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CALORIMETRIC STUDY OF THE IMMERSION ENTHALPIES OF ACTIVATED CARBON CLOTHS IN DIFFERENT SOLVENTS AND AQUEOUS SOLUTIONS

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The specific and non-specific interactions of twelve activated carbon cloth samples prepared from commercial cotton fabric, and that present different activation degrees are studied through the determination of immersion enthalpies in CCl_4 and H_2O, and in aqueous solutions of NaOH and HCl.

The immersion enthalpies found for the solvents CCl_4 and H_2O are in a range of 5.49–45.84 and 1.77–7.76 J g^{-1}, respectively. The enthalpic values for the materials in aqueous solutions of NaOH and HCl, allow characterizing the chemical surface of these materials, which are in a range of 6.63 and 21.49 J g^{-1}, finding through them important relations in company with other characterizing techniques used in the study of these materials.

Keywords: *acidity, activated carbon cloth, adsorption isotherm, basicity, immersion calorimetry*

Introduction

In the group of porous materials used actually in separation processes, we found the activated carbon fibers, these materials are promising adsorbents that can be used for the efficient separation, purification, recovery, and storage of different contaminants as have metals or VOC's. These materials can be incoporated in form of yarns, felts or cloths. These last ones, the activated carbon cloth, ACC, is a flexible form of activated carbon, that is mechanically weak but highly porous in nature, and because of this fact, it possesses unique characteristics as compared to the conventional activated carbon. Because of the thin fibrous shape in activated carbon fabric, a fast intraparticle adsorption kinetics takes place in gas- and liquid-phase adsorption [1, 2].

The main precursors used in the preparation of these adsorbents are woven materials of viscose rayon, phenolic resin, and fabrics from polymers like polyacrylonitrile and Nomex, and can be obtained through of the physical or chemical activation methods [3–8].

The adsorbent characteristics of these materials are determined by their high porosity and surface chemistry reactivity, the porosity is the result of the production process that involves a carbonization stage of a precursor material, and an activation stage of the product obtained in the first stage. In the activation, the porosity of the material is developed thanks to the action of diverse activation agents, and establishes the presence of superficial oxygenated groups, that together with porosity are the ones that determine the possible application of an activated and its acid or basic character [9].

In the immersion calorimetry technique, the resulting thermal effects of the interaction between a solid with a liquid can be measured; if the wetting liquid is a non-polar solvent, the amount of generated heat due to the physical interaction is proportional to the surface area of the solid, nevertheless, when a different liquid is used as the wetting liquid, the specific interactions between the liquid and the solid surface can be known, which in the case of activated carbons allows getting related information about the functional groups and let us establish important relations in the characterization of these materials [10–18].

In this work, the results of the immersion calorimety characterization of activated carbon cloths, prepared from chemical activation of cotton woven materials are presented, the discussion of the established relations between the calorimetric results with the adsorption isotherms, and the surface chemistry evaluated by the Boehm method is developed.

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Experimental

The activated carbon cloths used in this work, were prepared by chemical activation of two woven materials from, through of the impregnation with 1% (p/v) solutions of $ZnCl_2$, $AlCl_3$ and H_3PO_4, and the later carbonization in nitrogen and carbon dioxide atmosphere until a temperature of 1123 K [19]. For the textural characterization, the surface area were obtained by the BET method, and the micropore volume by the Dubinin Radushkevich equation and the αs method [20–22].

Oxygen surface groups determination

With the object of determining the total acidity and basicity of the prepared cloths, related with the presence of oxygen heteroatoms in the solid surface, the methodology proposed by Boehm was used [23, 24]. Approximately 0.1000 g of the cloths were place in contact with 25 mL of NaOH and HCl 0.05 M, in plastic recipients of 50 mL; the solution was stirred for five days, and occasionally nitrogen was bubbled over the solutions with the purpose of removing the atmospheric carbon dioxide. Finally, 10.0 mL aliquots were titrated with either an acid or basic solution previously standardized to determine by difference the μmol g^{-1}. For these titrations the automatic Schoot Titroline Alfa – Plus was used.

