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

J. Serafin¹, A.K. Antosik², K. Wilpiszewska³, 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 reduction. 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 times 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) which makes it expensive. Alternatively, CO₂ can be used to produce syngas in conjunction with methane by the dry reforming. This is alternative solution for CO₂ and CH₄ utilisation and especially zeolite membranes in conjunction with methane by the dry reforming. 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 deactivation. The production of hydrogen from methane by catalytic methane decomposition or utilizing membranes especially zeolite membranes was investigated deeply. Apart from hydrogen production other valuable product – carbon nanomaterials such as carbon nanotubes, carbon nanofibers, carbon nanocapsules, and metal nanowires encapsulated in carbon 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 formaldehyde and methanol is possible in presence of catalyst such as: niobium(V) oxide, Fe-ZSM-5, M/SiO₂ where M=Se, Nb, V, Fe, and Mo or in presence of Methylotomas trichosporium OB3b. Catalytic conversion of methane to esters in condensed phase was investigated at ambient and high pressure. As catalysts metals such as Pt, Pd, Ir, Ni, Zn and halogens mainly bromine and iodine were applied. The separation system of products obtained in condensed phase using membrane was developed. 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.

There are many attempts for CO₂ utilization as a raw material e. g. photocatalytic reduction to methanol 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. 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. The adsorption on solid sorbents seems more promising. Carbon materials are very good CO₂ sorbents. CO₂ adsorption on commercial activated carbons, modified commercial activated carbons, carbon nanosheets, carbon nanotubes, activated carbons produced from biomass and from molasses was investigated. Carbon materials have great potential. They can be applied also as sorbents of various chemicals and hydrogen and even catalysts or catalyst supports. They properties dependent on the carbon source and synthesis method.

Biodegradable film is environmentally friendly as it eventually degrades in the soil after about a month, and without the participation of microorganisms after year. If oxygen is present, aerobic biodegradation occurs and carbon dioxide is produced. If there is no oxygen, an anaerobic degradation occurs and methane is produced instead of carbon dioxide and water. 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 \( \mu \)m) 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 K\( \alpha \) radiation (\( \lambda = 1.5418 \) Å). 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 \( \mathrm{N}_2 \) 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 \( (V_{\text{tot}}) \) was determined at the highest value relative pressure \( (p/p_0 = 0.99) \). The volume of micropores \( (V_{\text{mic}}) \) and mesopores was obtained using the density functional theory (DFT).

Carbon dioxide sorption

\( \mathrm{CO}_2 \) 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 20 = 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.

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.
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 others materials were very similar.

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 demonstrate 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

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

| Sample | S_{text}/m²/g | V_{total}/cm³/g | V_{micropore}/cm³/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               |

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 m²/g and 1.188 cm³/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 CO₂ 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 CO₂ from the atmosphere.

LITERATURE CITED

1. Manan, Z.A., Nawi, W.N.R.M., Alwi, S.R.W. & Klemes, J.J. (2017). Advances in Process Integration research for CO₂ emission reduction - A review. J. Clean. Prod. 167, 1–13. DOI: 10.1016/j.jclepro.2017.08.138.
2. IPCC, Direct global warming potentials, IPCC fourth assess. Rep. Clim. Change 2007 (2007) 2.10.2.
Method Algorithm.

Carbon Nanomaterials over Ni/ZSM-5 Catalyst Using Simplex
333–345, DOI: 10.1080/1536383X.2011.613543.

over a Supported-nickel Catalyst.

wicz, B. (2013). Synthesizing Multi-walled Carbon Nanotubes
9936-6.

from methane catalytic decomposition over nickel supported
wicz, B. (2010). Low temperature growth of carbon nanotubes

formaldehyde using polymorphic T-, M-, and H-forms of

B. & Narkiewicz, U. (2008). Selective methane oxidation to
carbon.

ture one-step synthesis of cobalt nanowires encapsulated in

ZSM-5.

formaldehyde and methanol using molecular oxygen over Fe-

ZSM-5 catalyst.

hydrogen and carbon nanomaterials from methane using Co/

Methane Reforming with Carbon Dioxide.

DOI: 10.1023/B:KICA.0000009057.79026.0b

Michalkiewicz, B. (2003). Methane conversion to
methyl bisulfate from its solutions in fuming sulphuric
acid combined with hydrolysis to methanol.

