Heterogeneous Catalytic Chemistry by Example of Industrial Applications

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ABSTRACT: Worldwide, more than 85% of all chemical products are manufactured with the help of catalysts. Virtually all transition metals of the periodic table are active as catalysts or catalyst promoters. Catalysts are divided into homogeneous catalysts, which are soluble in the reaction medium, and heterogeneous catalysts, which remain in the solid state. A heterogeneous metal catalyst typically consists of the active metal component, promoters, and a support material. In some cases, the metallic state itself forms the active ingredient. However, this situation is largely restricted to precious metal catalysts and to some base metals used under reducing conditions. In most cases and especially in homogeneous catalysis, it is a metal compound or a complex that forms the active catalyst. Catalysis can be rather puzzling as a given metal can catalyze a variety of different chemical transformations, while the same substrate, passed over different catalysts, can give different products. It is therefore helpful to be familiar with the fundamentals of catalytic science before being exposed to the uncountable applications, which form the backbone of industrial chemistry. Examples of practical importance are used in this paper to highlight important principles of catalysis.

KEYWORDS: General Public, Public Understanding, Upper-Division Undergraduate, Curriculum, Inorganic Chemistry, Catalysis, Green Chemistry, Industrial Chemistry

A catalyst is a substance that accelerates the rate of a chemical reaction. The catalyst is not consumed and therefore does not appear in the overall reaction equation. A catalyst promoter is an additive that improves the performance of a catalyst, but has no catalytic activity for a given chemical conversion. Often the catalyst is written above the reaction arrow in square brackets. This indicates that a catalyst is needed for the reaction to attain equilibrium within a reasonable time. For example, the esterification of carboxylic acids with alcohols takes place in the presence of acids or bases, as does the reverse reaction, the hydrolysis of esters. In the equation below (Scheme 1), the acid shows above the reaction arrow to indicate that this reaction is acid catalyzed.

Scheme 1. Acid-Catalyzed Esterification

\[
\text{R}^\prime \text{OH} + \text{R}^\prime \text{OP} \xrightleftharpoons[^{\text{H}_2\text{O}}]^{\text{[H}_2\text{O}]^+} \text{R} ^\prime \text{O} \text{R}^\prime + \text{H}_2\text{O}
\]

ECONOMIC BACKGROUND

The economic importance of catalysis reflects in the following numbers:

- In 2005 the value of the goods produced with the help of catalysts amounted to $900 billion US$.\(^3\)

Looking at these figures, one has to keep in mind that catalysts employed for environmental abatement processes, such as automotive exhaust catalysts, do not produce any goods of economic value. A breakdown of catalyst usage by industry sectors indicates that there is an almost even distribution across four different sectors, namely, (i) the polymer industry (21%); (ii) coal, oil, and gas refining (22%); (iii) manufacturing of chemicals (27%); and (iv) environmental applications (30%).\(^2\)

INDUSTRIAL CATALYTIC CONVERTERS

Various reactor types have been designed to facilitate catalytic conversions on an industrial scale. Four examples are given in Figure 1.\(^4\) Reactor A is a stirred tank reactor operated batchwise. The catalyst is dissolved in the liquid phase, and it could be an acid or a base, a metal salt, or a metal–organic complex. Shown is a ruthenium alkylidene complex, which is active for the olefin metathesis reaction.\(^5\) Catalysis in solution is referred to as homogeneous catalysis. Homogeneous catalysts are usually more active and selective than heterogeneous catalysts. They are also easier to tailor for specific purposes, as the reaction mechanism is often well understood. The major disadvantage of homogeneous catalysis lies in the fact that it is difficult to separate the products from the catalyst, as the catalyst is present in the same phase. Also, homogeneous catalysts do not lend themselves easily for continuous operations. However, these problems can be overcome by

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immobilizing homogeneous catalysts onto heterogeneous supports. For a successful heterogenization of a transition-metal complex, the reaction mechanism should predict that the metal ligand chosen for bonding to the support remains firmly attached to the metal. The cyclopentadienyl ligand is an example for such a ligand.  

