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Preparation of activated carbon from the biodegradable film for CO₂ capture applications

J. Serafin^{1*}, A.K. Antosik², K. Wipliszewska³, Z. Czech²

West Pomeranian University of Technology, Szczecin, Faculty of Chemical Technology and Engineering, Pulaskiego 10, 70-322 Szczecin, Poland

¹Institute of Inorganic Chemical Technology and Environment Engineering

²Institute of Organic Chemical Technology

³Polymer Institute

Corresponding author: e-mail: Jaroslaw.Serafin@zut.edu.pl

In this work for the first time, activated carbons were prepared from carboxymethyl film (low-cost carboxymethyl film waste), using chemical activation with potassium hydroxide. The samples were characterized by nitrogen adsorption-desorption at 77 K, XRD, SEM methods. The high values of the specific surface area and total pore volume were achieved and were equal to 2064 m²/g and 1.188 cm³/g, respectively. Waste from the film can be immediately utilized without CO₂ production. This is the environmentally friendly way of waste utilization. Through this process, we can protect our environment. This study showed that the activated carbon obtained from carboxymethyl film waste can be used as a good adsorbent for CO₂ adsorption.

Keywords: A biodegradable film activated carbon, adsorption, CO₂, capture.

INTRODUCTION

Growing global concerns on the environmental, social and economic effect of greenhouse gases (GHG) emissions motivated the development various strategies for GHG reduction¹. The major GHG are CO₂ and CH₄. The main sources of CO₂ are fossil fuel combustion, deforestation, cement production. The main sources of CH₄ are fossil fuel production, agriculture, landfills. Methane has a global warming potential 25 times² that of CO₂ but it is also valuable raw material mainly for syngas production. The most widely practiced production route of syngas (hydrogen and carbon oxide) is steam reforming. Unfortunately this process requires high temperatures (800–900°C)³ which makes it expensive. Alternatively, CO₂ can be used to produce syngas in conjunction with methane by the dry reforming⁴. This is alternative solution for CO₂ and CH₄ utilisation and generation of value-added products but it cannot be applied in industry because of fast catalysts deactivation⁵. The production of hydrogen from methane by catalytic methane decomposition^{6–8} or utilizing membranes⁹ especially zeolite membranes¹⁰ was investigated deeply. Apart from hydrogen production other valuable product – carbon nanomaterials such as carbon nanotubes^{7–13}, carbon nanofibers⁸, carbon nanocapsules¹⁴, and metal nanowires encapsulated in carbon¹⁵ can be obtained from methane. Studies regarding the process of methane oxidation to products different from those obtained when preparing synthesis gas were conducted already at the beginning of the 20th century. Direct methane oxidation to oxygenates such as formaldehyde¹⁶ and methanol¹⁷ is possible in presence of catalyst such as: niobium(V) oxide¹⁶, Fe-ZSM-5^{18, 19}, M/SiO₂ where M = Se, Nb²⁰, V²⁰, Fe²⁰, and Mo²¹ or in presence of Methylosinus trichosporium OB3b²². Catalytic conversion of methane to esters in condensed phase was investigated at ambient^{23, 24} and high pressure^{25, 26}. As catalyst metals such as Pd^{27–29}, Pt^{24–31}, Ni³², Zn³² and halogens²⁶ mainly bromine³³ and iodine^{23, 24} were applied. The separation system of products obtained in condensed phase using

membrane was developed³⁵. Methane can be used as fuel in cars but good methane sorbent is needed. Adsorbed methane technology could allow methane consumption comparable to the other conventional petroleum-based fuels. Activated carbons can be applied as methane sorbents^{36–39}.

There are many attempts for CO₂ utilization as a raw material e. g. photocatalytic reduction to methanol⁴⁰ but the efficiency is usually very low. Carbon dioxide is applied in industry as raw material to urea production but the urea production scale is much smaller than that of synthesis gas^{5, 41, 42}. The most important commercially applied technology for CO₂ removal is the absorption process in amines. One major disadvantage of amine absorption processes is the high energy consumption, arising from high energy levels required to regenerate the sorbent^{41, 42}. The adsorption on solid sorbents seems more promising. Carbon materials are very good CO₂ sorbents³⁸. CO₂ adsorption on commercial activated carbons⁴³, modified commercial activated carbons^{44–47}, carbon nanosheets⁴⁸, carbon nanotubes^{49–51}, activated carbons produced from biomass^{52–56} and from molasses⁵⁸ was investigated. Carbon materials have great potential. They can be applied also as sorbents of various chemicals^{59–62} and hydrogen^{63–67} and even catalyst⁶⁸ or catalyst supports^{69–71}. Their properties dependent on the carbon source and synthesis method^{72–77}.

