Abstract

Water Gas Shift - WGS is one of primary processes for generating hydrogen. Although this process is applied on a large scale with producing important chemicals, its catalytic aspect it is still the object of intensive basic research. The well-known Fe-Cr-Cu based catalysts have numerous significant disadvantages including the presence of environmentally toxic Cr^{6+} with cancerogenic and mutagenic. Moreover, in case of those catalysts, there is also the necessity of conducting the steam reforming (preceding HT WGS) at the minimum steam/gas ratio lower than 2.8. The decrease of this value is connected with the risk of forming iron carbide catalyzing side reactions (Fischer-Tropsch reactions) as the result of which hydrogen is consumed causing a number of unfavorable consequences and leading to the decrease of process efficiency. Moreover, systems based on the promoted non-stoichiometric magnetite Fe_xO_y systems are gradually deactivated by recrystallization of Fe_xO_y caused by temperature and steam.

In this project, we intend to undertake research on completely different type of WGS catalysts i.e. on systems based on mixed oxides $ZnO\text{-}Al_2O_3$ with dominant spinel phase $Zn_xAl_yO_z$ promoted with alkali metals. Moreover, there are justifiable grounds for assuming that modification of mixed $ZnO\text{-}Al_2O_3$ by adding Cu and/or La leads to stability increase and improvement of catalytic effect durability. Our pioneering studies conducted so far indicate that there is possibility of replacing widely applied systems with the next generation catalysts with new formula which eliminate disadvantages of the conventional WGS catalysts.

The development of the new formula and the method of obtaining the highly active, stable WGS catalyst which would be resistant to deactivation and coking will allow for further development of innovative techniques of obtaining hydrogen determining miniaturization of energy sources (e.g. fuel cells) and feedstock feedstock flexibility of hydrogen generation processes.

The first stage of the works will be the development of the optimum preparation method of model $ZnO\text{-}Al_2O_3$ materials. Different synthesis techniques will be applied for comparative reasons i.e.: co-precipitation, co-precipitation with the addition of surfactants, method or reversed micro-emulsion (with pressure emulsification also). Additionally, depositing of nanometric grains of the formed spinel phase on different supports will be carried out. If synthesis parameters are selected properly, the obtained catalysts should show favorable structure and texture properties (i.e.: nanosize of $Zn_xAl_yO_z$ grains, mesoporosity and high surface area) - which can make them attractive for numerous catalytic applications, not only in the described WGS reaction.

Another equally interesting aspect of this project is research on the selection of the proper modification methods for model $ZnO\text{-}Al_2O_3$ with alkali metals salts, Cu and/or La.

The obtained materials will be thoroughly evaluated in terms of their physicochemical properties analysis using a wide range of experimental techniques: nitrogen adsorption/desorption, mercury porosimetry porosimetry, X-ray fluorescence, ICP-OES, X-ray diffraction analysis, X-ray photoelectron spectroscopy, UV-Vis-DR spectroscopy, thermogravimetric analysis, and High Resolution Transmission Electron Microscopy. These studies will allow for the specification of the impact of the method and preparation of modified and non-modified Zn-Al materials on morphology, chemical composition, structural and textural and surface properties.

The evaluation of activity and stability in the water gas shift reaction will be carried out by measurements in kinetic regime in gradientless and differential reactors. The complementary part of results will be attempt of evaluating the resistance to thermal and chemical deactivation as well as resistance to coking during conducting the WGS process at lower steam/gas ratio.

The results of proposed research will allow for the improvement of basic knowledge in the scope of promoted and non-promoted materials based on mixed $ZnO\text{-}Al_2O_3$ oxides with a dominant content of spinel $Zn_xAl_yO_z$ as catalysts for the WGS reaction. The collected results should allow for a more in-depth explanation of the role of spinel structure and the promoters' activity as factors determining the activity in the water gas shift reaction. The correlation of results related to kinetic and physicochemical studies creates the possibility of designing the catalytic material with desired properties dedicated to this process.