneous catalysts belong to the wider used in industry. Enzymatic catalysts are employed mainly in pharmaceutical and cosmetic technologies.

Generally, the main characteristic feature of heterogeneous catalytic systems is that they are in solid state and in a different phase than entrance compounds and reaction products. The most important advantages of these catalysts are a higher selectivity and reparability comparing to homogenous ones. The characteristic features of both catalysts types are compare in Table 1.

Table 1. Comparison of homogeneous and heterogeneous catalysts features

	Homogeneous	Heterogeneous
<i>Effectivity</i>		
Active centers	all metal atoms	only surface atoms
Concentration	low	high
Selectivity	high	lower
Diffusion problems	practically absent	present (mass-transfer-controlled reaction)
Reaction conditions	mild (50–200 °C)	severe (often >250 °C)
Applicability	limited	wide
Activity loss	irreversible reaction with products (cluster formation); poisoning	sintering of the metal crystallites; poisoning

Enzymes are classified as a separate class of catalysts. They have significant advantages (activity, selectivity, specificity), and disadvantages (costs) comparing to heterogonous and homogeneous catalysts. Enzyme-catalyzed reactions are very expensive. Enzymatic catalysis is used mainly in pharmaceuticals, dairy and food industries. Till now the main technologies preferably use heterogeneous catalysts or homogeneous.

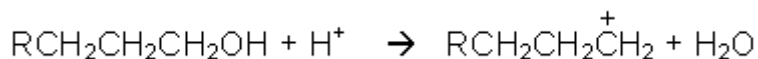
Depending on state aggregation catalyst are gases, liquids and solids. Industrially important are liquid and solid catalysts. It is worth to mention that around 75% of all chemicals are produced in processes employing catalysts. For example the production of synthetic fibers, plastics, pharmaceuticals, agents, resins, crop-protection, and pigments required catalytic processes. Moreover in such technologies as the crude-oil processing and petrochemistry catalysts are necessary on purification stages, refining and other. Catalysts have been used in inorganic technologies like synthesis of sulfuric acid, the conversion of ammonia to nitric acid. Finally, environmental protection measures such as automobile exhaust control, and purification of off-gases from power stations and industrial plant would be inconceivable without catalysts. Recently many selective catalysts like

multicomponent oxides and metallic catalysts, zeolites and metal complexes have been developed.

All catalytic process can be classified according to reaction mechanism as:

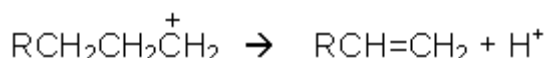
- oxidation-reduction reactions (redox reactions): hydrogenation, dehydrogenation, oxidation. The typical catalysts: metals, semiconducting metal oxides and sulfides.
- acid-base reactions: hydrolysis, isomerization, cracking, alkylation. Typical catalysts: the Brönsteds and Lewis's acids and bases, oxides: aluminium, magnesium, and aluminosilicates.
- reactions with coordinative mechanism: polymerization, oligomerization, carbonylation, hydrogenation, hydroformylation. Typical catalysts: metals complexes (usually transition metals) bimetallic systems.

From the historical point of view dehydration of ethanol to ethylene (in 1787 by Priestley's) is the first reaction performed with solid catalyst. Catalytic dehydration of alcohols is a simple method for alkenes obtaining. Al_2O_3 as a catalyst needs a specific preparation: hydrated aluminium oxide needs calcinations at temperature above 200°C (at this temperature in dehydroxylation water molecules and oxide ions O^{2-} are created). Dehydroxylation causes a surface defects as Lewis acidic centers (unsaturated Al^{3+} ions) and basic Lewis centers (O^{2-} ions) creation. Water molecules deactivate Lewis centers and create strongly acidic Brönsted's centers. Alcohols dehydration reaction performs on Brönsted's active centers where hydroxyl groups disconnect proton from alcohol molecule. During reaction alcohol molecule adsorbed on aluminium oxide surface reacts with proton. As a products carbo- cation and water molecules are created according to relation:



$\text{RCH}_2\text{CH}_2\overset{+}{\text{CH}}_2$ is called carbo-cation.

On catalyst surface carbo-cation decomposes according to relation:



Proton connects to catalyst and olefin is a product of reaction.

Above reaction is one of the possible mechanisms. At lower temperature is possible reaction in which as a product suitable ethers can be obtained.

Dehydration of alcohols with aluminum oxide (Al_2O_3) as a catalyst is a sample of olefins production.

*** glc basic principles are described below**

Gas-liquid chromatography is a form of column chromatography in which the absorbing medium is a liquid of low volatility, called the liquid phase, and this is dispersed over the surface of an inert solid support. The latter is usually a granular material which does not itself adsorb the components but which merely acts to hold the liquid phase in a stable dispersed form. A gas stream, known as a carrier gas, flows continuously through the column and the temperature of the system is controlled. When a small quantity of a volatile mixture is applied to the column the components are distributed between two phases and therefore moved more slowly than carrier gas stream, due to the retarding effect of the liquid phase. The column should be sufficiently long due to separating components as a result of differences in this retarding effect. When the separated components are eluted from the column a sensitive device, known as a detector, converts the concentration or mass substance contained in the exit gas stream into an equivalent electrical or other measurable signal (depending on detector type). This signal is usually measured by some continuous recording device to produce a chromatogram. Typical chromatogram consists of a number of peaks each of which corresponds to a component of the mixture. The position of each of these peaks is characteristic of the component to which it is due. These characteristic positions are measured in terms of the volume of carrier gas which has passed through the column between the time application of the sample to the column and the time of emergence of the component. This gas volume is called the retention volume, V_R , and is a fundamental gas chromatography property in qualitative analysis. The size of each peak (its area or height), is normally proportional to the amount of component causing it. This property is an important prerequisite for accurate quantitative analysis.