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POSTER COMMUNICATION

Methane removal from ventilation air on a copper oxide catalyst

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Abstract
The work concerned the preparation of catalytically active copper oxides by electrochemical oxidation. The obtained catalysts were tested for the oxidation of methane with a concentration below 1% vol. in the air.

Keywords
methane combustion, copper oxide, coal mine ventilation

1. INTRODUCTION

The poster presented at the UCRA3 in 2024 conference discusses the catalytic oxidation of methane with a concentration below 1% vol. in the air. Copper oxides obtained in the electrochemical oxidation of copper were tested as a catalyst.

In general, removing methane from ventilation air is a big challenge for companies producing this type of pollution due to emission fees. This problem is also troublesome for engineers designing air treatment installations. The difficulty in this case is mainly not the lack of availability of technology enabling methane removal, but ensuring low operating costs of the installation. Methane is a non-toxic gas whose emissions should be reduced to a minimum due to its high global warming potential (GWP). Methane in ventilation air in Poland occurs mainly in hard coal mines, even in those no longer exploited. Although its concentration in the air is usually below 1% by volume, considering the high air flow rate in the ventilation shaft, which reaches several thousand m^3/min, it causes the emission of huge amounts of methane into the atmosphere every year. Currently, existing methane removal technologies can be divided into thermal and catalytic (Pawlaczyk-Kurek and Suwak, 2021). The thermal process is carried out at temperatures usually above 800 °C. In catalytic methods, methane oxidation occurs at a lower temperature, usually below 500 °C. Noble metals such as palladium and platinum doped with cobalt and cerium oxides are used as catalysts (Oh et al., 2024).

The motivation to conduct the research was to experimentally check whether copper oxides obtained by electrochemical methods exhibit catalytic activity in the oxidation of dilute methane and whether this activity depends on the preparation method. Moreover, copper oxides can be a much cheaper alternative to palladium catalysts (Feng et al., 2011). The poster communication compares oxides obtained electrochemically using three different solutions with commercially available copper(II) oxide (analytical grade, Chempur, Poland).

2. METHODS

Catalytically active copper oxides were obtained as a result of electrochemical oxidation of the surface of copper plates. The oxidation process was carried out using three different methods (i.e. using three different electrolytes). In "Method 1", 0.02 M potassium hydroxide solution was used as electrolyte. The voltage between the electrodes was 6–8 V. In "Method 2", the electrolyte was a solution of 0.15 M KOH + 0.1 M NH4F, and the voltage in the electrolyser was set in the range of 6–8 V. The electrolyte in "Method 3" was 0.1 M ammonium fluoride solution. The process was carried out at a constant current density of 5 mA/cm^2, then the sheet (from Method 3) was transferred to a 10% hydrogen peroxide solution to reach the final layer of copper oxides.

The catalytic properties of the obtained oxides were tested in a gradientless reactor. In each measurement series, 0.33 g of the oxide tested was placed in the reactor. Measurements

were carried out for air containing 4000 ppm of methane in the temperature range from 250 to 470 °C. The value of the maximum temperature used in these measurements was determined based on preliminary tests carried out for an empty reactor. These tests were carried out to determine the temperature of homogeneous oxidation of methane. The gas flow rate used in catalytic tests under standard conditions ranged from 200 ml/min to 800 ml/min. To determine the conversion of methane, concentration was measured at the inlet and outlet of the reactor using infrared spectroscopy.

A scanning electron microscope (SEM) was used to morphologically evaluate the obtained oxides. SEM images are shown in Figures 1–3 of the poster. The analysis of the chemical composition of the formed oxides was carried out using X-ray diffractometry (X'Pert Pro, Malvern Panalytical, Great Britain), Fig. 4, and Raman spectrometry (alpha300 M+ WITec, Germany), Fig. 5.

3. RESULTS

Fig. 6A shows the methane conversion obtained for a flow rate of 200 ml/min. and Fig. 6B for a flow rate of 800 ml/min. The presented data show that copper oxides gained in the electrochemical oxidation process are characterized by catalytic activity in the methane oxidation reaction in ventilation air. The oxides received with Methods 1 and 2 are more active compared to the oxides obtained with Method 3. Moreover, copper oxides obtained in the electrochemical oxidation process are more active compared to commercially available copper (II) oxide. Methane conversion of about 50% for the best catalysts was observed at a temperature of about 350 degrees Celsius and flow rate of 200 ml/min.

4. CONCLUSIONS

Based on the measurements performed, the catalytic properties of copper oxides obtained in the electrochemical process were demonstrated. Moreover, the received oxides were characterized by greater catalytic activity than CuO available on the market.

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Introduction

Methane is one of the most common pollutants emitted into the atmosphere with ventilation air from coal mines. This gas is dangerous not because of its toxicity, but because of its global warming potential (GWP). Its concentration in air is below 1% by volume, but considering the high gas flow rate, which can reach up to several thousand m^3/min, this results in the emission of huge amounts of methane into the atmosphere every year. Currently, there are two main methods of methane removal: thermal and catalytic. The thermal process is carried out at temperatures usually above 800°C. In catalytic methods, methane oxidation is carried out at a lower temperature, usually below 500°C.