Immersion enthalpies determination

Immersion enthalpies of the activated carbon cloths prepared for these study were developed in different liquids like CCl_4, water and NaOH and HCl solutions 0.1 M, with the aim to evaluate the specific an non-specific interactions between these liquids and the solid. For these purpose, around 0.1000 g of activated carbon were weighed and set in a calorimetric cell designed for this purpose, later, 10.0 mL of the mentioned solvents, HCl and NaOH were added. The cell is placed in the primary heat deposit and for approximately 2 h the temperature of the calorimetric assembly is let to stabilize, after that the immersion of the sample in the solution and the thermal changes are registered until a baseline is again reached, a post-period of 30 min is recorded and a final electric calibration is done.

The calorimeter used in the determinations is an adapted heat conduction equipment, built by the investigation group. The glass cell with lid has a 25 mL capacity, surrounded on its two faces by thermoelectric modules from Tellurex Co. with dimensions of 20.0×40.0×3.8 mm connected in series, which measures the heat flow by the Seebeck effect, and generates an electric potential signal proportional to the heat flow that comes from the calorimetric cell. To stabilize the outcoming signal of the calorimeter, other two thermoelectric modules were adapted in electric opposition, and it was packed with a shield material.

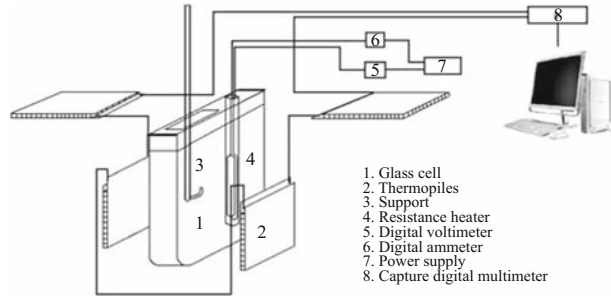

Fig. 1 Scheme of the equipment used in the calorimetric determinations

The scheme of the used calorimeter in the determinations is presented in Fig. 1.

Results and discussion

The textural and chemical characteristics of the materials used for this study are presented on Table 1; the nomenclature used includes the precursor, chemical agent used, and carbonization atmosphere. In that way, the first letter, F, indicates fiber, the second letter indicates the cotton precursor material, I for Indigo or D for Drill, the third letter indicates the chemical agent used, Z for the $ZnCl_2$, P for the H_3PO_4 and A for $AlCl_3$ and finally, the fourth letter indicates the carbonization atmosphere, N for nitrogen and C for carbon dioxide.

On Table 1, we report the results of the textural characterization of the activated carbon cloths, the materials show significant properties taking account the impregnant agent concentration and the short time the impregnation employed.

The results on Table 1 shows that the behavior of the different treatments done in the twelve samples are related with the textural differences of each material. The yield percentages are associated with the apparent surface area that indicates that the mass loss is related with the porosity development. In that way, the carbonized materials in carbon dioxide atmosphere, even though are materials with great losses of mass, are the ones that develop more porosity.

The micropore volume results calculated by the αs method, are related with the ones calculated by the Dubinin Radushkevich method, taking up values between 0.08 and 0.23 $cm^3\ g^{-1}$ for the carbonized samples in nitrogen atmosphere and 0.37 and 0.52 $cm^3\ g^{-1}$ for the carbonized samples in carbon dioxide atmosphere, since all of the carbonized samples under this atmosphere have an increasing values compared to the ones carbonized under nitrogen, however, micropore volume values for the samples FIZN and FIAN are lower than the ones calculated by the αs method, and it could be associated to the small porosity development in these samples. The

Table 1 Carbon cloths characterization results

ACC	Yield/%	Textural characterization				Surface chemistry	
		S_{BET}/ $m^2\ g^{-1}$	W_0 DR/ $cm^3\ g^{-1}$	αs method		Acid sites/ μmol g^{-1}	Basic sites/ μmol g^{-1}
				W_0/$cm^3\ g^{-1}$	S_{ext}/$m^2\ g^{-1}$		
FIZN	22.3	384	0.24	0.22	7	774.5	28.9
FIZC	14.9	790	0.38	0.46	100	957.4	70.5
FIPN	32.2	–	–	–	–	428.1	13.2
FIPC	20.8	709	0.38	0.41	19	580.2	26.7
FIAN	22.1	243	0.13	0.08	30	514.7	86.8
FIAC	11.0	848	0.41	0.49	92	1014.3	81.5
FDZN	24.8	430	0.22	0.25	21	488.1	71.1
FDZC	19.8	639	0.27	0.37	129	892.1	34.7
FDPN	31.4	346	0.17	0.20	35	545.0	4.3
FDPC	21.7	897	0.46	0.52	52	580.0	60.7
FDAN	25.6	411	0.20	0.23	47	578.3	77.3
FDAC	16.6	652	0.31	0.38	83	714.3	77.5

