

# TOPOGRAPHY AND MORPHOLOGY OF CARBON DEPOSITS ON CARBONIZED ADSORBENTS AND MINERAL CATALYSTS

*R. Leboda and B. Charmas*  
*Faculty of Chemistry, Maria Curie-Skłodowska University,*  
*M. Curie Skłodowska Sq. 3, 20-031 Lublin, Poland*

## Introduction

Carbon-mineral adsorbents (CMA) can be considered as a new generation of complex adsorbents of great applicability in the industrial and laboratory processes [1]. The interest developed in such adsorbents results, among others, from the possibility of carbonized adsorbents and catalysts utilization. Depending on the conditions of complex adsorbents preparation it is possible to obtain the adsorbent completely covered with the carbon deposit or the materials of the surface mosaic topography [2]. Such adsorbents can be used as model ones possessing random or patchwise topography of adsorption centres [3]. Knowledge of the characteristics, particularly of the adsorbents possessing a mosaic structure of adsorption centres can enable their rational application in adsorption of complex mixtures of organic and inorganic substances as well as carriers of multicomponent catalysts [1].

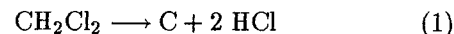
There are only few papers dealing with the studies of topography and texture of carbon deposits on the surface of mineral adsorbents and catalysts. They are described in [4,5]. The papers by Kamegawa and Yoshida [6,7] show application of measurement of p-nitrophenol (PNP) adsorption from the aqueous solutions for estimation of the size of selective surface of the complex carbon-silica adsorbents i.e. their total area of carbon 'patches' in the complex mosaic adsorbents. The method of PNP adsorption to study topography of carbon deposits in carbosils of various carbon contents is used in this paper. Theoretically these amounts should provide both entire and mosaic coverage of the surface with the carbon deposit.

## Experimental

The relative concentrations to the saturated concentration of PNP up to 0.4 were prepared in the way described in [6]. Silica gel Si-60 (Schuchardt, Germany) was the parent substance used in the studies. It was preliminarily washed away from the surface mineral impurities. The sample of it was heated at 550°C for 6 hours in order to obtain the heat-treated silica gel to be compared with the carbon-coated silica gels.

Carbon-coated silica gels (carbosils) were prepared in the rotational reactor which provides good reproducibility of the prepared adsorbents. The sample was subjected to the action of the modifying agent, CH<sub>2</sub>Cl<sub>2</sub>, fed into the reactor. The rate of CH<sub>2</sub>Cl<sub>2</sub> feeding was

0.6 cm<sup>3</sup>/min for the periods of 0.5, 1, 2, 3, 4 and 6 hours depending on the successive sample. Carbon was deposited on the silica because methylene chloride underwent pyrolysis according to the equation:



and the products are presented as carbosils Nos 1, 2, 3, 4, 5 and 6, respectively. The surface areas of carbosils S<sup>cs</sup> calculated from the adsorption data of argon at 77 K by the BET equation are shown in Table 1. Those for original silica gel and heat-treated silica gel are 330 and 320 m<sup>2</sup>/g, respectively.

## Results and Discussion

The adsorption amount of PNP on the powdered sample was calculated from the reference curve and difference of the absorbance of the diluted solution and the solution after adsorption. After [6] we assume that the BET model is the model corresponding to PNP adsorption on carbosils.

**Table 1.** Surface areas of the adsorbents obtained by carbon deposition on the silica adsorbent.

Carbosil	Coating time h	S <sup>cs</sup> m <sup>2</sup> /g	X <sub>C</sub> %	S <sub>C</sub> <sup>cs</sup> m <sup>2</sup> /g	P <sub>C</sub> %	S <sub>C</sub> m <sup>2</sup> /g
N <sup>o</sup> 1	0.5	304	0.77	5.7	1.9	740
N <sup>o</sup> 2	1	302	4.37	9.3	3.1	213
N <sup>o</sup> 3	2	267	14.89	18.4	6.9	124
N <sup>o</sup> 4	3	228	20.32	19.6	8.6	96
N <sup>o</sup> 5	4	205	26.70	20.6	10.0	77
N <sup>o</sup> 6	6	146	35.00	19.7	13.5	56

The amount of PNP adsorbed on carbosil is the sum of those on the surface of the carbon and silica gel. So, one can calculate the surface area of carbon of the carbosil,

$$S_C^{cs} = S^{cs} \cdot \frac{a_{\text{mon}}^{cs} - a^{sg}}{a_{\text{mon}}^{cb} - a^{sg}} \quad (2)$$

where S<sub>C</sub><sup>cs</sup> is the surface area of carbon of the carbosil (cm<sup>2</sup>/g carbosil); S<sup>cs</sup> is the total surface area of the carbosil measured by the adsorption of Ar at 77 K (cm<sup>2</sup>/g carbosil); a<sub>mon</sub><sup>cs</sup> is the amount of monolayer adsorption of PNP on carbosil (g PNP/cm<sup>2</sup> carbosil); a<sub>mon</sub><sup>cb</sup> is the amount of monolayer adsorption of PNP on graphitized carbon black (g PNP/cm<sup>2</sup>); a<sup>sg</sup> is the amount of

PNP adsorbed on the heat-treated silica gel at a concentration at which the monolayer adsorption on the carbosil is completed (g PNP/cm<sup>2</sup> silica gel).