Catalytically active copper oxides were obtained as a result of electrochemical oxidation of the surface of copper plates. The oxidation process was carried out using three different methods. Electolytes: Method 1 – 0.02 M potassium hydroxide solution; Method 2 – 0.15 M KOH + 0.1 M NH_4F; Method 3 – 0.1 M ammonium fluoride solution.

The catalytic properties of the obtained oxides were tested in a gradientless reactor. In each measurement series, 0.33 g of the oxide tested was placed in the reactor. Measurements were carried out for air containing 4000 ppm of methane in the temperature range from 250 to 470°C. The gas flow rate used in catalytic tests under standard conditions ranged from 200 ml/min to 800 ml/min. Concentration was measured at the inlet and outlet of the reactor to determine the conversion of methane.

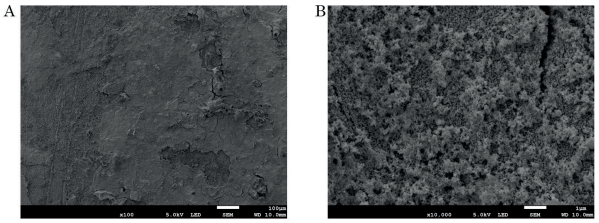

Fig. 1. SEM pictures of copper oxide obtained by Method 1. Magnification A) 100x, B) 10000x

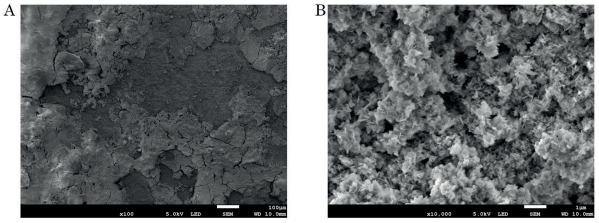

Fig. 2. SEM pictures of copper oxide obtained by Method 2. Magnification A) 100x, B) 10000x

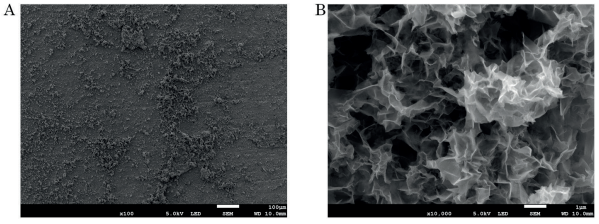

Fig. 3. SEM pictures of copper oxide obtained by Method 3. Magnification A) 100x, B) 10000x

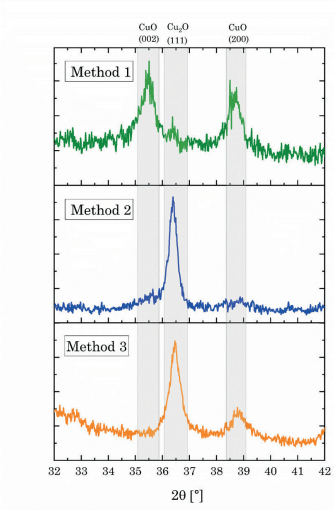

Fig. 4. XRD spectra.

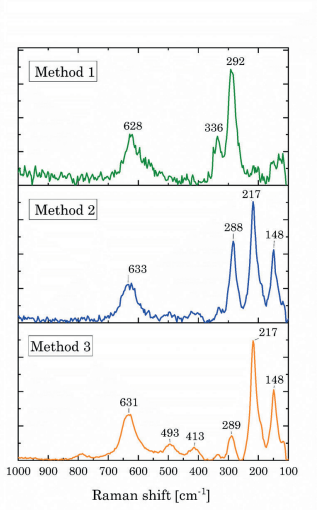

Fig. 5. Raman spectra.

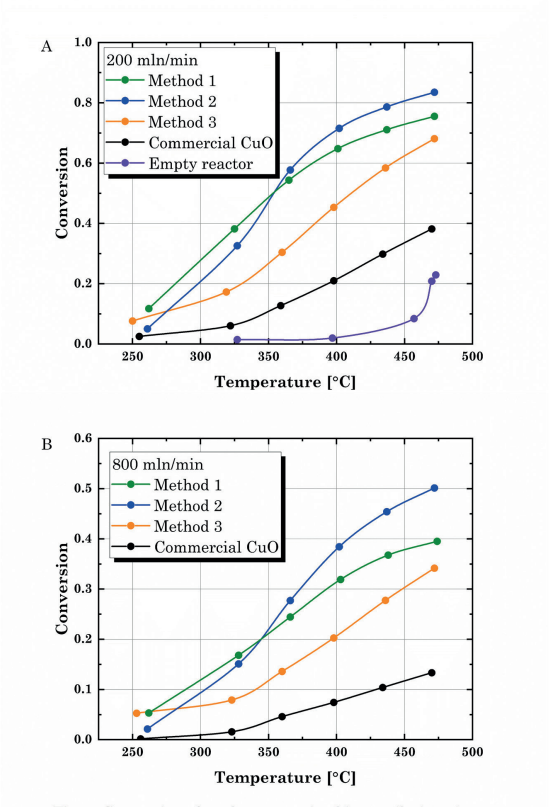

Fig. 6. Conversion of methane contained in ventilation air. Gas flow rate: A) 200 mln/min, B) 800 mln/min.

Acknowledgments

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