Reactors B, C, and D (Figure 1) are used for heterogeneous catalytic processes. Example B represents a sparged stirred tank reactor for gas-liquid reactions. The catalyst is suspended in powder form. Shown below the reactor is a precious-metal catalyst supported on activated carbon. The catalyst can readily be filtered off and reused until it is no longer of sufficient activity. Spent metal catalysts are normally returned to the catalyst manufacturer for metal recovery. Examples C and D show fixed-bed reactors. These operate in a continuous mode. The solid catalyst is stationary and the gaseous or liquid feed is passed over the catalyst bed. Multitube reactors (D) allow for efficient heat removal in the case of exothermic reactions. Heterogeneous catalysts for fixed-bed operations come in many different forms, as determined by the macro- and the microkinetics of the process. The artistic composition of examples shown below the two reactors was taken from a Clariant, formerly, SÜD-Chemie catalogue, with permission. Clariant is a catalyst manufacturer. Other companies producing catalysts for the chemical industry and other applications include BASF, Evonic, Johnson Matthey, Heraeus and Haldor-Topsoe. Reactor types used for catalytic conversions are not limited to those shown in Figure 1. See Henkel for a more comprehensive selection.

**ENVIRONMENTAL IMPACT OF CATALYSIS**

Catalysis is inherently a green technology. This is clearly demonstrated by the influence catalysis has on the environmental factor (E-factor). The E-factor is defined as mass of waste produced per mass of desired product.

\[
E = \frac{\text{kg of waste}}{\text{kg of desired product}}
\]

In the oil refining industry, almost all chemical conversions are catalyzed, and the E-factor is less than 0.1. However, when ascending the value creation chain in the chemical industry, the impact of catalysis decreases. The synthesis of pharmaceuticals, for example, is clearly dominated by traditional, multistep, stoichiometric organic chemistry, and burdened with a high E-factor; the quantity of waste produced can exceed the quantity of the targeted active pharmaceutical ingredient by a factor higher than 25 (see Figure 2).

The usefulness of the atom utilization for the comparison of different chemical processes is demonstrated by example of two routes to niacin or niacinamide. Niacin or nicotinic acid is a vitamin of the B group. In vivo, the acid is converted into the amide and both can be used as nutritional supplements. Lonza AG (Switzerland) is a major supplier and has developed two routes. The classical route is used in Switzerland, while a new catalytic route is operated by Lonza Guangzhou in China. The classical route starts with acetaldehyde and ammonia (Scheme 2). These are converted into 5-ethyl-2-methylpyridine by a  

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Scheme 2. Classical Route to Nicotinic Acid (Lonza AG, Switzerland)
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Another convenient measure for the environmental impact of chemical conversions is the atom utilization. Calculation of the atom utilization (AU) is based on molecular weights (MW) and defined as follows:

\[
AU = \frac{\text{MW of desired product}}{\text{Sum of MWs of all products formed in the stoichiometric equation}}
\]

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Tschitschibabin pyridine synthesis, followed by oxidation with nitric acid. As Scheme 2 shows, the environmental impact of this route is contained by recycling of the nitrous oxide, but two carbons are lost as carbon dioxide. The overall atom utilization is 37%. It is important to keep in mind that the atom utilization (in contrast to the E-factor) does not account for losses caused by low selectivities, as these are not reflected in the overall reaction equation. If a reactant A undergoes a variety of parallel
or consecutive reactions and B is the desired product, the selectivity \( S \) to B (in %) is defined as

\[
S_B = \frac{\text{Number of moles of A converted to B}}{\text{Total number of moles of A converted}} \times 100\%
\]