results corresponding to the surface chemistry, also presented in Table 1, show that the values of acidity expressed in μmol g^{-1} are larger for all the samples carbonized under carbon dioxide where the values are 545 and 1014 μmol g^{-1}.

In general, in spite of the lower acid character presented by the samples carbonized in nitrogen atmosphere, with regard to the ones carbonized in carbon dioxide, the samples impregnated with phosphoric acid have lower acid concentrations compared to both chlorides, which lets differentiate the effect the impregnant and the carbonization atmosphere has in each of the samples.

In the basic groups concentration information provided for this technique, it is observed that the concentrations are almost twenty times less than the expressed for total acidity, and that the basicity increases when the carbonization atmosphere is changed, even though in the impregnated samples the aluminum chlorides have a similar value is between 70–85 μmol g^{-1}.

Carbon tetrachloride enthalpies

The quantification of the energetic interactions generated by solid surface in the adsorption processs was developed by the respective immersion enthlapies, on Fig. 2, the curve corresponding to the immersion of the cloth FDPC in CCl_4 is shown; here an exothermic process is exposed, where the first peak corresponds to the effect of the generated heat by the contact of the carbon material with the liquid, while the rest of the peaks correspond to the electric calibration of approximately 2.4 J in the system done for each one of the try outs.

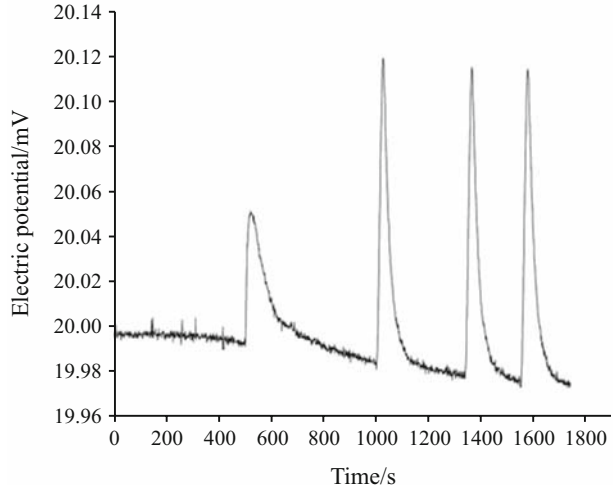

Fig. 2 Curve obtained in the immersion of an ACC in CCl_4

On Table 2 the enthalpic values obtained for the twelve prepared samples are presented. It is observed that in all the samples the immersion enthalpy increases when the carbonization atmosphere changes from nitrogen to carbon dioxide.

The enthalpic values for the samples carbonized under nitrogen are between –5 and –17 J g^{-1}; it is observed that the lowest value is for the FIAN that particularly presents a lower micropore volume as seen in the results presented in Table 1.

For the enthalpic values for samples FIPC, FIAC and FDPC, which have the highest porosity development according to the characterization by gas adsorption, the proportionality is observed, for which the calorimetric technique again allows to establish differences between each material. On Fig. 3 the determined relation between the immersion calorimetries in carbon tetrachloride according to the surface area

Table 2 Results for the calorimetric study

ACC	$-\Delta H_{CCl_4}$/J g^{-1}	$-\Delta H_{H_2O}$/J g^{-1}	$-\Delta H_{NaOH}$/J g^{-1}	$-\Delta H_{HCl}$/J g^{-1}
FIZN	12.21±0.67	1.77±0.10	9.86±0.54	14.15±0.77
FIZC	42.28±2.30	3.63±0.20	15.87±0.87	18.83±1.03
FIPN	11.62±0.63	2.68±0.15	9.59±0.53	12.72±0.69
FIPC	27.35±1.49	6.29±0.34	16.79±0.92	9.21±0.50
FIAN	5.49±0.30	3.83±0.21	13.95±0.76	17.74±0.97
FIAC	42.30±2.31	7.55±0.41	18.68±1.02	21.91±1.20
FDZN	15.60±0.85	3.01±0.16	9.42±0.52	6.63±0.36
FDZC	45.84±2.50	4.46±0.24	18.29±1.00	16.22±0.88
FDPN	17.28±0.94	5.01±0.27	14.12±0.77	7.39±0.40
FDPC	33.92±1.85	8.76±0.48	14.30±0.78	21.49±1.17
FDAN	17.73±0.97	3.92±0.21	11.40±0.62	6.86±0.37
FDAC	22.57±1.23	5.74±0.31	13.10±0.72	11.86±0.64

