

Structure dynamics of surface of catalytic systems based on nanocrystalline gold loaded on oxide supports in chemoselective Reduction of (Volatile) α,β -Unsaturated Carbonyl compounds (R-(V)ABUC)

This project **focuses on nanocrystalline gold** (Au) catalysts based on oxide supports: silica (SiO_2), ceria (cerium (IV) oxide, CeO_2) and titanium (IV) oxide (TiO_2). These systems exhibit different chemical properties in Reduction of (Volatile) α,β -Unsaturated Carbonyl compounds (R-(V)ABUC) with gaseous hydrogen. Utilisation of gold-based systems creates the possibility to **precisely control the hydrogenation pathway** and, thus, to obtain desired products. This capability favours gold among other metal catalysts. **The main scope of this project is to describe features of the catalyst surface and its structural changes that lead to intended chemical effect.**

Hydrogenation of conjugated unsaturated carbonyl compounds (i.e. aldehydes and ketones) is the process of great importance in which valuable compounds are obtained, to mention just printer inks and medicines. In the first step, unsaturated alcohol (so called allylic alcohol) or saturated carbonyl compound are produced. Next step leads always to the same product: saturated alcohol. **Allylic alcohols production is of special interest of manufacturers, as currently these compounds are synthesised in costly stoichiometric reactions.** Although gold catalysts exhibit desired properties, **exhaustive answers** covering lack of long-time stability of catalysts and key physicochemical features responsible for observed phenomena **are still not provided.**

The **activity of gold** surface in the key step of the hydrogenation reaction which is activation of hydrogen molecule **is proposed here to be the result of cyclic structural changes of this surface.** They are the consequence and trigger, at the same time, of surface interactions with hydrogen molecules and the proceeding reaction. **Primary results** confirm that the real behaviour of nanocrystals would remain unspotted if they are approximated just as a part of ideal crystal structure. The diminishing crystal size gives the surface interactions the power to disturb the energetic equilibrium and electron cloud distribution of the whole particle. Under the influence of physical or chemical adsorption taking place on the surface, the crystal structure also adapts to the new energetic and electronic conditions, but, only after the reaction products are removed (desorbed), the crystal structure will restore its initial state and will be ready for the next reaction act.

Tool which allows for investigation of crystal structure evolution is ***in-operando* Nanocrystalline X-Ray Diffraction (NXRD)** technique – established and developed in the laboratory that I work in. It is based on Powder X-Ray Diffraction (PXRD), however, it utilises: a dedicated measurement chamber in which gas atmosphere composition is controlled (*operando* conditions); special measurement strategy regarding correlation of structural data with chemical output of the reaction; and adapted results interpretation method. Statistical analysis of several diffraction patterns (DP) measured under the same conditions and comparison of the differences in DP, rather than estimation of absolute values, minimize the influence of apparatus errors. Evolution of parameters which reflects crystal structure changes, e.g. angle of X-Ray radiation diffraction on the catalyst sample, is presented as a function of the composition of the gas stream going out from the chamber. This evolution is then interpreted through their comparison with simulation results which calculate the expected experimental values. This unique approach to classic techniques **enabled construction of dynamic model of** catalyst structure and to monitor its changes during studies on carbon monoxide oxidation reaction catalysed by **Au/CeO₂**.

The choice of reaction in the gas phase was based on its numerous advantages. Lack of solvent eliminates the necessity of taking it into account in preparation of the experiment and during data analysis. It is also beneficial from the point of view of future technology, as the process as a whole can be designed to be more economically efficient. It is also more feasible to scale it up to the required production yield. The gaseous stream of products is ready as such to be fractionated by temperature-controlled condensation into subsequent collectors. The catalyst itself is less prone to mechanical degradation what increases its durability necessary during time-consuming diffraction experiments or factory plant operation. Selected systems containing different supports allow to track surface structure changes of catalysts working on different reaction pathways, including that leading to allylic alcohol.

Analysis of catalyst activity and performance combined with physical structural research shows dynamics of the surface which is as a whole the active centre of the catalyst. **New point of view on the catalytic systems together with new data are likely to be the crucial step towards development of this branch of chemistry.**