The catalytic route (Scheme 3) starts with 2-methylpentanediamine, which is cyclized to 3-methylpiperidine over an acidic catalyst. 3-Methylpiperidine is dehydrogenated to 3-picoline over palladium. It follows an ammonoxidation reaction to 3-cyanopyridine using a vanadium oxide containing catalyst. Finally, selective enzymatic nitrile hydrolysis leads to pharma-grade niacinamide. Notably, the ammonia set free in the first step is re-incorporated in the third step. The only byproducts are hydrogen and water, and the overall atom utilization is 75%. Hydrogen can be recovered for further use, and water is environmentally beneficial. The process shown is therefore a prime example of modern green chemistry. The starting material, 2-methylpentanediamine, is marketed by Invista (previously DuPont) under the trade name Dytek A. It is obtained by hydrogenation of 2-methylglutaronitrile, which is a structural isomer of adipodinitrile and, therefore, a byproduct of the Nylon 6.6 manufacturing route.

■ THERMODYNAMIC AND KINETIC ASPECTS OF CATALYSIS

The thermodynamic and kinetic implications of catalysis are schematically demonstrated in Figure 3. A catalyst provides a new route with a lower Gibbs energy of activation \( \Delta G^\ddagger \) for the product formation from given starting materials (reactants). In this way, a catalyst accelerates the reaction. The Gibbs energy for the reaction \( \Delta G^\ominus \) remains unchanged. This means a reaction that is thermodynamically unfavorable cannot be made favorable with the help of a catalyst. (Catalysis is a kinetic, not a thermodynamic, phenomenon.) All the catalytic intermediates of the reaction must be less stable than the product. If an “intermediate” is more stable than the desired product, the reaction will stop there (dotted line in Figure 3), and this intermediate will be the final product.

The addition of hydrogen to the double bond of ethylene, for example, is thermodynamically favorable, but does not proceed at room temperature at any appreciable rate. At the turn of the 19th century, Paul Sabatier discovered that such reactions could be greatly accelerated by the addition of finely divided nickel. However, he maintained that this would only be possible with substrates in the gas phase. Wilhelm Normann proved him wrong; in 1902, he patented the catalytic hydrogenation of fats and oils in the liquid phase. By 1914 not less than 25 plants for the saturation of fats and oils (fat hardening) were running worldwide, mainly for the production of margarine and shortening.

■ MECHANISTIC ASPECTS OF CATALYSIS ON METAL SURFACES

Today’s understanding of double-bond hydrogenation is based on the mechanism originally proposed by Horiuti and Polanyi for the hydrogenation of ethylene on a Pt(111) surface (Figure 4). This mechanism is instructive, as the principle reaction steps involved offer a good starting point for the understanding of many other reactions taking place on metal surfaces.

The following steps describe the mechanism:
- Physisorption of the reactants on the metal surface. (Physisorption takes place via van der Waals forces.)
- Chemisorption of the reactants. (Chemisorption involves the formation of chemical bonds with the catalyst surface.) Ethylene forms an equilibrium between the π-bonded and the di-σ-bonded form, and the H–H bond of hydrogen is cleaved. According to Somorjai, it is
mainly $\pi$-bonded ethylene that, in the following step, reacts further to the ethyl intermediate.

- Formation of the ethyl intermediate. This step must be reversible, as the complete range of deuterated ethanes (and not only DH$_2$C–CH$_2$D) is observed in case D$_2$ is used instead of H$_2$.
- Formation of the second C–H bond.
- Desorption of the product.

The key step is the activation of the reactants by chemisorption to the platinum surface. This facilitates the catalytic route of lower activation energy for the formation of the products. Sabatier postulated that a good catalyst provides an optimum strength of bonding between the reactants and the catalyst surface (Sabatier’s principle). Both too weak and too strong bonds will slow down or prevent the reaction. This principle was convincingly demonstrated by Rootsart and Sachtler, as illustrated in Figure 5. The model reaction is the decomposition of formic acid to carbon dioxide and hydrogen over various metals. It is reasonable to assume that the metal formate shown corresponds to the top of the volcano curve at the lowest temperatures required to achieve the preset reaction rate. To the left (Au and Ag), bond formation between the catalyst surface and the formate is too weak, as indicated by the corresponding $\Delta H^\ominus$ values; to the right (W, Fe, Co, Ni, and Cu), the enthalpy of formation is highly negative and bond formation is too strong. In the first case, the intermediate does not form at a sufficiently high rate; in the second case, the intermediate is too stable and does not decompose at a sufficiently high rate. The platinum group metals in the middle strike the correct balance and provide the optimum strength of bonding between the reactant and the catalyst surface for the reaction to occur.

