

# ELEMENTARY PROCESSES IN HETEROGENEOUS CATALYSIS

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Over the past decade the production rate of (synthetic) fertilizers parallels the drastic increase of the world population. This would not have been possible without the development of a chemical process (Haber-Bosch process) which enables the large scale production of ammonia ( $\text{NH}_3$ ) from nitrogen ( $\text{N}_2$ ) and hydrogen ( $\text{H}_2$ ).

Air pollution from automobile exhausts is substantially reduced by catalytic converters transforming toxic substances like nitric oxides ( $\text{NO}_x$ ) and carbon monoxide ( $\text{CO}$ ) into more harmless ones such as nitrogen, water or carbon dioxide.

These are just two examples for the operation of a phenomenon called 'heterogeneous catalysis' which inter alia underlies the vast majority of processes of chemical and petroleum industries and without which the modern world would certainly look quite different.

The principle underlying heterogeneous catalysis is the following: The transformation of molecules into new ones is very often a very slow process, i.e. the probability of reaction upon encounter (e. g.  $2\text{N}_2 + 3\text{H}_2 \rightarrow 4\text{NH}_3$ ) is very low, but may be accelerated by the use of a catalyst. The latter forms intermediate compounds with the reacting molecules and thus offers an alternative reaction pathway with an overall higher rate. In heterogeneous catalysis this role is played by the surfaces of solid materials (frequently metals) which form bonds with molecules arriving from the gas phase ('chemisorption'), and hence the study of chemisorption phenomena offers the key for elucidating the mechanism underlying heterogeneously catalyzed reactions. This task is, however, seriously hampered by the following two facts which still are the reason why this field has an odor of 'black art'.

1. Processes occurring in direct contact with the surface of a solid represent essentially a two-dimensional scenario whose investigation requires experimental tools different from regular (three-dimensional) chemistry.

2. The surfaces of 'real' catalysts are generally quite non-uniform with respect to their chemical composition as well as structure. Small concentrations of additives may act as 'promoters' which enhance the catalytic activity, and the small catalyst particles expose surface planes with different atomic configurations as deter-

mined by the respective termination of the crystalline solid.

Both problems may now be overcome: the development of a whole arsenal of surface physical methods enables the study of the structural, electronic and dynamical properties of solid surfaces and of chemisorbed particles on the atomic level, and the complexity of 'real' catalyst surfaces is replaced by using well-defined single crystal surfaces as model systems.

One of the most recent and most powerful experimental techniques is scanning tunneling microscopy (STM) which enables direct imaging of surfaces even with atomic resolution. Several examples will serve to illustrate the kind of information which may be provided by this method: The atomic configuration of the top-most layer of a solid may correspond to the bulk termination, but often it may also deviate and the surface is reconstructed. Chemisorbed species are frequently forming two-dimensional phases with long-range order as a consequence of interaction between them as can most conveniently be probed by low energy electron diffraction (LEED). The strength of the chemisorption bond is usually comparable to that between the surface atoms of the substrate, and as a consequence the latter may become displaced from their original positions under the influence of chemisorbed species. The results may even be macroscopic restructuring of a catalyst's surface under the conditions of steady-state reaction.

Most important is the ability of a catalyst's surface to break bonds within molecules ('dissociative chemisorption') by offering a net energy gain through the formation of chemisorption bonds with the fragments. This will also become evident with the two examples of reactions whose mechanisms could be elucidated along the sketched strategy, namely the oxidation of carbon monoxide and the synthesis of ammonia.

The reaction  $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$  is most favourably catalysed by metals of the platinum group and exhibits probably the simplest mechanism of all catalytic processes. It involves chemisorption of CO as well as dissociative chemisorption of oxygen ( $\text{O}_2$ ). Like on other transition metal surfaces, CO chemisorbs on platinum by coupling of its C-atom end and tends to form a densely packed configuration. This bond is of moderate strength and hence in the temperature range of catalytic reaction

(>200°C) the thermal energy is sufficient to initiate also release of this molecule back into the gas phase (desorption), so that at given temperature and CO partial pressure a steady-state coverage of the surface by CO will result. The O<sub>2</sub> molecule, on the other hand, interacts with the surface with bond breaking into chemisorbed O atoms. This step requires an ensemble of several unoccupied neighboring surface platinum atoms which might, however, already be blocked by chemisorbed CO molecules. In order to reduce the CO coverage (at a given partial pressure in the gas phase) below a critical value, hence a high enough temperature of catalyst operation is required. (The chemisorbed O atoms, on the other hand, form a rather open configuration on the surface which does not appreciably affect the additional uptake of CO). Once a chemisorbed O atom is neighboring a chemisorbed CO molecule these two surface species may recombine into CO<sub>2</sub> which molecule is immediately released into the gas phase, whereby the previously occupied surface sites become again available for chemisorption of the reactants so that the reaction can continuously go on.

Somewhat more complex is the ammonia synthesis reaction which is a large-scale industrial process using an iron-based catalyst. In this case, the primary steps consist in dissociative chemisorption of both reactants, N<sub>2</sub> and H<sub>2</sub>. While this process is quite rapid for hydrogen (H<sub>2</sub>), bond breaking of the nitrogen molecule occurs only with rather low probability and represents hence the rate-limiting step of the overall reaction. In this context a particular role is played by the (111) crystal plane of iron. The incoming N<sub>2</sub> molecule is at first bonded 'end-on' to this surface with the N-N bond remaining practically unaffected. As a next step the molecular axis may become inclined so that both N atoms interact with the surface. In this state the N-N bond is appreciably weakened so that this species represents the precursor for complete dissociation. Once the chemisorbed N atoms are formed they may successively recombine with chemisorbed hydrogen atoms (via NH and NH<sub>2</sub> surface species as intermediates) to chemisorbed NH<sub>3</sub> which eventually is released into the gas phase.

The dissociation probability of the N<sub>2</sub> molecule

is enhanced by the presence of potassium on the surface. Although the overall content of this element in the actual catalyst is very small (<1%), it becomes strongly segregated to its surface which is in fact covered by it to a substantial extent. The role of this 'electronic' promoter consists in a modification of the nitrogen chemisorption bond whereby the dissociation probability is increased.

Based on quantitative information about the individual elementary steps sketched, even the theoretical evaluation of the overall rate of ammonia production in an industrial plant became feasible, and the predicted data were found to be indeed in close agreement with the actual yields measured.

It has thus to be concluded that heterogeneous catalysis needs no longer to be a 'black art', but that this field now became accessible to atomic level research.