HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

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Contents

1. Introduction

The term "catalysis" was first employed by Berzelius in 1836 to identify a new entity capable of promoting the occurrence of a chemical reaction by a "catalytic contact". In his view, the catalyst was seen as something that is added to the reaction to speed up the rate of the reaction (catalytic force) without being consumed or produced in the process. It is important to recognize that the catalysis can be traced back to ancient terms if we consider for example the fermentation processes, which are examples of biocatalysis. As for the industrial catalytic processes, catalytic production of sulfuric acid, i.e. lead chamber process, where oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) was performed in the presence of a mixture of nitric oxides (NO/NO_2) as catalyst, dates back to eighteenth century. However, catalysis started to play a major impact on the chemical industry starting from the beginning of the twentieth century, nowadays more than 95% of chemicals being produced via a process that includes at least one catalytic step. The volcano-like shape reported in Figure (data from ref. (Kieboom et al. 1999)), which illustrates the introduction of major industrial catalytic processes as a function of

time, could suggest that catalysis could be considered to be a mature technology, where major developments have already been achieved. However, an overview of the catalytic technology that has been introduced on the US market in the 1990s, reported over 130 examples of new catalysts or catalyst improvements for operating processes (both in some advanced stage of scale up or commercialized) (Armor 2001), indicating the vital role of the catalytic technology to many industrial processes. Consistently, world catalysts sales accounted for some $ 7.4 billion in 1997. In summary, catalysis nowadays plays a key role in the production of chemicals and materials.
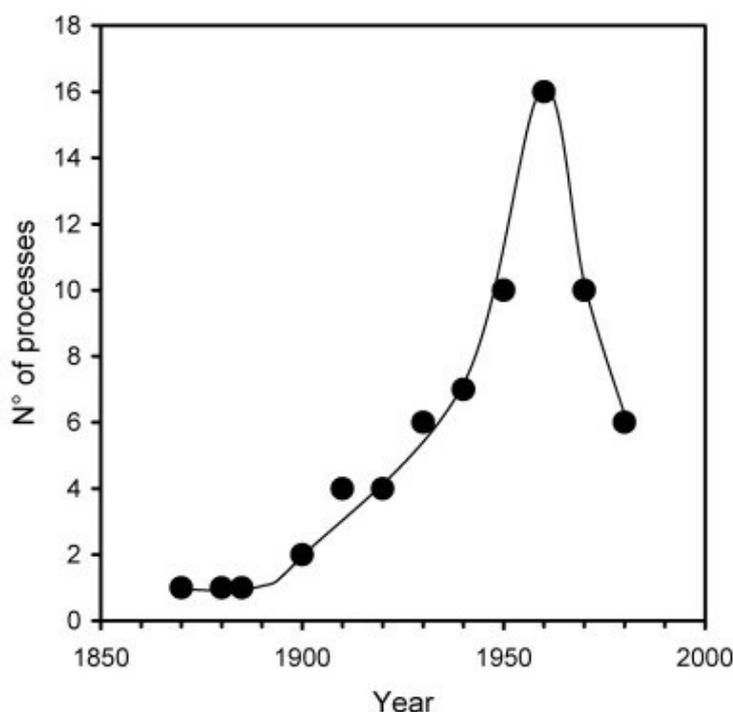

Figure 1: Summary of the historical development of the major industrial catalytic processes number of major commercialized industrial processes per decade (in the 20th century)). The line is only an eye-guide. After (Kieboom *et al*. 1999)