For ethylene hydrogenation the situation translates into the picture shown in Figure 6. First-row transition metals and second- and third-row transition metals appear on separate volcano curves. The group VIII metals (periodic groups 8–10) are most active and among these the platinum group metals.

It is well-known from practical applications that base metals are less active hydrogenation catalysts than the more expensive platinum group metals (PGMs). Base metals generally require more stringent reaction conditions than PGMs to achieve acceptable results. However, for bulk chemical applications, the catalyst price is a determining factor, and for this reason, nickel and cobalt are often preferred to precious metal catalysts (Ru, Rh, Pd, and Pt).

It should be mentioned that the exact chemical nature of the chemisorbed species that play an active role in a given catalytic conversion is often difficult to establish. The precise molecular structure of the intermediates depends on many factors. These include

- Composition of the catalytically active metal or alloy.
- Crystallite size of the metal or alloy.
- Exact metal surface structure (e.g., type of exposed crystal phase, presence of kinks and steps).
- Adsorbate induced restructuring.
- Presence of other chemisorbed species.
- Nature of the catalyst support.
- Presence of catalyst promoters.
- Temperature and pressure.

A catalyst surface must be seen as a flexible, dynamic system that is able to accommodate a sequence of catalytic intermediates. The multiplicity of possible surface sites makes it difficult to determine the exact chemical environment of each intermediate that contributes to the catalytic cycle. For an advanced treatment of this important aspect of heterogeneous catalysis, see van Santen and Neurock.

### CONVERSIONS BY METALLIC-STATE CATALYSIS

It is necessary to clearly distinguish between catalysis by metals and catalysis in the metallic state. The general term “metal catalysis” is usually understood to include catalysis by metal compounds, such as metal oxides, salts, and organometallic complexes. Homogeneous transition-metal catalysis is always facilitated by metal compounds. A border case between
Homogeneous and heterogeneous catalysis would be the catalysis induced by colloidal nanoparticles kept in suspension. Only groups VIII and IB of the periodic table (all the metals shown in Figure 7) display catalytic activity of practical significance in the metallic state, especially for hydrogenation and oxidation reactions. Other transition elements are too difficult to reduce and to maintain in the metallic state. In the metallic state, iron, cobalt, nickel, copper, and ruthenium catalyze hydrogenation reactions, including the hydrogenation or hydrogenolysis of carbon monoxide. (Hydrogenolysis, in contrast to hydrogenation, involves the cleavage of an interatomic connection in the substrate.) Iron and ruthenium are unique in their capability of converting nitrogen to ammonia, a reaction that can be regarded as the hydrogenolysis of N$_2$. Silver is used for some large-scale selective oxidation reactions, such as the conversion of ethylene to ethylene oxide and the oxidation of methanol and ethanol to the corresponding aldehydes. In contrast, oxidations over Rh, Pd, Ir, and Pt are prone to result in deep oxidation, which is the total oxidation to CO$_2$ and water. These four metals are also extremely useful for many conversions involving hydrogen, such as hydrogenations, dehydrogenations, hydrogenolyses, and naphtha reforming. The catalytic activity of gold appears to be restricted to the nanostate, as confirmed by numerous more recent reports.

Metallic-state catalysis over group VIII and IB elements includes many important large-scale processes. Examples are ammonia synthesis (Fe), ammonia oxidation (Pt–Rh), Fischer–Tropsch synthesis (Fe, Co), methanol synthesis (Cu), and refinery processes such as platforming.

