Adsorption 11: 715–718, 2005

Influence of Presence of Inert Impregnant (NaCl) on Adsorptive Characteristics of Activated Carbon

STEFAN ZIETEK*
Military Institute of Chemistry and Radiometry, 00-910 Warsaw, Poland
stefan.zietek@wp.pl

ANDRZEJ SWIATKOWSKI
Military Technical Academy, 00-908 Warsaw, Poland

RADOSLAW SZMIGIELSKI AND DOROTA PALIJCZUK
Military Institute of Chemistry and Radiometry, 00-910 Warsaw, Poland

JADWIGA SKUBISZEWSKA-ZIEBA
Maria Curie-Skłodowska University, 20-031 Lublin, Poland

Abstract. Influence of presence of inert impregnant (NaCl) on adsorptive properties of activated carbon was studied by breakthrough dynamics, and nitrogen adsorption. It was noticed that contribution of inert impregnant (NaCl) had fundamental influence on volume of micro-, mesopores and breakthrough times.

Keywords: activated carbon, adsorption, breakthrough

1. Introduction

Many catalysts consist of metals or metal compounds supported on an appropriate support, the basic role of which is to maintain the catalytically active phase in a highly dispersed state. It is well documented that the role of the support is not merely that of the carrier; it may actually contribute catalytic activity ingredients during the manufacturing process. Further, the interaction between the active phase and the support phase can affect the catalytic activity. The selection of the support is based on a series of desirable characteristics: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; appropriate physical form for the given reactor; high surface area (which is usually, but not always, desirable); porosity and chemical nature. Of a wide range of possible supports, in practice only three combine these characteristics optimally, and they account for the most commonly used supported catalysts: alumina, silica and carbon. Although many types of carbon materials have been used to prepare carbon-supported catalysts (graphite, carbon black, activated carbon, activated carbon fibers, carbon-covered alumina, graphite intercalation compounds, glassy carbon, pyrolytic carbon, polymer-derived carbon, fullerenes, nanotubes, etc.) (Rodriguez-Reinoso, 1998), high surface area activated carbons are the carbon materials of choice for most carbon-supported catalysts, and they are the common materials in industry, environment protection and special applications. Example of this is Cu-Cr-Ag/Activated Carbon—Whetlerite used in respiratory protection devices for military purposes. It is known that adsorption mainly take place in the micropores of activated carbon. Meso- and macropores play very

*To whom correspondence should be addressed.

important roles in any adsorption process, because they serve as a passage route for the adsorbate to the micropores, since only a few of these are placed in the outer surface of the carbon particle.

Therefore the aim of this work is to elucidate the influence of presence of inert impregnant (NaCl) on adsorptive properties of activated carbon was studied by breakthrough dynamics, and nitrogen adsorption. It was noticed that contribution of inert impregnant (NaCl) had fundamental influence on volume of micro-, mesopores and breakthrough times.

Application of NaCl as impregnant allows to explain behavior of other type of catalysts (e.g., Cu-Cr-Ag/Activated Carbon) on carbon surface. The interaction between carbon surface and catalyst components can change their chemical state as well as thermal treatment during preparation process. There are many types of adsorbates (e.g., ClCN, HCN) which react with impregnant and in this way can change their chemical structure. The use of natrium chloride (in below described experiments) instead of Cu-Cr-Ag eliminates its chemical interactions with carbon surface and/or adsorbate. Thermal stability of NaCl allows to introduce it on the carbon without any change during thermal treatment.

2. Materials and Methods

Activated carbon Norit R 0.8 Extra has been used as support for incipient-wetness impregnation with different amount of sodium chloride. Commercial carbon was previously deashed with concentrated HCl acid and methanol. Obtained impregnated carbon samples had NaCl percentage as follows: 0, 5, 10, 15, 20. They were labeled AC-0, AC-5, AC-10, AC-15 and AC-20 respectively. Their structural and adsorptive characteristics were studied by means of nitrogen adsorption and desorption isotherms determined at 77.4 K using a Micromeritics ASAP 2405N analyzer. Tert-butylbenzene (TBB) breakthrough dynamics was analyzed by using a modified Wheeler-Jonas model (Jonas et al., 1972) describing the breakthrough time versus the carbon bed height and gas flow parameters. Compressed air was purified on columns with activated carbon, molecular sieves and silica gel. The TBB vapor was generated by means of an infusion pump with a syringe. Dry air, challenged with required amounts of TBB vapor, was supplied through a glass tube (internal section 5.187 cm^2) filled with a tested carbon. An initial concentration of TBB was $c_0 = 1 \pm 0.1$ mg dm^{-3}. The carbon bed depth was constant $L = 1.5$ cm. The carbon bed was temperature-controlled at 293 K. The volumetric flow rate was $Q = 5.19$ $dm^3 min^{-1}$ (1.0 $dm^3 min^{-1} cm^{-2}$), resulting in a linear velocity $v_L = 1000$ cm min^{-1}. The outlet concentrations were analyzed in cycles of 3 min by using a CP 9001 CHROMPACK gas chromatograph with a flame ionization detector (FID). The breakthrough times were determined at the outlet concentration (after the carbon bed) of TBB $c_x = 10^{-5}$ mg dm^{-3} (Palijczuk et al., 2002). The micrographs were made using AFM Digital Instruments NanoScope III.