1.1. Catalyzed vs Non-Catalyzed Reaction

From a chemical point of view, the concept of catalyst is intimately linked to the mechanism of the chemical reaction. The catalyst is capable of accelerating the reaction rate or to change the selectivity of the reaction towards different products with respect to the situation when the reaction occurs in the absence of the catalyst. To explain these concepts, let us consider a general chemical reaction which is described by the following equation:

$$aA + bB \xrightarrow{r_1} cC + dD \tag{1}$$

where A, B and C, D represent respectively the reagents and the products and the

terms a, b, and c, d, represent the stoichiometric coefficients of the reaction.. For such a reaction we can define the reaction rate as:

$$r = -\frac{1}{a} \times \frac{d[A]}{dt} = -\frac{1}{b} \times \frac{d[B]}{dt} = \frac{1}{c} \times \frac{d[C]}{dt} = \frac{1}{d} \times \frac{d[D]}{dt}$$

where the use of square brackets is conventionally employed to indicate the concentration of the different species in mol L^{-1}. For the sake of simplicity, we will consider the reaction rate for a process occurring in a single homogeneous phase. This case can be described by a kinetic law, which is measured experimentally and represents the relationship between the reaction rate and the reactant concentration:

$$r_1 = k_1[A]^m[B]^n \tag{2}$$

where m and n represent the reaction order with respect to reagents A and B. $k_1\left((mol/L)^{-m-n+1}s^{-1}\right)$ is the kinetic constant for the reaction (1). Notice that in this simple description we do not consider the contribution of the reverse reaction to the overall reaction rate. This contribution would be of the type:

$$r_{-1} = k_{-1}[C]^p[D]^q \tag{3}$$

where the sign minus is conventionally used to indicate the reverse process. Under conditions where the contribution of the reverse process to the overall reaction rate cannot be neglected, Eq. (3) must obviously be subtracted from Eq. (2) to obtain the net reaction rate.

The dependency of the reaction rate on the temperature is described by the Arrhenius law:

$$k_1 = A \times e^{-\frac{\Delta E_a}{RT}} \tag{4}$$

where A is the geometric factor, R the universal gas constant (8.32 J mol^{-1} K^{-1}), T reaction temperature (K) and ΔE_a is the activation energy (J mol^{-1}) for the reaction. As a matter of fact, when we consider a hypothetical reaction pathway leading from reagents to products, the activation energy for the reaction considered is defined as the energy barrier which must be overcome by the system so that products are formed in the reaction. The energy profile for the reaction as a function of the reaction coordinate, i.e. moving from the reagents to products, is schematically illustrated in Figure (dotted line). Clearly, in order to transform the reagents into products, molecules must overcome the energy barrier represented by the activation energy. The role of the catalyst is therefore to modify this energy profiles so that alternative reaction pathways, featuring lower activation energy compared to non-catalyzed system, can be offered, resulting in higher reaction rates under comparable reaction conditions, as dictated by Eq. (4). It is important to realize that the presence of a catalyst can modify also the product distribution as illustrated in Figure for a hypothetical catalyst offering a new reaction pathway leading to products B. Such products may not be reachable in the

