

NO₂ REMOVAL ON ADSORBENTS OBTAINED BY PYROLYSIS OF CARDBOARD

Marta Supłat, Piotr Nowicki, Helena Wachowska,
Robert Pietrzak

Laboratory of Coal Chemistry and Technology,
Faculty of Chemistry, A. Mickiewicz University,
Grunwaldzka 6, 60-780 Poznań, Poland

Introduction

The development of many branches of industry and the use of modern technologies that are accompanied by tougher and tougher requirements for environmental protection justify the ceaseless search for possibly cheap and most effective adsorption materials. From among many products used for this purpose the most promising are carbonaceous adsorbents, because of low cost of production and abundant resources as well as specific beneficial properties, such as: high mechanical, chemical resistance and ease of degradation of the used material.

Precursors for the manufacture of carbonaceous adsorbents can be different materials, for instance lignin, cellulose, peat and coals [1-2]. The reasons for use of coals as precursor material is the high content of carbon and their primary porous structure, which permit get materials characterised by well-developed porous structure. The pore structure present in natural coals is poorly developed and can not be accessible to many adsorbates. Therefore coals must be subjected to carbonisation and/or activation which can be realized by physical method or by chemical method [3-4].

Economy and the measures aimed at the environment protection instigate the search for new precursors and new technologies for production of carbonaceous sorbents. For these reasons recently certain waste products have been used as precursors, for example waste tyres, polymers, resins, sawdust as well as agricultural byproducts such as: stones, shells and corncobs [5-6]. The use of these raw products permits obtaining adsorbents of new physicochemical properties and convert these waste materials to valuable products.

The aim of the study was to obtain carbonaceous adsorbents from cardboard and to check the effect of the temperature of pyrolysis on their sorption performance towards NO₂.

Experimental

The carbonization of the cardboard (C) was carried out in a horizontal furnace under argon with a flow rate of 170 mL/min. The samples were heated (5°C/min) from room temperature to the final carbonization temperature of 400 (C4), 500 (C5), 600 (C6) or 700°C (C7). In the final temperature, samples were kept 30 min and then cooled in inert atmosphere.

The elemental analysis of the chars obtained were performed on an elemental analyser CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany).

Characterization of the pore structure of was performed on the basis of low-temperature nitrogen adsorption-desorption isotherms measured on a sorptometer ASAP 2010 manufactured by Micrometrics Instrument Corp. (USA). Surface area and pore size distribution were calculated by BET and BJH methods, respectively. Total pore volume and average pore diameter were determined as well.

The surface oxide functional groups were determined by the Boehm method [7].

Evaluation of NO₂ was carried out according to the procedures described in [8] with some modifications. Samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume 2 cm³). Dry air with 0.1% of NO₂ was passed through the column of adsorbent at 0.450 L/min. The breakthrough of NO₂ was monitored using electrochemical sensor.

Results and Discussion

According to the data presented in Table 1, carbonisation of cardboard led to important changes in the elementary composition of the precursor. The content of carbon increased by 20.8-31.6 % accompanied by a significant decrease in the content of hydrogen and especially oxygen by 19.1-27.7 %. Moreover, with increasing temperature of the carbonisation process significantly increases the content of ash.

Table 1. Characteristics of Raw Cardboard and Chars Obtained at 400 - 800°C (wt.%).

Sample	Ash ^d	C ^{daf}	H ^{daf}	O ^{daf*}
C	6.6	45.5	6.1	48.4
CC4	26.0	66.3	4.4	29.3
CC5	27.9	68.8	3.2	27.9
CC6	31.9	75.0	2.5	22.5
CC7	35.1	77.2	2.1	20.7

The surface area measured for samples obtained, presented in Table 2, clearly illustrate a considerable influence of the temperature of activation on the porous structure of final products. The best textural parameters reveals CC7 sample carbonized at 700°C, which has about 17 times more developed surface area, than analogous sample CC4 obtained at 400°C.

To get the information on the surface properties of the samples obtained, the content of the oxygen functional groups of acidic and basic character was determined by the Boehm method. Analysis of the data collected in Table 3 has shown that the materials studied are characterised by different content of surface oxygen functional groups, from 4.22 to 5.48 mmol/g.

Table 2. Textural Parameters of Samples Obtained.

