The polymerization is a chemical reaction during which small molecules, called monomers, form larger ones by binding to each other. The products of such reactions are called polymers. Although this process, in specific cases, can take place spontaneously, it usually requires use of special substances, among others, the catalysts are worth mentioning. The latter are the chemical systems, which added to the mixture of reactants allow the process to occur.

The Phillips catalyst is a catalytic system, in which the chromium containing active phase was supported on the silica surface (Cr/SiO_2). The polymerization of the simplest alkene, namely ethylene over this catalyst is one of those chemical reactions that we know a lot, but still not everything. In principle, we do not know the most important thing. We do not know the mechanism of this reaction.

It is widely known that this Cr/SiO_2 system very effectively catalyzes the polymerization of ethylene. This reaction results in the so called high-density polyethylene (HDPE), a polymer produced in huge quantities, accompanying us in our everyday life. Using the polyethylene, various things can be made, i.e., the plastic bags or the food storage containers. Importantly, it is estimated that nearly 50% of total world's production of HDPE is directly related to the Phillips catalyst. One might therefore conclude that since this polymer is produced in such big quantities, the reaction leading to its formation is well known. Nothing can be further from the truth than this. It turns out that despite many years of extensive research studies on this catalyst, a number of questions of fundamental importance still remain unanswered. As mentioned above, the mechanism of ethylene polymerization over the Phillips catalyst is not established, as well as the structure of the active sites, i.e., that piece of the catalytic system that directly takes part in the process.

According to the experimental studies, the reduced Cr oxide species are the precursors of the active sites. This is well established, because before the polymerization starts, the reduction of the Cr surface species occurs. This reduction takes place with an observed induction period, which is the initial stage of the reaction when the rate is very small. However, the mechanism of this transformation is not unambiguously determined. Thus, the first objective of this project is to study the reduction of the Philips catalyst, assuming ethylene as a reducing agent. The expected results of this project can reveal some interesting aspects of initial stages of reaction between ethylene and the Phillips catalyst. In particular, it is expected that the reason of induction period will be explained.

After formation of the reduced Cr species, ethylene polymerization takes place immediately, therefore experimental studies on the reaction mechanism are a challenging task and often lead to contradictory conclusions. Various reaction mechanisms have been proposed in the literature, however, none of these proposals is widely accepted. The initiation reaction, during which the active sites are formed from their oxide precursors, still remains unexplained, as well as the propagation and termination reaction, i.e., chain growing and chain ending reaction, respectively. Thus, the second objective of this project is to understand the full mechanism of ethylene polymerization taking the initiation, propagation and termination reaction into account. One cannot exclude that a new reaction mechanism will be proposed, which could be widely accepted in a whole scientific community.

In this project, the theoretical approach will be used to study ethylene polymerization over the Phillips catalyst. It means, that quantum chemical calculations will be carried out. Nowadays, such approach is commonly used, in parallel to the experimental studies. The reason why the theoretical approach is so important today is that the additional information, not available at this moment from the experimental techniques, can be obtained. The still growing computational power enables to study systems with increasing complexity and reliability. In this project, it is planned to perform computer simulations of a large systems using density functional theory (DFT) approach, a powerful tool in the hands of theoretical chemists. We expect that the results of these calculations will provide an additional knowledge about the examined oxide precursors and the active sites. Moreover, we belive that our efforts to determine the mechanism of ethylene polymerization over the Phillips catalyst will bring a great impact in the literaure.

Study on this reaction mechanism seems to be fully justified taking into account the widespread use of the Phillips catalyst, and the fact that we still do not know what is the mechanism of ethylene polymerization over the Phillips catalyst. Moreover, it is anticipated that the work carried out in the project should explain how different Cr oxide precursors affects the catalytic activity, separately at the initiation and propagation stages. The results obtained in this project will also allow to explain many other contentious issues and provide unique knowledge about the Phillips catalyst and its activity in the polymerization of ethylene.

In general, the project will contribute to the development of heterogeneous catalysis and computational catalysis.