

SORPTION PROPERTIES OF CARBON COMPOSITE MATERIALS FORMED FROM LAYERED CLAY MINERALS

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Abstract—The sorption properties of carbon-composite materials based on montmorillonite and hydroxalcalite matrices have been studied using nitrogen adsorption isotherms and inverse gas chromatography. Carbon composite materials derived from both types of inorganic precursors contain pore structure accessible for adsorbate molecules. Adsorption capacity per unit mass of these composite adsorbents is larger in the case of hydroxalcalite than in montmorillonite-based materials. Exposing these materials to ambient conditions results in their hydration. Subsequent water removal by heating under vacuum increases nitrogen adsorption capacity, which is explained by the opening of the adsorption space. The water content of hydrated samples and its effect on adsorption capacity is greater for the case of hydroxalcalite-based materials. No direct relationship between carbon content and adsorption properties of the materials studied is observed.

Key Words—Carbon, Hydroxalcalite, Inverse gas chromatography, Montmorillonite, Nitrogen sorption, Surface energy.

INTRODUCTION

Recent years have seen a renewed resurgence in adsorption research. Three reasons for these developments are: 1) increasing emphasis on environment, health and safety; 2) emerging new technologies; and 3) escalating energy costs. New materials are needed to meet these demands. One example is a program that uses gases such as hydrogen or methane as fuels for car engines. This end use requires microporous structures that can serve as adsorbents for gas storage. For practical applications, it is desirable to prepare materials that allow high adsorption capacity per volume and weight of the adsorbent. Submicroporous activated carbon is expected to be of particular interest.

One class of submicroporous carbons are Carbon Molecular Sieves (CMS) currently prepared by adsorption of hydrocarbons and carbonization of them in porous structures of other carbons acting as a matrix (Verma and Walker, 1992; Gaffney *et al.*, 1992). However, other techniques based on calcination of organic precursors between the layers of clay minerals have been discussed (Sonobe *et al.*, 1990; Bandosz *et al.*, 1992). In this case, organic material creates a thin film in the interlayer space of inorganic matrices so the size of pores is limited by the interlayer distance of the precursor mineral.

Microporous materials based on inorganic matrices and carbonized polymers were introduced and de-

scribed in our previous work (Bandosz *et al.*, 1993). It has been found that cationic (intercalated montmorillonites) and anionic (synthetic hydroxalcalite-like structures) clays are useful candidates as molecular matrices for carbons. Their layered framework and small interlayer spacing (about 1 nm), ion-exchange properties, and varied structural porosity are factors that can make it possible to control syntheses and final properties of composite structures. The aim of this preliminary study is to compare the sorption properties of two composite materials (layered mineral-activated carbon) prepared on the basis of two different inorganic precursors.

EXPERIMENTAL METHODS

Materials preparation

The montmorillonite samples and their carbonized counterparts have been prepared according to the methods described elsewhere (Bandosz *et al.*, 1992). Briefly, the sodium form of montmorillonite was intercalated by hydroxyaluminum oligocations (A). A portion of this sample was heat-treated at 673 K. Heating resulted in dehydroxylation of the aluminum complex producing a sample (AH) with a rigid structure. Both samples were saturated by polyfurfuryl alcohol and calcined in a nitrogen atmosphere at 973 K (samples AC and AHC, respectively).

Synthetic Mg-Al-CO₃ hydroxalcalite was prepared by the reaction of aqueous sodium aluminate solution with stoichiometric amounts of basic magnesium carbonate, 4MgCO₃·Mg(OH)₂·5H₂O. The reactions were carried out using two different Mg/Al ratios, 2:1 (H2) and 3:1 (H3), respectively.

The 4-styrenesulfonate anion was incorporated between the layers of hydroxalcalite by methods described

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previously (Dimotakis and Pinnavaia, 1990; Putyera, 1991). Accordingly, mixed magnesium-aluminum oxide solid solution prepared by calcination of carbonate hydroxalcalite is hydrothermally reconstructed to crystalline organic derivatives of hydroxalcalite through the meixnerite phase. The 4-styrenesulfonate anion in the interlayer spaces of hydroxalcalites was polymerized in a 0.1 M water solution of potassium persulfate at 358 K (Geismar *et al.*, 1991) (samples H2P and H3P). Carbonization of the intercalated polymer was carried out in a flow of nitrogen at 873 K for 3 hr (samples designated H2C and H3C).