Michalkiewicz, B., Ziebro, J. & Tomaszewski, M. (2006).
Preliminary investigation of low pressure membrane distillation
of methyl bisulphate from its solutions in fuming sulphuric acid
combined with hydrolysis to methanol. J. Membrane Sci.
213(1–2), 223–227, DOI: 10.1016/j.memsci.2006.02.046.

Michalkiewicz, B., Ziebro, J. & Srenscek-Nazzal, J. (2006).
Direct oxidation of methane to formaldehyde. Przem. Chem.
85(8–9), 624–626.

Kałucki, K., Michalkiewicz B., Morawski A.W., Arabczyk
W. & Ziebro J. (1995). Przem Chem. 74(4), 135–136.

Markowska, A. & Michalkiewicz, B. (2009). Biosynthesis
of methanol from methane by Methylosinus trichosporium
OB3b. Chem. Pap. 63(2), 105–110, DOI: 10.1007/s11696-008-
0100-5.

Michalkiewicz, B. (2011). Methane oxidation to methyl
bisulphate in oleum at ambient pressure in the presence of
iodine as a catalyst. Appl. Catal. A-Gen. 394(1–2), 266–268,
DOI: 10.1016/j.apcata.2011.01.014

Michalkiewicz, B. & Kosowski, P. (2007). The selective
catalytic oxidation of methane to methyl bisulphate at
ambient pressure. Catal. Commun. 8(12), 1939–1942,
DOI: 10.1016/j.catcom.2007.03.014

Michalkiewicz, B. & Kałucki, K. (2002). Direct conversion
of methane into methanol formaldehyde and organic acids.
Przem. Chem. 81(3), 165–170.

Jarosinska, M., Lukbowski, K., Sosnicki, J.G. &
Michalkiewicz, B. (2008). Application of Halogens as Catalysts
for the methane to methyl bisulfate reaction. Appl. Catal. A-Gen.
349(1–2), 407–412, DOI: 10.1016/j.apcata.2006.04.006.

Michalkiewicz, B. (2006). Assessment of the possibility
of the methane to methanol transformation. Pol. J. Chem.
Technol. 10(2), 20–26, DOI: 10.2478/v10026-008-0023-5.

Michalkiewicz, B. (2006). Esterification of methane
as the first stage in converting the natural gas to methanol.
Przem. Chem. 85(8–9), 620–623.

Michalkiewicz, B. & Balcer, S. (2012). Bromine catalyst
for the methane to methyl bisulphate reaction. Pol. J. Chem.
Technol. 14(4), 19–21, DOI: 10.2478/v10026-012-0096-z

Michalkiewicz, B., Jarosinska, M. & Lukasiewicz, I.
(2009). Kinetic study on catalytic methane esterification
in oleum catalyzed by iodine. Chem. Eng J. 154(1–3), 156–161,
DOI: 10.1016/j.cej.2009.03.046

Michalkiewicz, B., Ziebro, J. & Tomaszweska, M. (2006).
Preliminary investigation of low pressure membrane distillation
of methyl bisulphate from its solutions in fuming sulphuric
acid combined with hydrolysis to methanol. J. Membrane Sci.
286(1–2), 223–227, DOI: 10.1016/j.memsci.2006.09.039.

Srenscek-Nazzal, J., Kaminska, W., Michalkiewicz, B. &
Koren, Z.C. (2013). Production, characterization and methane
storage potential of KOH-activated carbon from sugarcane
molasses. Ind Crop Prod. 47, 153–159, DOI: 10.1016/j.indcrop.2013.03.004

Duda, J.T., Kwiatkowski, M., Milewska-Duda, J. (2010).
Application of clustering based gas adsorption models to
analysis of microporous structure of carbonaceous materials.
Appl. Surf. Sci. 256(17), 5243–5248, DOI:10.1016/j.apsusc.2009.12.111.

Kwiatkowski, M., Duda, J.T. & Milewska-Duda, J. (2014).
Application of the LBET class models with the original fluid
state model to an analysis of single, double and triple carbon
dioxide methane and oxygen adsorption isotherms. Colloids Surf. A: Physicochem. Engine. Asp. 457(1), 449–454, DOI:
10.1016/j.colsurfa.2014.06.021.
69. Wroblewska, A., Makuch, E., Młodzik, J. & Michalkiewicz, B. (2017). Fe-carbon nanoreactors obtained from molasses as efficient catalysts for limonene oxidation. *Green Porsec Synth* 6(4), 397–401. DOI: 10.1515/gps-2016-0148.