reported on Table 1. On this graph it is again observed the effect the carbonization atmospheres has, and the almost linear relation between the developed area and the first enthalpic values, even though the tendency changes in the right part of the graph, the behavior has a good adjustment to the showed tendency.

Taking in account that the experimental results can be compared with the calculated values for the Stoeckly–Kraehenbüehl (SK) equation [12] which involves the characteristic energy of the adsorbent and the calculated micropore volume for the physical vapor adsorption, the relation is shown in Fig. 4.

The marked tendency on the graph can confirm that the experimental results complement the textural characterization of these materials, and that the experimental enthalpic value product of the non-specific interactions between the carbon and the non-aqueous solvent, is related to the calculated one in a linear way. The marked points on the figure, and that are not in the tendency, correspond to the samples FDZC, FIAC and FIZC, samples that have an increased porosity development and a lower percentage of micropores than the rest of the cloths.

In that way, it can be concluded that the enthalpic values reported in this work have a direct relation with the ones obtained in the characterization by gas adsorption isotherms, taking in account that the comparison was done with the values of E_0 and W_0 from the N_2 77 K isotherm, this way the calorimetric immersion technique offers satisfactory results, which complement the textural characterization for the prepared activated carbon cloths.

The enthalpic values in water, which establish the specific interactions between the solid surface and the polar solvent, is between –1.77 and –8.76 J g^{-1}. Just as the reported values of the textural characterization and immersion calorimetry in CCl_4, an in-

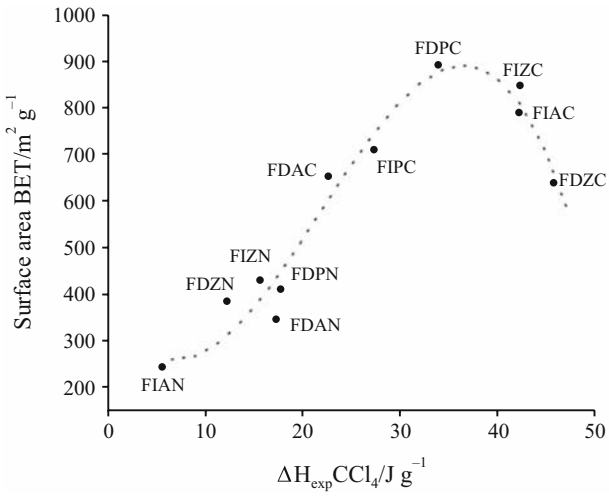

Fig. 3 Relation between the immersion enthalpies in CCl_4 and the BET area

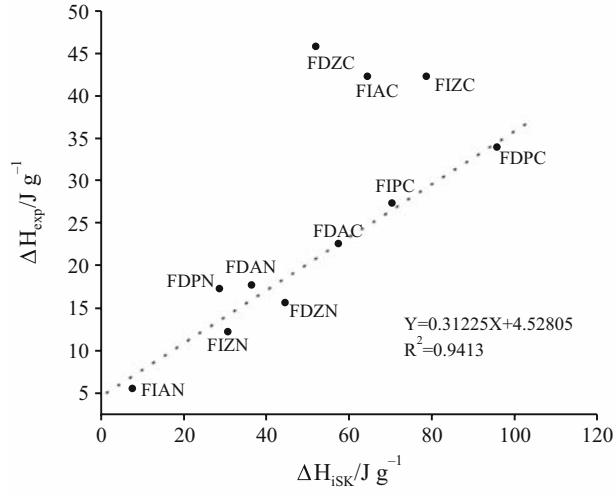

Fig. 4 Relation between the experimental enthalpy and the calculated one by SK equation

crease in the enthalpic value is observed when the carbonization atmosphere is changed, therefore, the enthalpic values of the carbonized samples under carbon dioxide, duplicate the values from the samples carbonized under nitrogen atmosphere, even though this behavior is not so evident as when the chemical impregnant was phosphoric acid that according to the textural characterization, this was the impregnant that generated higher micro-porosity in the materials.