absence of the catalyst due to high activation energy for their formation. However, it should be observed that high yields of products B can be obtained in the presence of the catalyst only when the reaction is run under kinetic control, i.e. the reaction is stopped before the equilibrium conditions are attained. In summary, the presence of the catalyst affects the kinetic aspects of a reaction by lowering the activation energy, without affecting its thermodynamics, *i.e.* the product distribution at equilibrium. As a result of this, catalytic reactions occur under milder conditions and, when carried out under kinetic control, with higher or different selectivity compared to non catalytic processes.
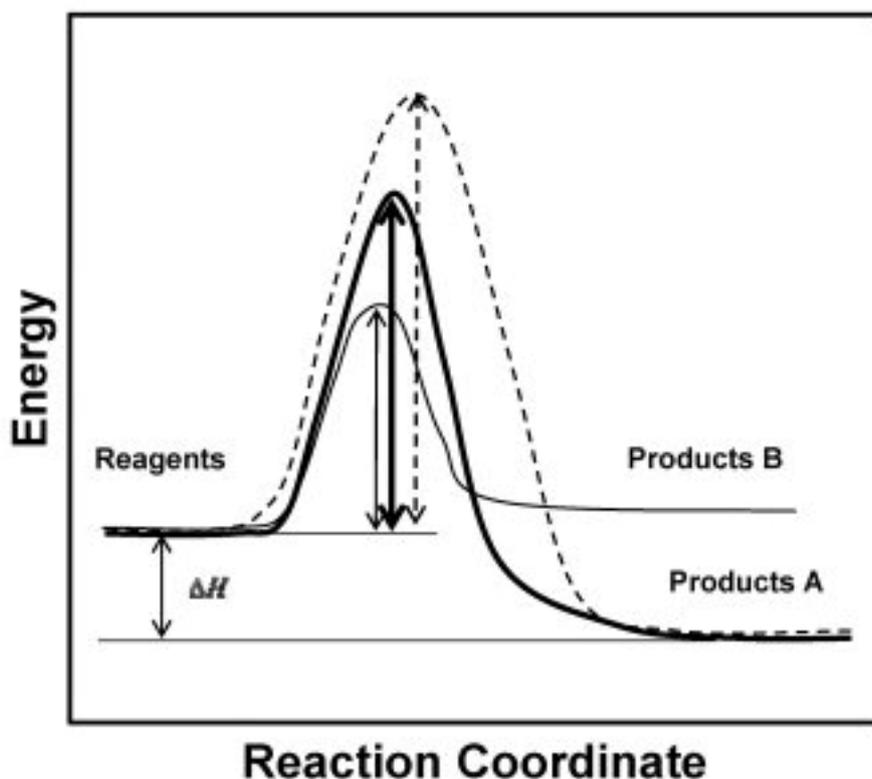

Figure 2: Energy diagram for a generic reaction and the effects of a catalyst on the reaction profile: dotted line: uncatalyzed reaction; solid thick line: catalyzed reaction leading to the same products, solid thin line: catalyzed reaction leading to different products (see text for details). The differences in the energies indicated by the arrows represent the activation energy barrier $\left(\Delta E_a\right)$ for the forward reaction and enthalpy of the reaction $\left(\Delta H\right)$.

1.2. Homogeneous vs. Heterogenized and Heterogeneous Catalysts

Traditionally catalysts were distinguished into homogeneous and heterogeneous; subsequently, heterogenized catalysts were also introduced. This distinction is linked to the fact that the catalyst operates respectively in the same phase where the reaction occurs (homogeneous catalysts) or in a different phase (heterogeneous or heterogenized

catalysts). In principle, there is no limitation on the phase to be considered, as a matter of fact the fist industrial catalyzed reaction (1750) was the oxidation of SO_2 to SO_3 using NO as a homogeneous catalyst, which occurs in the gaseous phase. On the other hand, most of the processes using homogeneous catalysts occur in a liquid phase whereas for the heterogeneous catalysts, the catalyst is usually in a solid form, and the reaction occurs either in the liquid or gaseous phase. The fact that the catalysts is in a distinct phase with respect to the reaction medium, accounts for the major advantage of the heterogeneous catalysts over the homogenous as it makes the separation e re-utilization of heterogeneous catalysts simple and cheap compared to the homogenous catalysts.

A great variety of homogeneous catalysts are known, ranging from Brønsted and Lewis acids widely used in organic synthesis, metal complexes, metals ions, organometallic complexes, organic molecules up to biocatalysts (enzymes, artificial enzymes, etc). However, nowadays the term homogeneous catalyst is often referred to organometallic or coordination complexes, which will be treated in Section 2.

The major advantages/disadvantages of heterogeneous vs. homogeneous catalysts are summarized in Table 1. As a general picture, the main difference is the fact that in the case of homogeneous catalysts, every single catalytic entity can act as a single active site. This makes homogeneous catalysts intrinsically more active and selective compared to traditional heterogeneous catalysts such as oxides or supported metal particles. The heterogeneity of the surface sites is, in fact, a common feature of the heterogeneous catalysts.