### METAL-DEPENDENT PRODUCT FORMATION FROM SYNTHESIS GAS

The conversion of synthesis gas (mixtures of CO/H$_2$ in different ratios) provides an interesting case concerning the change in product selectivity depending on the catalytic element used. This is demonstrated in Figure 7. The product selectivity changes along the first transition-metal series from left to right. Iron and cobalt (and also ruthenium) convert synthesis gas into a mixture of hydrocarbons by a process known as Fischer–Tropsch synthesis. Nickel is a selective methanation catalyst, and copper is used for methanol synthesis. As indicated in Figure 7, a line drawn across the periodic table separates copper and nickel, separates the base metals from the PGMs up to ruthenium, divides ruthenium from rhodium and osmium, and finally crosses down between osmium and rhenium. Under normal catalytic reaction conditions, metals to the left of this line dissociatively chemisorb carbon monoxide, whereas metals to the right will chemisorb CO molecularly (without breaking the carbon–oxygen bond). In other words, on iron, cobalt, and nickel CO dissociates, whereas it remains undissociated on the coinage metals (Cu, Ag, and Au) and the PGMs (except Ru). Regardless of the detailed mechanisms involved, the full hydrogenation of undissociated CO over a copper catalyst leads to methanol, whereas the hydrogenation over the base metals iron, cobalt, and nickel leads to hydrocarbons and water. The fact that commercial nickel catalysts can produce methane with a selectivity of up to 96% is explained by the high abundance of chemisorbed hydrogen relative to chemisorbed carbon (carbidic surface carbon) on a nickel surface. As a result, almost all the surface carbon is rapidly hydrogenated to methane. This is in contrast to the situation found on iron (and cobalt). The coverage by carbidic carbon is extensive and the reduced availability of hydrogen favors hydrocarbon chain growth to give alkanes, and unsaturated compounds (olefins) form as byproducts. In terms of Sabatier’s principle iron and cobalt provide the optimum bond strength for the chemisorbed species to form Fischer–Tropsch products, whereas nickel provides the optimum bond strength for the formation of methane.

The reverse reaction of methanation (double arrow in Figure 7) is known as steam reforming and is of even greater industrial importance. Most of the synthesis gas used for processes such as methanol synthesis, Fischer–Tropsch synthesis, and hydroformylation (the conversion of olefins into aldehydes) is produced by nickel-catalyzed steam reforming.

### AUTOMOTIVE EXHAUST CATALYSIS

As indicated above, oxidations over Rh, Pd, Ir, and Pt are prone to result in deep oxidation. Environmental abatement catalysts make use of this. The most important single application is probably automotive exhaust catalysis. It is a remarkable achievement that the deep oxidation of hydrocarbons and carbon monoxide and the reduction of nitrous oxides can be done in a single catalytic converter. This is possible by the use of platinum or palladium or both combined with rhodium. A schematic presentation is given in Figure 8. Rhodium is able to dissociatively adsorb NO in preference to O$_2$, whereas palladium and platinum are responsible for the splitting of oxygen. The chemisorbed nitrogen atoms combine to N$_2$, whereas the chemisorbed oxygen atoms oxidize carbon monoxide and hydrocarbons (HC) to CO$_2$ and water.
The introduction of the automotive exhaust catalyst shows that legislative pressure can trigger innovative solutions and create business opportunities on a large scale (even for metal brokers and speculators). To understand some of the price fluctuation seen for rhodium over the last four decades,32 it has to be kept in mind that the annual mining output of rhodium is only about 25 tons. This constitutes ca. 1% of the annual gold production. The annual production of platinum amounts to approximately 130 tons. In 2008, more than 75% of the total rhodium output was used for the manufacturing of autocatalysts.33

### SELECTIVE OXIDATION CATALYSIS UNDER MILD CONDITIONS

Deep oxidation, or over oxidation, is likely to occur with PGMs under oxidative conditions, unless special precautions are taken. However, for selective oxidation reactions, high-oxidation-state base-metal oxides can be used as catalysts. These must be able to switch between two oxidation states (redox catalysis). Examples are MoO₃, V₂O₅, and Sb₂O₅. The reactions take place at elevated temperatures in the gas phase. These conditions can be prohibitive for fine chemical applications, due to the temperature sensitivity of complex organic molecules. However, for applications in the fine chemicals industry, palladium and platinum catalysts can be modified by incorporation of bismuth or lead, resulting in improved selectivity for partial oxidations. Although the exact role of bismuth and lead is still a matter of speculation, Besson et al.34 provided an instructive suggestion by example of the selective oxidation of an hydroxyl group (see Scheme 4).