The results for neutralizing enthalpy for the acid and basic groups located over the carbon surface present a similar behavior to those values of water, an increase in the enthalpic values for the carbonized samples in carbon dioxide is observed, gas that not only performs as oxidant degrading the porose surface, but also produces oxidizing reactions in the functional groups. In this way, the results for the immersion enthalpies, which are between –9.42 and –18.29 J g^{-1} for a NaOH solution, and 6.39 and 21.91 J g^{-1} for a HCl solution, allow establishing differences in the superficial chemistry of each one of the samples.

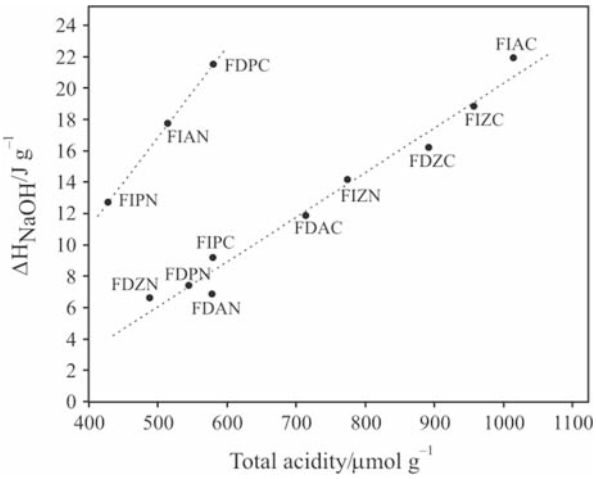

Fig. 5 Relation between immersion enthalpy in NaOH and total acidity

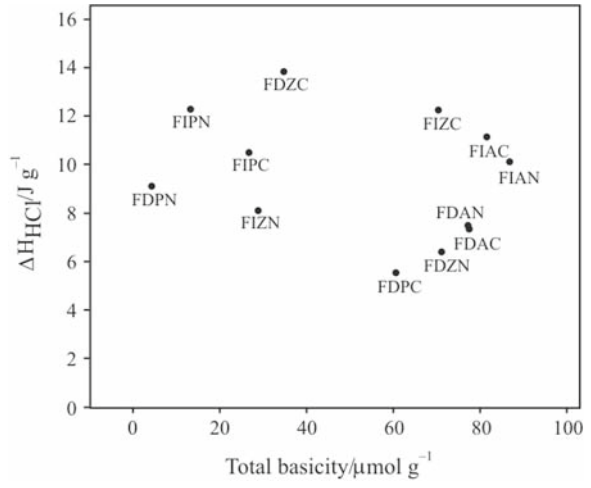

Fig. 6 Relation between the immersion enthalpy in HCl and total basicity

On Fig. 5 the established relation between the enthalpic values of the total acidity and the reported values of total acidity on Table 2 are shown.

On Fig. 4 the linear relation between the enthalpic values in NaOH according to the total acidity calculated values through the Boehm method is observed. Even though on Fig. 5 there are two linear tendencies, which can allow concluding that the calorimetric technique establishes the differences between each one of the treatments done over the samples and helps to complement the information offered by the volumetric technique.

On Fig. 6 the relation between the total basicity through the Boehm method and the enthalpic values in HCl is illustrated.

In this graph there is no significant relation, even though, the results by the calorimetric technique allows to establish the differences between every sample by the values reported on Table 2, the basicity of an activated carbon is yet an investigation topic, and for this reason, in the carbon cloth samples, the points of view.

Conclusions

The specific and non-specific interactions were determined for the twelve simples of activated carbon prepared from chemical activation of weaved cotton materials, through the measure of the immersion enthalpy of CCl_4, water, NaOH and HCl.

