

In the face of climate change, the scientific community is looking for effective solutions that could replace existing technologies of negative impact on the environment. At the same time, taking into account the continuous increase in global energy demand and accompanying projected depletion of fossil fuel reserves, the implementation of alternative energy sources becomes necessary. In this context, hydrogen is an important raw material, the production of which is becoming essential. Currently, it is used primarily in refining processes and in the production of ammonia. However, hydrogen is also gaining importance in the car industry, which is currently facing major changes related to the introduction of automotive fuel cells. Thus, the oil concern Grupa LOTOS S.A. is running PURE H<sub>2</sub> project, which shall be finalized by 2023. Its scope is to develop infrastructure to produce and sell high purity hydrogen as a feed for fuel cells. Lotos is planning to build stations for fuelling buses and trucks, stations for fuelling personal vehicles, as well as installations for fuelling deep-sea vessels and trains. Similarly, the concern PKN Orlen S.A. has started the Hydrogen Eagle program, which involves the construction of an international network of hydrogen hubs fuelled with renewable sources of energy and installations converting municipal waste into green and blue hydrogen.

Although the production of hydrogen from renewable sources does not yet have a significant share in global production (~ 95% of hydrogen comes from natural gas and coal), changes are coming. What is worth mentioning, the hydrogen production by steam reforming, among others of ethanol, which can be derived from biomass. Much attention has been paid to the ethanol steam reforming process over the past two decades. A wide range of catalytic systems based on both noble and non-noble transition metals was investigated as potential catalysts. Currently, the most commonly used catalysts are based on cobalt or nickel - elements much cheaper and more widely available than noble metals. Unfortunately, they are quickly deactivated during the process, mainly due to coke production. Therefore, the market still lacks a catalyst that ensures a satisfactory practical hydrogen production efficiency.

Of the several different strategies used to improve the stability of the catalysts in the ethanol steam reforming process, modification by the addition of alkali dopants deserves special attention. It is also worth emphasizing that bioethanol, produced by pretreatment of biomass using alkali hydroxide, may contain residual amounts of alkali metals. The positive effect of alkali is explained in the literature by reducing the amount of formed coke, modifying the acidity of the catalyst, the dispersion of the active metal phase, and/or their effect on the active metal oxidation state in the catalyst. Nevertheless, despite extensive research, there is still a lack of a comprehensive, unambiguous interpretation of the promotional effect of alkali. It is associated with difficulties in characterizing them, caused by their low content in catalysts and changes in their chemical state and location at reaction conditions.

Therefore, the project aims at understanding the role of alkali doping on the surface-structure-performance relationship for the cobalt catalysts for the ethanol steam reforming process. Systematic, multi-faceted studies for a wide range of alkali doped cobalt-based supported catalytic systems will provide new knowledge about the influence of alkali on the catalysts. The effects on the cobalt oxidation state, catalyst/carrier acidity, catalyst electron-donor properties, cobalt phase interaction with the carrier, and mechanism of deactivation will be determined. Then, to gain an insight into the reaction mechanism over the investigated samples the *in situ* and *operando* IR studies will be carried out. The detection of intermediate reaction products formed during ethanol transformation will allow to vary the detailed reaction networks and determine the impact of alkali on the ESR mechanism. These results will be validated by thermodynamic modeling for model cobalt phase surfaces. In turn, a thorough understanding of the surface state of alkali promoters, which is of key importance, will be achieved by the application of the dedicated experimental methods and taking advantage of the new vacuum system integrating the unique in the country and the world species resolved – thermal alkali desorption apparatus (SR-TAD) and Kelvin probe setup for determination of work function changes. The new vacuum system constructed for the needs of the project will create a new quality in catalysis, enabling *in situ* studies of the reduced/spent catalysts thanks to the possibility of their transfer without air exposure. The experimental studies of the work function modifications upon alkali doping will be supported by the DFT calculations.

The outcome of the project will allow for a fundamental understanding of the impact of alkali and thus will help for the rational design of an active and selective catalyst for hydrogen production, exhibiting long-term stability, so crucial in this application.