Methods

Elemental analysis. Elemental analyses of the composite samples were determined by Carlo Erba CHNS-O EA1108 Elemental Analyzer.

X-ray analysis. Oriented sample mounts were made by settling a suspension of each mineral onto glass slides. All mineral mounts were dried at room temperature and heat treated at 673, 823 and 973 K; the mounts were rehydrated at humidity below 50% after calcination. X-ray diffractograms were produced with a Philips PW1729 diffractometer using filtered CuK_α radiation. Relative humidity during measurement was below 50%.

Inverse gas chromatography. The thermodynamic parameters that we use to characterize gas-solid interactions are derived from gas chromatographic results. The net retention volume, V_N , of a molecular probe injected into the stream of a carrier gas flowing through the chromatographic column filled with the investigated material is calculated from the measured net retention time (Kiselev and Yashin, 1969). Using this quantity the standard free energy of adsorption at infinite dilution is calculated as

$$\Delta G^0 = -RT \ln \frac{V_N}{S_m} + C \quad (1)$$

where R and T are the gas constant and temperature, m and S are mass and specific surface area of the adsorbent, C is a constant related to the standard states of gas and adsorbed phases.

Values of V_N measured at different temperatures are also used to calculate the enthalpy of adsorption, ΔH^0 ,

$$\Delta H^0 = -R \frac{\delta \ln(V_N)}{\delta(1/T)} \quad (2)$$

where δ stands for partial derivative.

Both ΔG^0 and ΔH^0 obtained under conditions of infinite dilution are dependent only on the gas-solid interaction since interaction between adsorbed molecules can be neglected.

Alkanes were used in this work to assess dispersive gas-solid interactions. It is well known from the chromatographic literature (Kiselev and Yashin, 1969) that

the logarithms of V_N for n -alkanes vary linearly with their number of carbon atoms; therefore, the quantity, ΔG_{CH_2} , which is defined as the difference in the ΔG^0 of two subsequent n -alkanes represents the free energy of adsorption of a CH_2 group. This quantity is not related to any particular alkane molecule; and due to its incremental character, it is not dependent on the choice of the reference state.

The chromatographic experiments were performed with an ANTEK 3000 gas chromatograph (from Antek Instruments Inc.). Details are described elsewhere (Bandosz *et al.*, 1992). Helium was used as a carrier gas with a flow rate of about $30 \text{ cm}^3/\text{min}$. The samples were conditioned at 473 K in the chromatographic column under helium gas flow for 15 hr prior to the measurements. The experiments were done in the temperature range 423–623 K. Under these conditions all chromatographic peaks were symmetrical and retention times did not depend on the amount injected (Henry's Law region). Retention volumes were corrected for the gas compressibility. The error of the measurement of retention time was 5%, and the temperature was stabilized with an accuracy $\pm 0.1 \text{ K}$.

Gas adsorption experiments. Nitrogen adsorption isotherms at 77 K were determined gravimetrically in the pressure range of 1 to 700 mmHg using a CAHN RG Electrobalance. The samples were outgassed at 423 K under vacuum (10^{-3} mmHg). The nitrogen isotherms were also determined for composites after their heat pretreatment under vacuum at different temperatures between 423 and 773 K. The apparent surface areas were calculated from nitrogen adsorption isotherms by using the BET equation in the p/p_0 range from 0.05 to 0.30.

RESULTS AND DISCUSSION

The X-ray results characterizing structural parameters of our samples are collected in Table 1. The heat treatment of intercalated montmorillonite (A) at 673 K resulted in the release of water and caused the hydroxaluminum oligocations to transform into aluminum oxide pillars (Pinnavaia, 1983; Ocelli and Tindwa, 1983). This resulted in a small decrease in the d_{001} distance. After carbonization both samples have about the same value for d_{001} (1.4–1.45 nm). At the temperature of carbonization, regardless of the content of the interlayer material, the spacing of samples A and AH decreased. In the case of the A sample we found that the structure swelled after saturation by polyfurfuryl alcohol because the inorganic matrix retained its swelling properties. However, after heat treatment, the structure became rigid as a result of cross-linking of aluminum oxide pillars so that polymer could only fill the space between pillars. Although the mechanism of creation of a carbon deposit was likely different in these two cases, the final product appears to be similar in

Table 1. Results of X-ray diffraction analysis and IGC (423 K).