Property	Homogeneous	Heterogeneous
Catalyst recovery	difficult and expensive	easy and cheap
Thermal stability	poor	good
Selectivity	excellent/good – single active site	good/poor - multiple active sites

Table 1: Comparison of main advantages/disadvantages of homogeneous vs. heterogeneous catalysts.

As exemplified in Figure 3 for a cubooctahedron *f.c.c.* metal particle, not only the nature of the catalyst, i.e. chemical composition, plays a role in defining the properties of the heterogeneous catalysts, but also the dimension and the form of the particle plays a role in determining the relative number and type of exposed surface atoms (Anderson 1975). Catalytic oxidation of carbon monoxide at low temperatures over gold-containing catalysts, pioneered by Haruta and co-workers (Haruta 1997, Haruta & Date 2001), is a nice example of such importance: gold particles larger than 5 nm were essentially catalytically inactive for CO oxidation, whereas gold particles with an optimum size of about 2-3 nm showed extremely high catalytic activity and were able to fully oxidize CO even at -100°C. This example highlights the paramount importance of strict control of the preparation of the heterogeneous catalysts in order to ensure reproducible and well-defined systems.
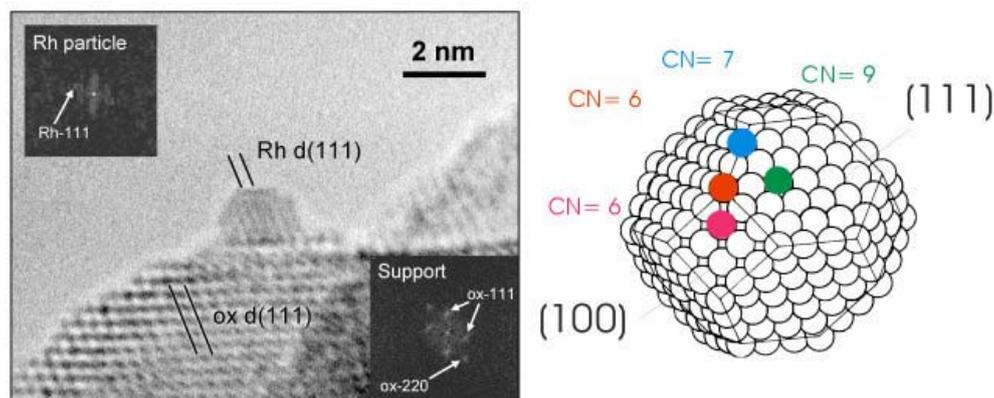
Figure 3: High resolution transmission electron micrograph and digital diffraction patterns of a Rhodium metallic particles deposited on a $Ce_{0.68}Zr_{0.32}O_2$ mixed oxide as support. Notice the cubo-octahedron-like form of the Rhodium particle, which exhibits different surfaces (indicated) and Rhodium atomic sites with different coordination number (CN) as evidenced in the right part. Rhodium crystallizes in the *f.c.c.* structure and has a CN=12 for bulk metal atoms.
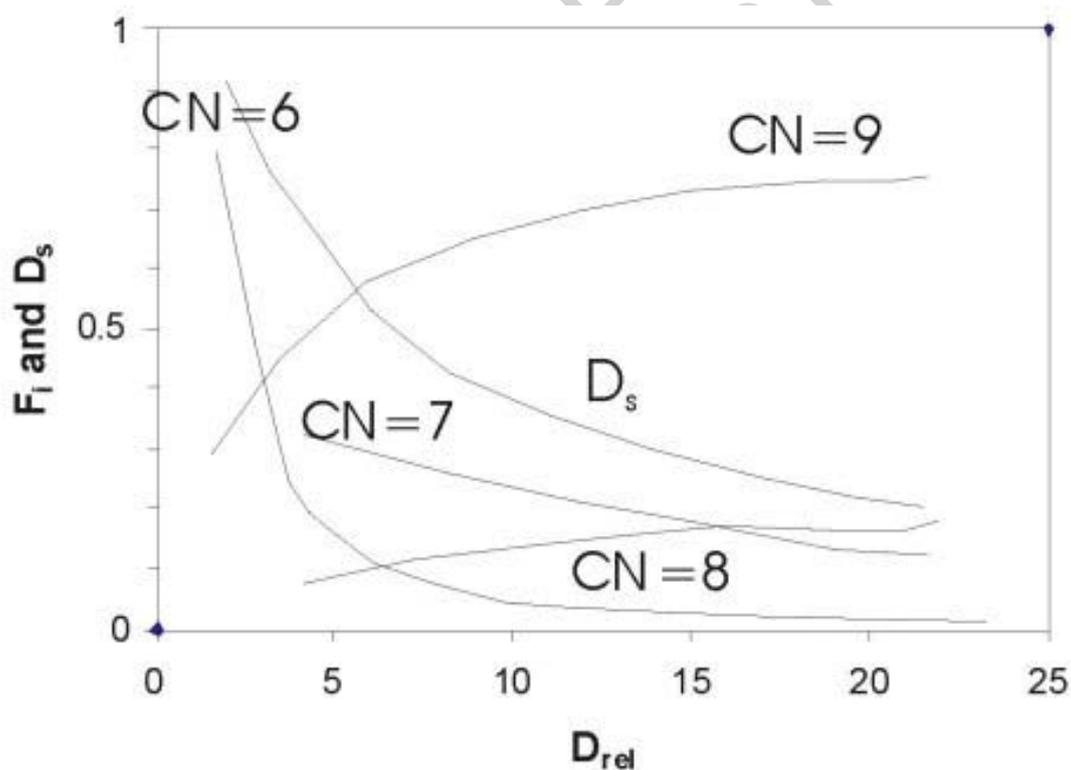