**Scheme 4. Speculative Mechanism for the Pt–Bi Catalyzed Oxidation of Alcohols (adapted from ref 34)**

According to this proposal, dehydrogenation of the alcohol to the aldehyde takes place on the noble metal surface. The chemisorbed hydrogen reacts with a higher-oxidation-state bismuth oxide species, giving water and a lower-oxidation-state bismuth species. The lower-oxidation-state bismuth is oxidized by the oxidizing agent used for the overall reaction. The addition of bismuth keeps the platinum surface free of excess oxygen, thus preventing over oxidation of the substrate. The left part of the catalytic cycle exemplifies the action of a common base-metal oxidation catalyst: bismuth switches between two oxidation states and (in the case of Scheme 4) oxidizes hydrogen to water. Depending on the substrate, Pt–Bi catalysts allow for very high selectivities under mild reaction conditions. Instead of air, hydrogen peroxide can also be used as the oxidizing agent. Examples for the oxidation of hydroxymethylimidazoles to formylimidazoles are shown in Scheme 5.35,36 Formylimidazoles are important intermediates in the synthesis of pharmaceuticals. Further examples for the successful application of Pt–Bi oxidation catalysts were reported by Anderson et al.37

### PEDAGOGICAL ASPECTS

The content of this article can be used as the basis for an introduction to heterogeneous catalysis. For example, it could lay the foundation for a course on descriptive heterogeneous catalysis or industrial process chemistry. It also could serve as an amendment to a course on homogeneous catalysis. Students are provided with a background on economic and ecological aspects of catalysis, types of catalysts used in industrial practice, modification of catalysts (to improve selectivity), the importance of surface chemistry for the understanding of catalytic reactions at a molecular level, and thermodynamic and kinetic implications. Examples of industrial importance are used for demonstration purposes. After they have been introduced to catalysis using the concept of this paper, learners should be able to answer the following question: Why do certain metals selectively catalyze certain transformations?

Parts of this paper could be given as exercises. Depending on their level, students could be asked to match catalyst types to given catalytic converters (Figure 1). After Scheme 2 has been explained, students should be able to calculate the atom utilization for the reaction of Scheme 3 and compare the two processes. After they have been introduced to one of the Figures 5 and 6, they could be asked to find an interpretation for the remaining figure. On the basis of the information contained in Figure 7, students should be able to propose possible catalysts for other reactions of carbon monoxide. Examples for other reactions, including those of CO₂, are found elsewhere.38

### CONCLUSION

Catalysis, and heterogeneous catalysis in particular, is a mature field of science. Catalysis grows and diversifies further as the world economy grows and diversifies. It contributes significantly to value creation in the real economy. From an environmental point of view, it impacts positively on the viability of many human activities, not only those of a pure chemical nature. To continue educating the catalysis experts of tomorrow at schools and universities and to raise public awareness for the importance of catalysis is therefore of great significance. To the lay person and to many undergraduate students, catalysis appears as a rather complex field, not the least because of the huge number of different catalytic materials and the many different catalytic processes that go with them. Often students are exposed to specific applications of catalysis (e.g., descriptive heterogeneous catalysis) before they have been exposed to the basic principles of the relevant surface chemistry. This often contributes to the perception that catalysis is a “magic” art, rather than a science. Teaching important fundamentals of catalysis at an early stage can be expected to contribute to a deeper understanding. This, in turn, will allow the student to put forthcoming information into perspective. In the paper at hand, an attempt was made to explain some important concepts of catalysis in a brief, but
understandable manner. Applications of industrial and general importance were used for demonstration purposes.

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**Notes**

The author declares no competing financial interest.

**REFERENCES**