Sample	d_{001} [nm]	Interlayer space [nm]	ΔG_{CH_2} [kJ/mol]	ΔH^0 hexane [kJ/mol]
H2	0.75	0.28	2.93	—
H3	0.78	0.31	2.06	—
H2C	0.88	0.41	5.51	67
H3C	0.94	0.47	4.66	60
A	1.70	0.72	5.09	—
AH	1.60	0.62	4.74	—
AC	1.40	0.42	5.12	69
AHC	1.45	0.47	4.40	53

that the interlayer distance after calcination is the same, and this presumably is limited by the thickness of the carbon layer deposited.

For the H2 and the H3 samples the initial values of d_{001} are very small. The poly(4-styrenesulfonate) polyanion introduced between the layers of hydrotalcite causes a significant increase in d_{001} limited only by the size of the 4-styrenesulfonate molecule that is cross-linked between sheets by chemical bonds. The interlayer space increased up to 1.5 nm (Bandosz *et al.*, 1993) which is a significant value if we consider the structure of clay minerals (Barrer, 1978). Calcination of the hydrotalcite samples in the presence of poly(4-styrenesulfonate) polyanion lead to an increased interlayer distance compared to the initial carbonate forms. The calculated interlayer spacing for these materials is found to be the same as in the case of montmorillonite based composites. This finding is consistent with our hypothesis that carbonized structures will control the sheet separation regardless of the nature of the matrices.

The X-ray results alone do not confirm the existence of a porous network accessible for adsorption. The adsorption properties of investigated materials should depend on the volume and sizes of their free interlayer spaces. However, possible structures of these materials can be deduced from: the chemical composition of the precursors, the known thermal behavior of the inorganic matrices, and the calcination conditions. Since the calcination of montmorillonite based samples had been carried out at 973 K, a temperature which ensures the carbonization of the polymer (between mineral layers) but does not cause the breakdown of the mineral layer structure, we can expect a stable microporous structure where pores are created between the carbonaceous material and mineral layers.

The temperature of calcination of the other composite materials (H2C and H3C) based on hydrotalcite precursors was slightly lower because the recrystallization of the hydrotalcite matrix structure starts at 923 K. However, the 873 K treatment was high enough for carbonization of the intercalated polymer chemically bound to mineral layers. The Mg/Al ratios for H2 and

Table 2. Results of CHN-S analysis [wt. %].

Sample	C	H	N	S
H2C	13.62	3.01	—	5.77
H3C	9.50	2.96	—	4.64
AC	3.84	0.18	0.12	—
AHC	4.12	0.82	0.30	—

H3 precursor samples determine the charge of the layers in accordance with the basic structural unit $[Mg_{1-x}Al_x(OH)_2]^{x+}$. Thus the amount of the intercalated polymer, which is related to the carbon content in the final composite should be higher for the H2C sample, which it is (Table 2). Now in contrast to montmorillonites, calcined hydrotalcite samples are expected to be metastable. The metastability is due to the unbalanced charge on the layers caused by collapse of the organic intercalate. Thus, during carbonization, new functional groups must be created and/or the old retained on the carbonized polymer to compensate the charge balance on the layers. The presence of these groups can influence the adsorption behavior of the hydrotalcite-based samples, especially after exposure to an atmosphere at normal humidity.

In order to further investigate the properties of our carbon-matrix materials, systematic sorption experiments were carried out. Nitrogen adsorption isotherms of montmorillonite-based samples are collected in Figure 1. These isotherms are characterized as type I or type II in the lower pressure region, where the adsorption space is limited to a restricted number of nitrogen adsorption layers. But the isotherms "bend up" in the higher pressure region. This suggests that some of the pores formed in the montmorillonite based samples are in a micro- to small mesopore region. Apparent BET surface areas calculated from nitrogen adsorption isotherms are about 300 m²/g for samples intercalated by hydroxyaluminum polycations. Saturation by furfuryl alcohol, polymerization, and carbonization re-

