

Institute of Chemical Engineering

Adres artykułu: <https://iich.gliwice.pl/en/article/electrochemical-preparation-of-catalytically-active-copper-oxides-for-methane-oxidation-in-ventilation-air>

Electrochemical preparation of catalytically active copper oxides for methane oxidation in ventilation air

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Description

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The search for effective and economically viable gas purification methods is extremely important in today's world, plagued by excessive emissions of harmful substances and legal restrictions. One of the more serious threats is methane, a greenhouse gas with a global warming potential (GWP) of approximately 23 over a hundred-year period. Huge amounts of this gas are released into the atmosphere from the ventilation systems of underground mines. The fundamental difficulty in utilizing methane contained in ventilation air is its low concentration, below 1% by volume, and often even below 0.3% by volume. From a chemical point of view, methane is characterized by low reactivity resulting from the nature of the carbon-hydrogen bond, which is nonpolar and has a high dissociation energy (at 25°C ~ 439 kJ/mol). Currently, thermal methods are primarily used for methane utilization, which require the process to be carried out at temperatures above 800°C. An alternative to thermal methods is catalytic methane oxidation. The catalytic process is carried out at a lower temperature, making it safer and more economical. Catalysts that are active at temperatures below 500°C are mainly based on nanoparticles of noble metals, such as palladium and platinum, often doped with cobalt and cerium oxides. The difficulties and costs associated with the production of these catalysts limit their use on a larger scale. Furthermore, noble metal nanoparticles undergo thermal deactivation due to a strongly exothermic reaction and are very sensitive to pollutants present in ventilation air. A solution to this situation is to find cheaper alternatives. The use of copper oxides (CuO, Cu₂O) appears promising, as there are reports in the literature about the possibility of carrying out the oxidation of methane at low concentrations on a catalyst based on copper oxides at a temperature of ~500°C. These oxides can be obtained, for example, in the process of electrochemical oxidation of copper; this method allows for the precise and repeatable production of catalytically active oxides in the assumed shape and size. This is

important because the morphology of the nanoparticles is an important factor determining the activity and selectivity in the considered oxidation reaction. The aim of the project is to produce a catalytically active oxide layer on the surface of thin copper sheets by means of electrochemical oxidation (in a two-electrode system) and to determine the rate of methane oxidation reaction as a function of temperature. The most desirable oxide structures are nanoneedles and nanowires due to their high specific surface area. The oxidation process of the copper sheet will be carried out in two stages. In the first stage, electropolishing will be performed in a bath of orthophosphoric acid with the addition of alcohols. In the second stage, the surface of the sheet will be oxidized, resulting in it being covered with active forms of oxides. The process is planned to be carried out using electrolytes containing: (i) a 2 M KOH solution, (ii) a KOH solution with the addition of NH₄F, (iii) a 3 M NaOH solution. The process will be conducted in the temperature range of 20°C to 40°C. The voltage, which determines the shape and size of the obtained copper oxides, will be in the range of 4V to 10V [3]. The morphology of the obtained coatings will be continuously evaluated based on images taken with a scanning electron microscope (SEM), which will allow determining the most favorable process conditions (current-voltage parameters, electrolyte composition, temperature) for obtaining the assumed oxide structures (nanoneedles or nanowires). For the qualitative and quantitative assessment of the generated copper oxides, methods such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) will be used. The specific surface area of the obtained oxide coatings will be determined using nitrogen physisorption. The next step will be to perform measurements of the methane oxidation reaction rate in a gradientless reactor. The gas supplied to the reactor will contain air with the addition of methane at a concentration of 0.2 to 0.8 % by volume. The process will be analyzed in the temperature range of 300°C to 600°C. The concentrations of reagents will be monitored using Fourier transform infrared (FTIR) absorption spectroscopy. The results obtained from measurements in the gradientless reactor will allow comparing the change in activity of the obtained catalysts resulting from their preparation method. Furthermore, the results from the morphological studies of the obtained copper oxides, combined with catalytic tests, will allow for the evaluation of their suitability for the methane oxidation process at a concentration below 1% by volume in air.

Metryczka

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