The relation between the enthalpic values in CCl_4, and the surface area estimated by adsorption isotherms was established, where the effect of the carbonization atmosphere for each material is also observed. Of these form, the carbonized samples in carbon dioxide atmosphere present higher enthalpic values in both solvents against the nitrogen carbonized samples. Immersion enthalpies in CCl_4 and water present higher values for the non-polar solvent in a range of 5.40 and 45.84 J g^{-1}.

A linear relation is found between the neutralization enthalpic values and the acid groups located on the surface, and the values of total acidity found through the volumetric characterization.

The immersion enthalpies given by the specific interaction from the basic groups of the activated carbon cloths, and that are in between 6.6 and 21.9 J g^{-1}, allows to demonstrate the differences between each material, and even though no appreciable relations were found with the volumetric techniques, it does allow to observe the effect the impregnants and the carbonization atmosphere have on these materials.

The results gathered through the immersion calorimetry in solvents and different nature solutions

over activated carbon cloths, allows complementing the information obtained through other characterization techniques for these materials.

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References

1 K. P. Sing, D. Mohan, G. S. Tandom and G. S. D. Gupta, Ind. Eng. Chem. Res., 41 (2002) 2480.
2 J. M. Valente Nabais, T. Canário, P. J. M. Carrott and M. M. L. Ribeiro Carrott, J. Porous Mater., 14 (2007) 181.
3 A. C. Pastor, F. Rodriguez-Reinoso, H. Marsh and M. A. Martinez, Carbon, 37 (1999) 1275.
4 S. Y. You, Y. H. Park and C. R. Park, Carbon, 38 (2000) 1453.
5 M. Wu, Q. Zha, J. Qiu, Y. Guo, H. Shang and A. Yuan, Carbon, 42 (2004) 205.
6 J. M. Valente Nabais, P. J. M. Carrott and M. M. L. Ribeiro Carrott, Mater. Chem. Phys., 93 (2003) 100.
7 F. Suárez-García, A. Martinez-Alonso and J. M. D. Tascón, Carbon, 42 (2004) 1419.
8 A. Huidobro, A. C. Pastor and F. Rodriguez-Reinoso, Carbon, 39 (2001) 389.
9 F. Rodríguez-Reinoso, Activated Carbon: Structure, Characterization, Preparation and Applications, In Introduction to carbon technologies, Universidad de Alicante (Publicaciones), Alicante, Spain 1997, p. 60.
10 F. Stoeckli and T. A. Centeno, Carbon, 43 (2005) 1184.
11 M. V. López-Ramón, H. F. Stoeckli, C. Moreno-Castilla and F. Carrasco-Marín, Carbon, 37 (1999) 1215.
12 J. Silvestre-Albero, C. Gómez, A. Sepúlveda-Escribano and F. Rodríguez–Reinoso, Colloids Surf. A, 187 (2001) 151.
13 J. Angel Menéndez, Termochim. Acta, 312 (1998) 79.
14 J. C. Moreno and L. Giraldo, Instrum. Sci. Technol., 28 (2000) 171.
15 L. Giraldo and J. C. Moreno, J. Therm. Anal. Cal., 89 (2007) 589.
16 Y. Ladino-Ospina, L. Giraldo and J. C. Moreno-Piraján, J. Therm. Anal. Cal., 81 (2005) 435.
17 B. A. Finnin, M. A. A. O'Neill, M. Gaisford, S. Beezer, A. Hadgraft and J. Sears. J. Therm. Anal. Cal., 83 (2006) 331.
18 I. Wadsö and L. Wadsö, J. Therm. Anal. Cal., 82 (2005) 553.
19 F. Rouquerol, J. Rouquerol and K.Sing, Adsorption by Powders and Porous Solids, Academic Press, London 1999, p. 219.
20 G. A. Rodríguez, L. Giraldo, and J. C. Moreno, Rev. Col. Quim., 37 (2007) 43.
21 F. Rodriguez-Reinoso and M. Molina-Sabio, Adv. Colloid Interface Sci., 76–77 (1998) 271.
22 F. Rodríguez-Reinoso and H. Marsh, Activated Carbon, Elsevier Science, Oxford 2006, p. 143.
23 H. P. Boehm, Advances in Catalysis, Eley, D. D. H. Pines and P. B. Weisz, Eds, Academic Press, New York 1966, p. 192.
24 H. P. Boehm, Carbon, 40 (2002) 145.

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