Agata Suchora

Magnesium fluoride as a structure-determining component in nickel catalysts obtained by precipitation and combustion methods. Preparation, physicochemical characterization and catalytic activity in CO_2 methanation reaction

Climate change caused by global warming has long been the point of interest for many scientists. Carbon dioxide is the main cause of the greenhouse effect. One of the most promising ways to reduce CO_2 emissions is Power to Gas (PtG or P2G) technology, which involves using surplus electrical energy to produce hydrogen. The hydrogen is then used to convert CO_2 into methane. In the next stage, methane is injected into the gas network and becomes an energy carrier that can be used elsewhere and at another time. Among the many metals active in the CO_2methanation reaction, nickel is the most popular. In recent years, there has been a significant increase in interest in metal fluorides as well, including their use in catalytic reactions.

The presented doctoral dissertation titled "Magnesium fluoride as a structure-determining component in nickel catalysts obtained by precipitation and combustion methods. Preparation, physicochemical characterization, and catalytic activity in CO_2 methanation reaction" consists of three main parts: a literature review, an experimental section, and a section presenting research results and their discussion.

In the literature review section, the use of fluorides in catalysis is described, with a primary focus on magnesium fluoride. The crystalline structure of rutile-type of magnesium fluoride and nickel fluoride is presented. The influence of the unit cell size on formation of binary fluorides is emphasized. The Power to Gas technology is discussed in detail, which allows for the conversion of excess electrical energy into a more useful and flexible form – methane. The catalytic reaction of carbon dioxide hydrogenation to methane is presented in detail. The most important catalysts used in this reaction, as well as its mechanism and thermodynamics, are also discussed. An important part of the work is the preparation of catalysts using self-propagating high-temperature synthesis. Therefore, this section also provides a historical overview of this method and its main applications in preparation of catalysts.

The experimental section provides the methodology of work, with a detailed description of the preparation of catalysts obtained by precipitation and combustion methods. Furthermore, the parameters of the analytical techniques used for characterization of the obtained catalysts are presented. Additionally, the procedure for conducting the CO_2 hydrogenation to methane - is discussed.

In the final part of the work, the research results are presented. The main goal of this work was to obtain nickel catalysts for CO_2 methanation, in which magnesium fluoride serves as a structural component, and nickel fluoride is introduced as a secondary fluoride into the system. The synthesis of such materials assumes the formation of XYF_2-type systems, where both cations (X and Y) are divalent. This resulted in the preparation of two series of catalysts: one prepared by the precipitation method, and the other obtained through the combustion method.

A detailed physicochemical characterization of the magnesium-nickel systems synthesized by the precipitation method is discussed. Subsequently, the catalysts obtained by the combustion method are described. The characterization of both series of catalysts involved the following techniques:

- ICP-MS spectroscopy - providing information about the composition of catalysts;
- SEM-EDS microscopy - characterizing the morphology of catalysts;
- X-ray diffraction - providing information about the crystalline structures of catalysts;
- Nitrogen adsorption/desorption - providing information about the specific surface area (BET) and pore size and volume (BJH);
- Hydrogen chemisorption - determining the surface area of metallic nickel;
- Temperature-programmed reduction with hydrogen (TPR-H_2) - determining the reducibility of obtained catalysts;
- Temperature-programmed desorption of CO_2 (TPD-CO_2) - analyzing the basicity of materials.

Based on the conducted research, it was confirmed that all obtained catalysts have a structure and composition consistent with the initial assumption – they consist of MgF_2 and nickel nanoparticles. The progress of the combustion synthesis was documented in the form of video clips. Key frames illustrating the reaction progress were included in the thesis, along with a provided link where the complete video clips can be viewed (they were also included on the DVD).

In the final stage, the catalytic activity of the obtained catalysts in the CO_2 methanation reaction was examined. It was observed that magnesium-nickel systems obtained by both methods exhibited activity in this reaction, with a maximum conversion of 57% for precipitated catalysts and 70% for combustion catalysts at temperature of 450 and 350^{o}C, respectively. In the case of precipitated systems, the nickel content had the most significant impact on activity, while for combustion catalysts, the alkaline centers on the surface proved to be significant. Studies conducted with reduced mas of catalyst (GHSV=20,000 1/h; QT=60,000 ml/g·h), resulting in a significant increase in catalytic activity while maintaining high selectivity. Additionally, carbon balance for both systems was examined, and it was found that the phenomenon of carbon deposition was minimal.