Figure 4: Relative ratio (F_i) of surface atoms with different CNs and dispersion (D_s) *vs.* relative particle dimension defined as ratio of a radius of a sphere containing N atoms to the radius of the volume occupied by an atom in the unit cell. After (Anderson 1975).

In contrast to this surface heterogeneity, homogenous catalysts, due to their molecular

nature, are well defined systems, typically featuring a single catalytic site.

A major drawback of the homogeneous catalysts is the difficulty of their recovery from the reaction medium. Precipitation with subsequent recovery, e.g. elimination of the precipitating counter-ion, or distillation of the reaction products, which is an energy intensive process, are typically needed in order to re-utilize homogeneous catalysts. Such operation may often deactivate the catalyst. For example, homogeneous Rhodium phosphine catalysts are used on a scale of $4-5 \times 10^{12}$ g/year to catalyze hydroformylation of propene to volatile butanal where the product is continuously distilled off the reaction vessel. However, when the hydroformylation of long chain alkenes, typically 1-octene as depicted in (Scheme 1.1), used as starting materials for plasticizers, soaps and detergents, is attempted, the rhodium phosphine complex decomposes due to the higher distillation temperature in this case. Cobalt carbonyl complexes are therefore used industrially, despite the fact that rhodium complexes operate under much milder reaction conditions and achieve higher selectivity to the desired linear aldehyde compared to the cobalt catalyst (Cole-Hamilton 2003).
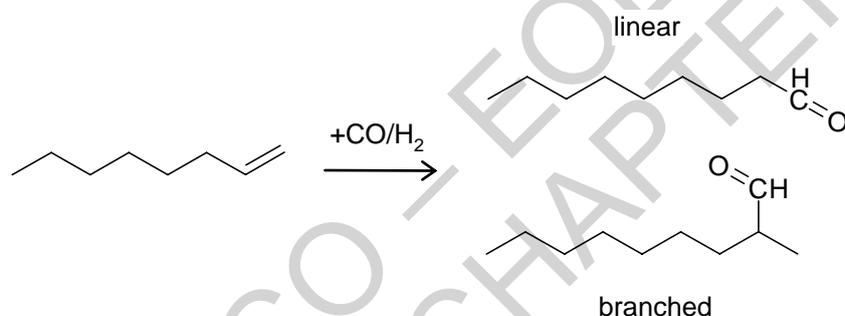
Scheme1.1: Hydroformylation of 1-octene to linear and branched aldehyde.

