

Heterogeneous catalysis, i.e. a catalysis in which the reactants and the catalyst are in a different physical state, plays a key role in the production of fine chemicals, conversion of toxic and greenhouse gases, as well as in processes aimed at production of the so-called “clean energy”. In particular, the reactions between gaseous species and solid catalysts are essential for many important oxidation and dehydrogenation processes, such as the conversion of ethylbenzene to styrene. The commonly used solid catalysts consist of supported noble metal nanoparticles, which are the active species in catalytic reactions. However, the reaction may only take place at the surface of nanoparticles, as the atoms residing in the deeper layers are inaccessible to the gaseous molecules. This results in a low atomic utilization efficiency, which is an important parameter determining the catalyst’s cost. Recently, the so-called single-atom catalysts (SACs), i.e. catalysts in which the active sites are composed of single metal atoms or few-atom clusters embedded in non-reactive support matrices, are intensively studied due to their high atomic utilization efficiency and superior activity in many industrially-relevant reactions. This activity is determined by various physical and chemical factors, such as charge transfer phenomena, which are still, to a significant extent, unknown.

The aim of the project is to determine the role of the electronic charge transfer between gaseous reactants and catalytically-active sites in the processes of conversion of selected greenhouse gases over solid SACs. The studies will be focused on determining the reaction mechanisms at the atomic scale, which will allow optimizing industrial catalysts. The transfer of electrons from the gas molecules to the catalyst, or the other way round, is believed to be responsible not only for the molecule binding, but also its dissociation and further chemical activity towards other molecules. The hypothesis of the project assumes that a controlled modification of the electronic structure of a SAC, through p- or n-doping, will allow maximizing its catalytic activity. The model reactions studied within the project will be the reduction of nitrous oxide (N₂O) and carbon dioxide (CO₂). N₂O and CO₂ are the two out of three most important greenhouse gases that are formed as side-products in many industrial processes. Their decomposition is not only important from the environmental point of view, but also constitutes an intermediate step in various oxidation reactions, such as the oxidation of carbon monoxide (CO) (another environmentally-harmful gas) to CO₂ with N₂O as the oxidizing agent. The molecules are thermodynamically stable, therefore, there is an intensive search for materials that would favor their catalytic decomposition (or at least interact with them, allowing their sensing). The model catalysts studied within the project will consist of single iron (Fe) atoms and few-atom clusters embedded in epitaxial graphene (Gr). Iron, thanks to its redox properties and low unit cost, is a superior metal candidate for SACs. However, proper matrices hosting Fe atoms and, preferably, consisting of Earth-abundant elements, are still to be developed. Graphene, a 2-dimensional hexagonal lattice of carbon atoms exhibiting unique physical properties, such as unusually high electrical and thermal conductivity, is one of the promising matrix materials for SACs. It is also characterized by a unique electronic structure, being a zero-bandgap semiconductor. When it comes to chemical properties, the surface of structurally-perfect graphene is considered chemically-inactive, with chemisorption occurring only at the edges and defect sites of graphene flakes. However, its unique electronic structure makes graphene very flexible for donating/accepting electrons to/from adsorbing molecules, when synthesized in a doped form. What is important from the point of view of the project, the electronic properties of Gr can be easily fine-tuned by growing the layer on different substrates and intercalating with various elements (thus promoting p- or n-doping). Recent theoretical reports indicate high catalytic activity of Fe-Gr SACs in N₂O and CO₂ decomposition, with the theoretically-predicted critical role of the catalyst-molecule charge transfer in the reaction course. These predictions will be experimentally verified within the proposed project.

The studies will be carried out using sophisticated measurements techniques: scanning tunneling microscopy (STM) and spectroscopy (STS) – allowing the determination of electronic structure of catalytically-active sites and chemisorbed molecules with atomic precision, as well as polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) – giving insight into the adsorption strength and geometry of adsorbed molecules. Through a systematic approach, the project will significantly broaden the knowledge on the role of the electronic charge transfer in catalytic processes and provide routes for rational designing of industrial SACs based on electronic considerations.