70. Serafin, J. (2017). Utilization of spent dregs for the production activated carbon for CO2 adsorption. *Pol J Chem Technol.* 19(2), 44–50. DOI: 10.1016/S1750-5836(07)00094-1.

71. Młodzik, J., Wroblewska, A., Makuch, E., Wrobel, R.J. & Michalkiewicz, B. (2016). Fe/EuroPh catalysts for limonene oxidation to 1,2-epoxylimonene, its diol, carveol, carvone and perillyl alcohol, *Catal. Today.* 268, 111–120, DOI: 10.1016/j.cattod.2015.11.010.

72. Kwiatkowski, M., Srenscek-Nazzal, J. & Michalkiewicz, B. (2017). An analysis of the effect of the additional activation process on the formation of the porous structure and pore size distribution of the commercial activated carbon WG-12. *Adsorption,* 23(4), 551–561, DOI: 10.1007/s10450-017-9867-4.

73. Kwiatkowski, M. & Broniek, E. (2017). An analysis of the porous structure of activated carbons obtained from hazelnut shells by various physical and chemical methods of activation. *Colloid. Surface. A.* 529, 443–453, DOI: 10.1007/s10450-017-9867-4.

74. Kwiatkowski, M., Fierro, V. & Celzard, A. (2017). Numerical studies of the effects of process conditions on the development of the porous structure of adsorbents prepared by chemical activation of lignin with alkali hydroxides. *J. Colloid. Interf. Sci.* 486, 277–286, DOI: 10.1016/j.jcis.2016.10.003.

75. Kwiatkowski, M., Kalderis, D. & Diamadopoulos, E. (2017). Numerical analysis of the influence of the impregnation ratio on the microporous structure formation of activated carbons, prepared by chemical activation of waste biomass with phosphoric acid. *J. Phys. Chem. Solids.* 105, 81–85, DOI: 10.1016/j.jpcs.2017.02.006.

76. Kwiatkowski, M. & Broniek, E. (2013). Application of the LBET class adsorption models to the analysis of microporous structure of the active carbons produced from biomass by chemical activation with the use of potassium carbonate. *Colloids Surf. A.* 427, 47–52, DOI: 10.1016/j.colsurfa.2013.03.002.

77. Srenscek-Nazzal, J. & Michalkiewicz, B. (2011). The simplex optimization for high porous carbons preparation. *Pol J Chem Technol.* 13(4), 63–70, DOI: 10.2478/v10026-011-0051-4.

78. Zee, M., Stoutjesdijk P.A.A. & Heijden, D.W. (1997). Structure-biodegradation relationships of polymeric materials. 1. Effect of degree of oxidation on biodegradability of carbohydrate polymers. *J. Polymer. Environ.* 3(4), 235–242.

79. Grima, S., Bellon-Maurel, V., Feuilloley, P. & Silvestre, F. (2002). Aerobic Biodegradation of Polymers in Solid-State Conditions: A Review of Environmental and Physicochemical Parameter Settings in Laboratory Simulation. *J Polymer Environ.* 8(4), 183–195. DOI: 10.1023/A:1015297727244.

80. Jayasekara, R., Harding, I., Bowater, I. & Lonergan, G. (2005). Biodegradability of Selected Range of Polymers and Polymer Blends and Standard Methods for Assessment of Biodegradation. *J. Polymer. Environ.* 13, 231–251. DOI: 10.1007/s10924-005-4758-2.

81. Spychaj, T., Wilpiszewska, K. & Zdanowicz, M. (2013). Medium and high substituted carboxymethyl starch: Synthesis, characterization and application. *Starch,* 65, 22, DOI: 10.1002/star.201200159.

82. Spychaj, T., Wilpiszewska, K. & Antosik, A. (2015). Novel hydrophilic carboxymethyl starch/montmorillonite nanocomposite films. *Carbohydr. polym.* 128. DOI: 10.1016/j.carbpol.2015.04.023

83. Serafin, J., Czech, Z., Antosik, A., Wilpiszewska, K. & Michalkiewicz, B. 2016 P 418159.

84. Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquérol, J. & Siemieniewska, T., 1985, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity *Pure Appl. Chem.,* 57, 603. DOI: https://doi.org/10.1515/pa-chem.57.0007.