The recognition of these inherent limitations of the homogeneous catalyst led to a flourishing activity attempting to heterogenize homogeneous catalysts. The aim is that of combining the advantages of the homogenous catalyst (activity and selectivity) with the facility of the heterogeneous systems to recycle the catalyst. Several routes to anchor or encapsulate the homogenous, below discussed, were suggested, however, it must be underlined that a major drawback of the heterogenized catalyst is the leaching of the catalyst during its use and recycle, leading to deactivation.

When a catalytic reaction is considered, one must always take into account that this process consists of different steps which, in the case of heterogeneous catalytic reaction, may include: 1) external diffusion, i.e. diffusion towards the catalyst body, e.g. pellet; 2) internal diffusion, i.e. diffusion within the pellet; 3) adsorption of reagents; 4) surface reaction; 5) desorption of products; 6) internal diffusion, i.e. diffusion towards the exterior of the pellet; 7) external diffusion.

The important aspect is that four of the seven steps are concerned with the diffusion and hence with the physical form of the catalyst bed within the reactor. Since the homogeneous catalysts are molecularly dispersed within the reaction medium, there is no internal diffusion.

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Bibliographic Sketches

Erica Farnetti studied chemistry at the University of Trieste – her birthplace – where she got her degree in 1983 with a thesis in homogeneous catalysis, which was awarded the Bracco-Salata price. After a 12-month period at the University of North Wales (Bangor, UK) in professor's C.J.M. Stirling's group, she went back to Trieste as a graduated student, working on the synthesis and characterization of homogeneous reduction catalysts; she got her Ph.D. in Chemical Sciences at the university of Trieste in 1989. In the same year she went to Zűrich as a postdoc at ETH with professor L.G.M. Venanzi, where her research topic was concerned with the synthesis and reactivity of heterometallic multinuclear hydrides. In 1990 she became assistant professor of inorganic chemistry at the University of Trieste where she is presently working.

Her main research interests are focussed on the study of organo-transition metal compounds and of their catalytic properties. Recent fields of research regard the oligo and polymerization reactions of alkynes homogeneously catalyzed by late transition metals, and on the other hand the study of organometallic compounds by means of electronic photoemission techniques using synchrotron radiation. Current interests include the transition metal speciation in the preparation of supported catalysts.

Roberta Di Monte obtained her PhD in Materials Engineering in 1995 at the University of Trieste. Currently, she is a researcher at the Department of Chemistry Sciences of the University of Trieste (Italy). Her research interests focus the synthesis and characterization of the nanostructured $CeO2-ZrO_2$ and $CeO_2-ZrO_2-Al_2O_3$ materials, which are widely used as critical ingredients of automotive catalytic converters. She is a co-author of over 35 papers, more than 20 industrial reports and three patents.

Jan Kaspar is a full professor of Inorganic Chemistry at the University of Trieste. He is a co-author of over 115 publications and five patents in the fields of homogeneous, heterogenized and heterogeneous catalysis. His research, in co-operation with leading industries such as Magneti Marelli (FIAT Holding, Italy) and MEL Chemicals (UK), has primarily been focused on advanced catalytic materials based on nanostructured CeO_2-ZrO_2 mixed oxides as oxygen storage promoters for the automotive three-way catalysts. He has given invited lectures on this topic at international conferences, leading automotive and catalyst industries, in addition to several invited reviews and papers. He has been a member of the editorial board of Catalysis Today and Journal of Rare Earths. He is a member of the executive board of the Interuniversity Consortium Chemistry for the Environment - INCA which joins researchers from over 30 Italian Universities.