Biodegradable film is environmentally friendly as it eventually degrades in the soil after about a month, and without the participation of microorganisms after year⁷⁸. If oxygen is present, aerobic biodegradation occurs and carbon dioxide is produced⁷⁹. If there is no oxygen, an anaerobic degradation occurs and methane is produced instead of carbon dioxide and water⁸⁰. An application of biodegradable film is obviously more advantageous than the traditional. It also has drawbacks: a) necessity for storage of the waste before decomposed; b) production of greenhouse gases (CO₂ or CH₄) to the atmosphere.

The goal of this work was to develop a method of preparing activated carbon using hydrophilic films based

on carboxymethyl starch (CMS) as a carbon precursor. Such method solves problems with storage of waste before they decompose and what more important with greenhouse gases emission. According to the our knowledge, production of activated carbon from CMS was not described up to know. In addition, activated carbons prepared by us are good CO₂ sorbents.

MATERIAL AND METHODS

MATERIAL

CMS with a degree of substitution 0.8 was prepared according to the method described elsewhere by Spychaj et al.⁸¹. Monohydrate citric acid (CA) (p. a.), and glycerol (p.a.), potassium hydroxide (KOH) (p.a.) were delivered from Chempur (Poland).

Preparation of biodegradable CMS-based film

The film was prepared in accordance with the method reported by Spychaj et al.⁸² namely: 3 g carboxymethyl starch, 2 g glycerol, and 1 g citric acid was introduced to 100 g of distilled water and stirred for 30 min. The final mixture was poured into polytetrafluoroethylene (PTFE) mold and dried for 48 h at 70°C. Obtained film (thickness 200–300 μm) was used for the production of activated carbon.

Preparation of activated carbon

Contained in film crosslinking CMS were used as a carbon precursor. CMS was crushed using an electric grinder. Chemical activation of the film powdered was done with saturated solution KOH (mass ratio KOH: carbon source, 1:1) during 3 h. The mixtures were dried at 200°C for 19 h. The next step was the carbonization of materials for 1h in a horizontal tube furnace under nitrogen flow at range 500–700°C. Cooled samples were washed with distilled water, treated with 1 M HCl for 19 h period, and then washed with distilled water until neutral. In the end, materials were dried at 120°C. The materials were denoted as CMS500, CMS550, CMS650, CMS700 (in accordance with the carbonization temperature). Method of activated carbon preparation was described in Polish patent application⁸³.

XRD

The structures of activated carbon were determined by XRD. Samples were recorded using PANalytical X-ray Empyrean diffractometer with Cu Kα radiation. The test results were analysed using the X'Pert HighStore diffraction program.

Nitrogen and sorption

The texture characterization of activated carbons was carried out by N₂ adsorption and desorption at 77 K using, a Quadrasorb automatic system (Quantachrome Instruments). Before the analysis samples were degassed overnight (16 h) under high vacuum at 250°C. The Brunauer–Emmett–Teller (BET) equation was used to determine surface areas (SBET). The total pore volume (V_{tot}) was determined at the highest value relative pressure (p/p₀ = 0.99). The volume of micropores (V_{mic})

and mesopores (V_{mes}), was obtained using the density functional theory (DFT).

Carbon dioxide sorption

CO₂ adsorption was provided at pressure up to 1 bar, at a temperature of 25°C. Before the analysis samples were degassed overnight (16 h) under high vacuum at 250°C.

SEM

Scanning electron microscopy (SEM) was used to investigate the morphology of the activated carbons (UHR FE-SEM Hitachi SU8020).

RESULTS AND DISCUSSION

Properties of the CMS film are shown Table 1.