Then the percentage of coating is given by  $P_C = (S_C^{cs}/S^{cs}) \cdot 100\%$ . The results of calculations using eq (2) are presented in Table 1 and in Figure 1.

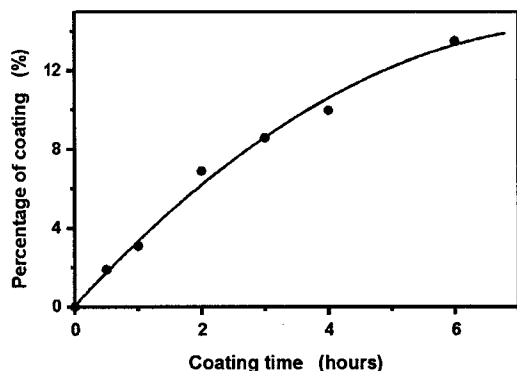


Figure 1. The changes of silica coating percentage as a function of coating time.

The value of the amount of monolayer adsorption of PNP on the graphitized carbon black,  $a_{\text{mon}}^{\text{cb}}$ , was accepted as that calculated by Kamegawa and Yoshida [6] from their adsorption data, i.e.  $5.28 \cdot 10^{-8}$  g/cm<sup>2</sup>.

Table 1 presents two values of carbon deposit specific surface area. One of them,  $S_C^{cs}$ , refers to the size of the surface calculated per gram of carbosil (silica support + carbon deposit), the other one,  $S_C$  is expressed for a gram of the carbon deposit (without the support mass). It was calculated from the following formula [4],  $S_C = (S_C^{cs}/X_C) \cdot 100$ , where  $X_C$  is the percentage of carbon (g of carbon/100 g of carbosil).

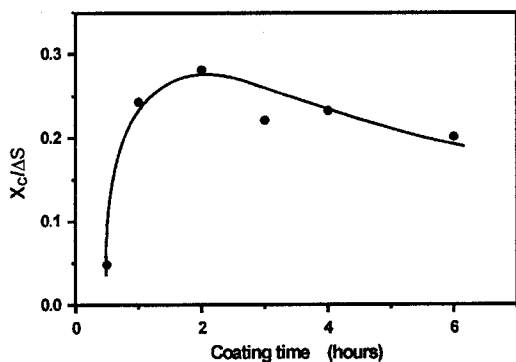


Figure 2. The changes of  $X_C/\Delta S$  for six carbosils as a function of coating time.

In Figure 2 the quantities  $\Delta S$  on the axis of abscissa indicate the differences between the size of specific surface area of silica used for carbonization (320 m<sup>2</sup>/g) and the specific surface area of a given carbosil. Thus, the quotient  $X_C/\Delta S$  means the amount of carbon deposit needed to change the unit of the modified adsorbent surface. It can be stated from Figure 2 that in the first

period of initial silica carbonization a small amount of the carbon deposit  $X_C$  is required for the elementary change of the surface size. This results from the fact that in the initial period of pyrolysis there are formed small globules of carbon deposit which can be settled in the narrowest pores of the modified silica. However, when the pyrolysis reaction time is over one hour more carbon deposit  $X_C$  is required for the same elementary change of the surface,  $\Delta S$ , the evidence of which is a gradual reduction of the relation under consideration.

Though comparable sizes of silica coverage with a carbon layer with those presented in papers [6,7] were obtained, the percentage values of coating for carbosils including over 20% w/w carbon (Nos 4-6) seem to be surprisingly small.

Carbosils prepared by a thermal decomposition of methylene chloride are most frequently characterized by very strong (local) energetic heterogeneity [3,8]. The application of the BET theory for heterogeneous surfaces was discussed in the monograph by Rudzinski and Everett [9]. The authors presented many adsorption systems showing the effect of energetic heterogeneity of the real adsorbent surface on the values of monolayer capacity and constant in the BET equation and, in consequence, on the size of the surface occupied by the adsorbed molecules of the adsorbate.

Therefore it is necessary to take into account the effects of energetic heterogeneity in further studies of topography of carbon deposits in the complex adsorbents.

### Acknowledgment

The research was supported by KBN Research Grant No. 3 T09A 036 11.

### References

1. Leboda, R., *Mater. Chem. Phys.*, 1992, 31, 243; 1993, 34, 123.
2. Gierak, A. and Leboda, R., *Mater. Chem. Phys.*, 1988, 19, 503.
3. Leboda, R. and Dąbrowski, A., in *Adsorption on New and Modified Inorganic Sorbents*, Studies in Surface Science and Catalysis, Vol. 99, eds. Dąbrowski, A. and Tertykh, V.A., Elsevier Science B.V., Amsterdam, The Netherlands, 1996, pp.115-147.
4. Felonov, V.B., *Porous Carbon*, Inst. Kat., Novosibirsk, 1995, pp.320-442.
5. Felonov, V.B., *J. Porous Materials*, 1996, 2, 263.
6. Kamegawa, K. and Yoshida, H., *Bull. Chem. Soc. Jap.*, 1990, 63, 3683.
7. Kamegawa, K. and Yoshida, H., *J. Colloid Interface Sci.*, 1993, 159, 324; 11995, 72, 94.
8. Gierak, A., Leboda, R. and Tracz, E., *J. Anal. Appl. Pyrol.*, 1988, 13, 89.
9. Rudzinski, W. and Everett, D.H., *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, New York, 1992, p.400.