3. Results and Discussion

The nitrogen adsorption isotherms for obtained activated carbon samples at 77.4 K are presented in Fig. 1.

The lower is isotherm position the higher is NaCl percentage. Calculated on the base of adsorption isotherms structural parameters i.e. total pore volume (V_p), mesopores volume (V_{mes}), micropores volume (V_{mic}), and specific surface area (S_{BET}) are summarized in Table 1.

The values of structural parameters given in Table 1 decreased parallel with rise of NaCl percentage in activated carbon samples. This tendency is especially

Table 1. Structural characteristics of tested adsorbents.

Adsorbent	V_p (cm^3/g)	V_{mes} (cm^3/g)	V_{mic} (cm^3/g)	S_{BET} (m^2/g)
AC-0	0.69	0.23	0.35	1362
AC-5	0.67	0.24	0.32	1313
AC-10	0.63	0.24	0.29	1237
AC-15	0.55	0.20	0.27	1092
AC-20	0.53	0.19	0.26	1048

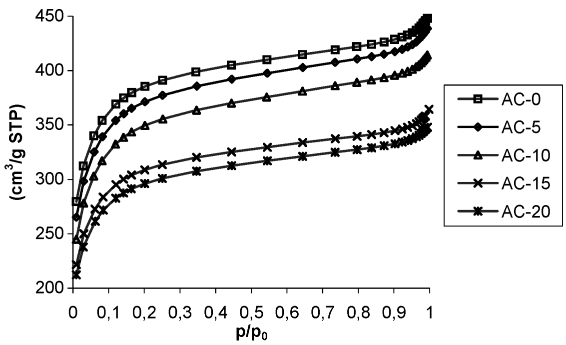

Figure 1. Nitrogen adsorption isotherms for Norit activated carbon samples with different quantity introduced NaCl at 77.4 K.

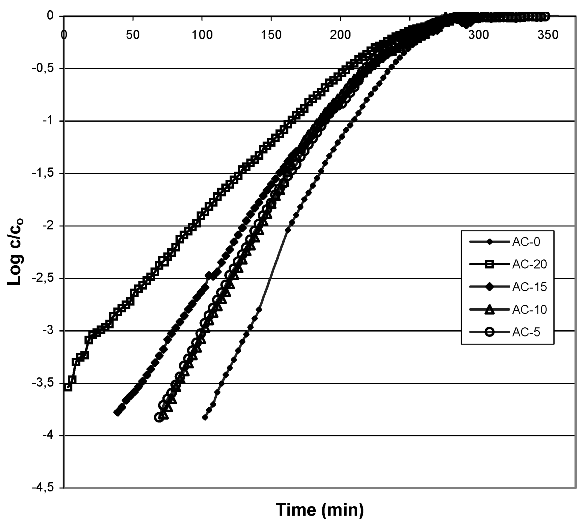

Figure 2. TBB breakthrough plots for tested carbons.

visible in case of micropore volume (in comparison with other parameters). For lower NaCl contents (5 and 10%) one can observe relatively small structural changes.

The results of tert-butylbenzene adsorption in dynamics conditions (breakthrough plots) are shown in Fig. 2. Stoichiometric time was neither calculated nor measured because in the scope of interest was investigation the dynamics characteristics at low breakthrough

Table 2. Dynamics parameters calculated based on modified Wheeler-Jonas equation.

Adsorbent	t_b (min)	A_{wb} (mg/g)	β_e^* (1/min)	W_e (mg/g)	m_o (g)	ρ_b (g/cm)
AC-0	64	102	$10{,}6 * 10^3$	371	3,268	0,42
AC-5	23	35	$8{,}6 * 10^3$	329	3,423	0,44
AC-10	24	36	$8{,}6 * 10^3$	326	3,501	0,45
AC-15	0	0	$7{,}03 * 10^3$	338	3,579	0,46
AC-20	0	0	$5{,}3 * 10^3$	310	3,657	0,47

t_b is the breakthrough time at the outlet concentration $c_x = 10^{-5}$ mg/dm^3; A_{wb} is the adsorption capacity of 1 g activated carbon at predefined breakthrough concentration $c_x = 10^{-5}$ mg/dm^3; m_o is the weight of bed; W_e is the kinetic adsorption capacity equal to the kinetic saturation capacity (mass of adsorbed vapor TBB)/(mass of adsorbent at concentration c_o); ρ_b is the bulk density of carbon bed; β_e^* is effective overall adsorption rate coefficient.

concentration (10^{-5} mg/dm^3). The reason of this is that the level of toxicity of some organophosphorus compounds (e.g., Sarin, Soman—which are chemical warfare agents CWA) are very high, so there is no need to consider behavior of fixed carbon beds at higher effluent concentration.