Table 1. Useful properties of CMS-based film

Properties	Results for CMS-film	Mechanical properties	Results for CMS-film
Moisture absorption	20% after 72 h	Elongation	78%
Solubility in water	58%	Young modulus	0.2 MPa
Contact angle	69.9 ° ± 1.4	Tensile strength	3 MPa

Figure 1 shows results of XRD measurements. Two peaks at about 26° and 45° were observed. The peak at 2θ = 26° corresponds to an interlayer distance of which graphene sheets (JCPDS by 26-1078). The lower temperature the broader peak at 26° indicating less and less ordered and structure. The peaks very broad indication of the random turbostratic stacking of layers.

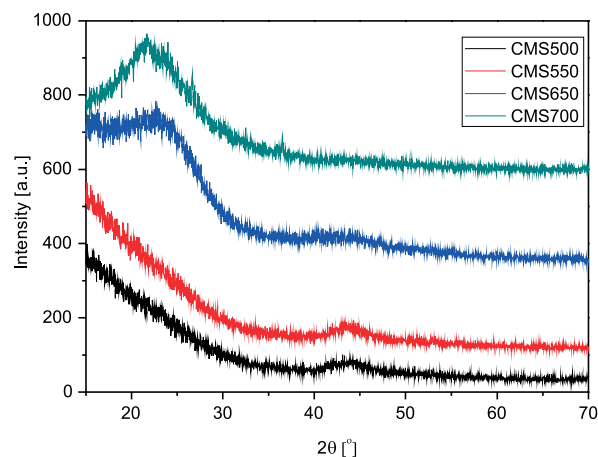


Figure 1. XRD diffraction pattern for activated carbons using Cu Kα radiation (λ = 1.5418 Å)

From Fig. 2 the nitrogen isotherm of CMS500 has the shape in between type I and type II according to IUPAC classification⁸⁴. This type of isotherm is characterized by the micropore and mesopore structures. The H4-type hysteresis loop in the CMS500 material reveals the formation of narrow slit-like pores. Samples CMS550, CMS650 and CMS700 show type II isotherm with small hysteresis type H4.

Table 2 shows the BET surface area, total pore volume, mesopores and micropores volume values. Note that the CMS500 sample showed the highest specific surface area 2064 m²/g and the highest micropore volume 0.417 cm³/g.

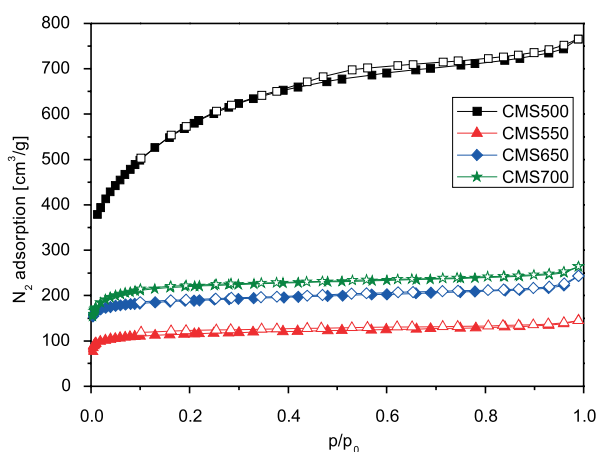


Figure 2. Nitrogen adsorption- desorption isotherms for activated carbons at 77 K

Table 2. The values of specific surface area, total pore volume and micropores volume of obtained activated carbons

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mikro} (cm^3/g)
CMS 500	2064	1.188	0.417
CMS 550	443	0.225	0.151
CMS 650	743	0.377	0.261
CMS 700	849	0.409	0.278

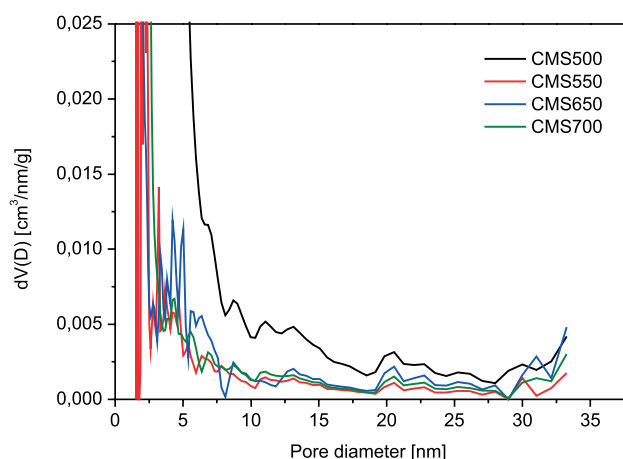


Figure 3. DFT pore size distribution derived from nitrogen adsorption at 77 K of activated carbons CMS