Sample	S_{BET} [m ² /g]	V_t [cm ³ /g]	A [nm]
CC4	13	0.02	5.4
CC5	58	0.04	2.9
CC6	226	0.12	2.2
CC7	228	0.13	2.3

All samples show distinctly basic character of the surface. The content and type of the surface oxygen groups is determined by the temperature of carbonization. An increase of temperature of carbonization contributes to a decrease of the acidic groups content, accompanied by significant increase in the content of groups of basic character.

Table 3. Acid-Base Properties of Chars Obtained.

Sample	Acidic groups [mmol/g]	Basic groups [mmol/g]	Total content [mmol/g]
CC4	0.87	3.35	4.22
CC5	0.55	4.66	5.21
CC6	0.25	4.48	4.73
CC7	0.10	5.38	5.48

All the samples produced were tested for the NO₂ adsorption in dry and wet conditions. The calculated breakthrough capacities for the chars obtained presents Table 4.

Table 4. NO₂ Breakthrough Capacities of the Chars Obtained.

Sample	NO ₂ breakthrough capacity [mg/g _{ads}]	
	Dry conditions	Wet conditions
CC4	2.7	5.2
CC5	4.3	6.9
CC6	8.4	25.3
CC7	23.2	65.9

According to these data, the chars obtained from cardboard are characterised by diverse sorption capacities of NO₂. The results indicate that the sorption ability of the samples obtained, both in dry and wet conditions, increases significantly with increasing temperature of carbonization. The highest NO₂ sorption capacities, both in dry and wet conditions (23.3 and 65.9 mg/g, respectively) were obtained for sample CC7 carbonized at 700°C. The least effective adsorbent of sorption capacity much smaller than those of the

other samples, proved CC4 sample, obtained from cardboard carbonized at 400°C, whose sorption ability towards NO₂ was only 2.7 and 5.2 mg/g, respectively.

Analysis of the data presented in Tables 2, 3 and 4 reveals that the sorption abilities of the samples studied depend significantly on the textural parameters and the acid-base character of their surface. The best sorption properties towards NO₂ shows sample CC7, which is characterised by the greatest surface area (228 m²/g) and the highest content of oxygen functional groups of basic character (5.38 mmol/g).

All the samples studied in our experiments showed much better sorption abilities in wet conditions. This difference was particularly pronounced for samples CC6 and CC7, which sorption capacity in wet conditions was almost 3 times greater than that in dry conditions. Greater sorption capacities in wet conditions most probably follow from a different mechanism of NO₂ adsorption, which is a consequence of presence of water in the system.

Conclusions

The results have shown that a suitable choice of the carbonization procedure for cardboard can produce adsorbents with high adsorption ability of nitrogen dioxide, especially in wet conditions.

Acknowledgments. This work was supported by The Polish Ministry of Science and Higher Education project No. N N204 277537.

References

- [1] Veksha A, Sasaoka E, Uddin MA. The influence of porosity and surface oxygen groups of peat-based activated carbons on benzene adsorption from dry and humid air. *Carbon* 2009;47: 2371-2378.
- [2] Nowicki P, Pietrzak R, Wachowska H. Influence of the precursor metamorphism degree on preparation of nitrogen-enriched activated carbons by ammoxidation and chemical activation of coals. *Energy Fuels* 2009;23:2205-2212.
- [3] Hsu LY, Teng H. Influence of different chemical reagents on the preparation of activated carbons from bituminous coal. *Fuel Processing Technology* 2000;64:155-166.
- [4] Nowicki P, Pietrzak R, Wachowska H. Comparison of physicochemical properties of nitrogen-enriched activated carbons prepared by physical and chemical activation of brown coal. *Energy Fuels* 2008;22:4133-4138.
- [5] Ahmedna M, Marshall WE, Rao RM. Production of granular activated carbons from select agricultural byproducts and evaluation of their physical, chemical and adsorption properties. *Bioresource Technology* 2000;71:113-123.
- [6] Crini G. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource Technology* 2006;97:1061-1085.
- [7] Boehm HP, Diehl E, Heck W, Sappok R. Surface oxides of carbon. *Angewandte Chemie International Edition in English* 1964;3:669-677.
- [8] Pietrzak R, Bandosz TJ. Activated carbons modified with sewage sludge derived phase and their application in the process of NO₂ removal. *Carbon* 2007;45:2537-2546.