On the basis of experimental results and modified Wheeler-Jonas model breakthrough dynamics parameters were calculated (Table 2).

As an example are shown AFM micrographs for samples AC-20 and AC-5 (Figs. 3 and 4).

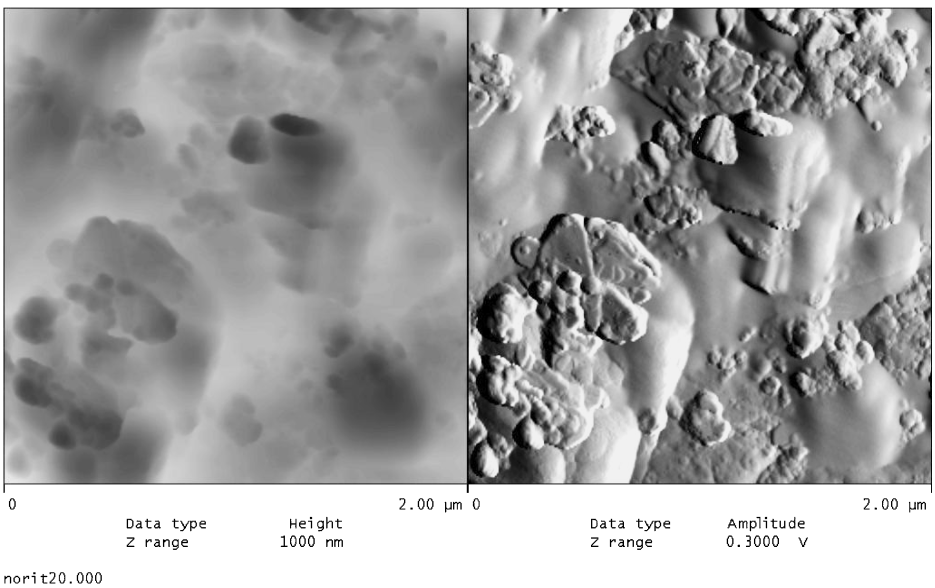

Figure 3. AFM micrographs for AC-20.

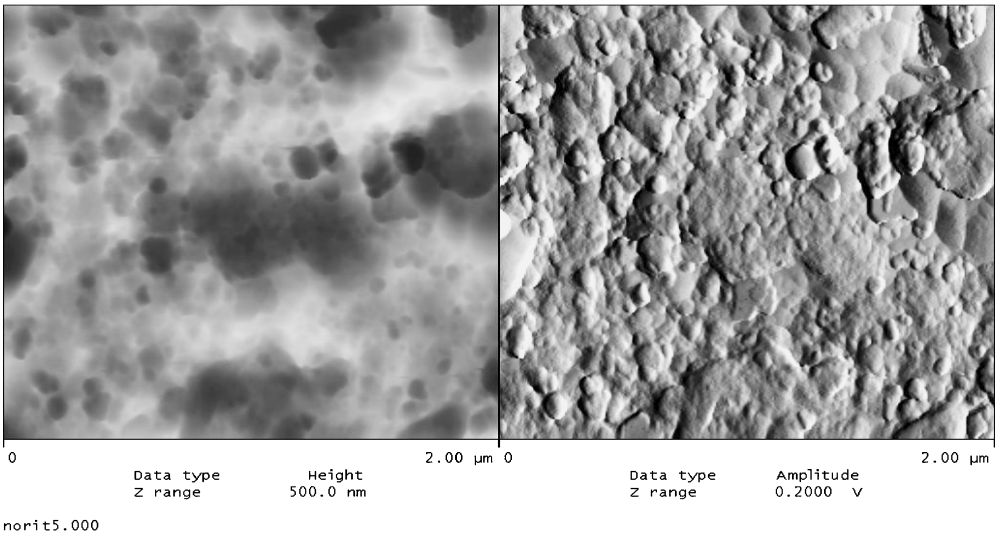

Figure 4. AFM micrographs for AC-5.

4. Conclusion

NaCl impregnation change porosity and dynamics adsorption parameters of activated carbon samples. Increasing amount of impregnant decrees micro- and mesopores volume, breakthrough time and effective overall adsorption rate coefficient. The most interesting is that the small change in NaCl concentration (from 0 to 5%, and from 10 to 15%) dramatically change breakthrough time but almost doesn't influence on static adsorption parameters (micropore volume and mesopore volume). Simultaneously kinetic saturation capacity are similar. On the basis of collected results, known kinetics adsorption theories as well as statics adsorption theories there is no possibility to fully explain observed phenomena. It was observed that probably the influence of NaCl deposition on dynamics and static parameters of activated carbon can be characterized not only by interaction between carbon surface and TBB but also by interaction between TBB and NaCl. AFM micrographs show that higher NaCl content could results in forming big microcrystals of impregnant and in this way decrees dispersion.

References

Jonas, L.A. et al., *Carbon*, **10**, 657–663 (1972).
Palijczuk, D. et al., *J. Colloid Interface Sci.*, **250**, 5–17 (2002).
Rodriguez-Reinoso, F., *Carbon*, **36**, 159–175 (1998).