DFT pore size distributions and cumulative pore volume curves are shown in Table 2, Fig. 3 respectively. The total pore volumes were estimated on the basis of the volume adsorbed at a relative pressure of about 0.95. The pore size distribution and micropore volume was obtained after application of the QSDFT model to the nitrogen adsorption data and assuming a slit-shape pore model. All samples have micropores located about 1.8 nm. Generally, the micropores result from the rapid volatilization of light organics and amorphization of carbonaceous segments during direct carbonization at a relatively high temperature of 500°C. The occurrence of mesopores is visible for each CMS in the whole range from 2 nm up to 35 nm where increasing. These pores are most demonstrating highest values in the range up to 7.5 nm. Obviously, CMS500 demonstrates a mesopore-dominant structure with a large mesopore value.

Figure 4 shows the sorption capacity of samples CMS. The highest sorption capacity was observed at activated carbon obtained at the temperature of 500°C and amounts to 3.52 mmol/g. The process of adsorption isotherms is typical for physical adsorption. Kinetics were not tested

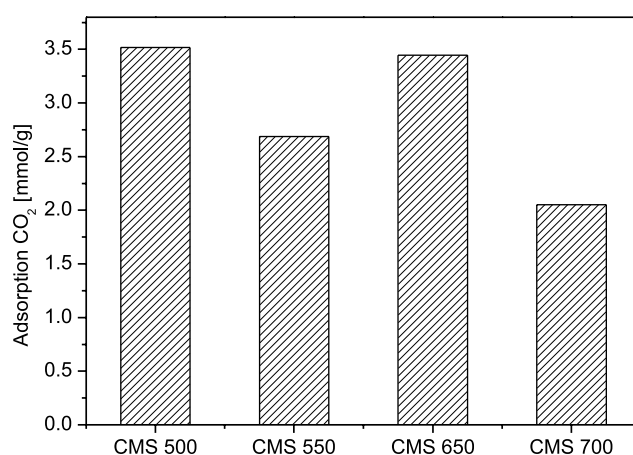


Figure 4. Adsorption of CO_2 at 25°C for CMS500, CMS550, CMS600, CMS650, CMS700

but the process was very fast. The balance was fixed after about a minute.

The SEM micrographs showed the presence of macropores on the surface of all tested materials. The only surface of CMS500 is shown in Fig. 5 because the micrographs of the other materials were very similar.

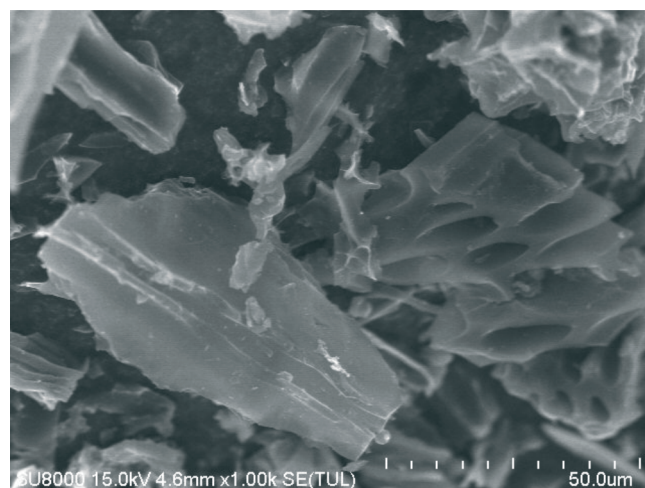


Figure 5. SEM micrograph of CMS500 surface

CONCLUSION

The new carbon precursor, namely carboxymethyl starch film was used for activated carbon production. Potassium hydroxide was used as an activating agent. The high values of the specific surface area and total pore volume were achieved and were equal to 2064 m^2/g and 1.188 cm^3/g , respectively. It is a good alternative to solve the problem of the foil storage until it decomposes. Waste from the film can be immediately utilized without CO_2 production. This is the environmentally friendly way of waste utilization. Through this process, we can protect our environment. The activated carbons described here are good materials for removing CO_2 from the atmosphere.

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