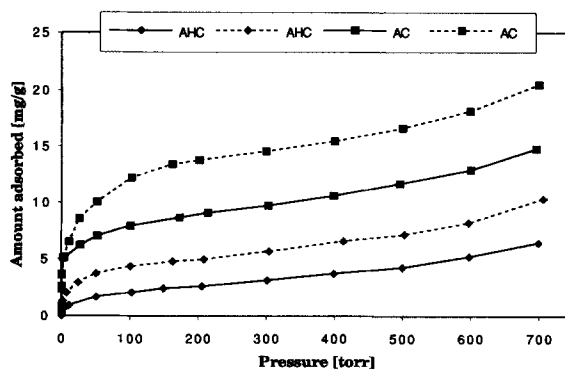


Figure 1. Nitrogen adsorption isotherms at 77 K of montmorillonite based materials before (—) and after heat treatment at 723 K (---).

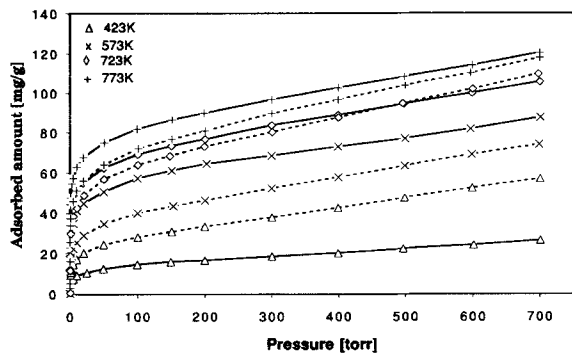


Figure 2. Nitrogen adsorption isotherms at 77 K of hydrotalcite based composite materials: H2C (—) and H3C (····) after heat treatment at four different temperatures.

sulted in a significant decrease of S_{N_2} , up to $60 \text{ m}^2/\text{g}$ for the AC sample and $30 \text{ m}^2/\text{g}$ for the AHC sample. The decrease observed is the result of filling of the interlayer space by the carbon deposit. The surface area of the AC sample is higher than for the AHC sample because in this case the matrix structure is characterized by hydroxylated pillars. Their presence resulted in the creation of new pores in the carbon present in the interlayer space. From the analysis of nitrogen isotherms, it is apparent that the internal surface of our composites is not available for N_2 molecules. The larger surface area observed for the AC sample may be the result of the presence of small pores that were created by water on the edges of inorganic crystallites. Whatever the case, the majority of internal surface is not available for adsorption.

Another characteristic feature of these composites can be revealed from adsorption results obtained after rehydration and outgassing at different temperatures. Almost twice the adsorption capacity of AC is found compared with the AHC sample. The carbon content of these samples (Table 2) is almost the same, and so is the free interlayer space. Therefore, the difference in adsorption properties could be attributed to their prep-

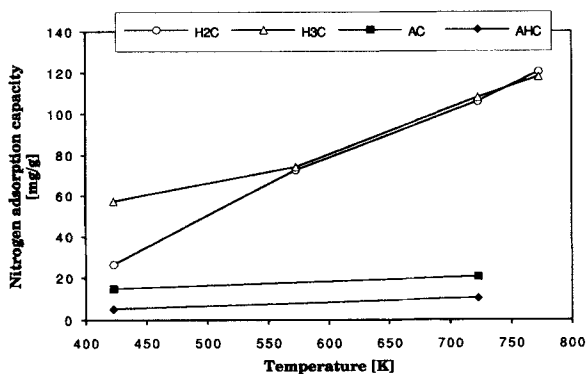


Figure 3. Relationship between nitrogen adsorption capacity and the temperature of heat treatment.

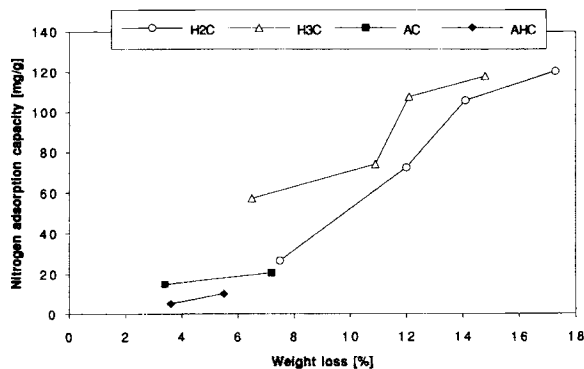


Figure 4. Relationship between adsorption capacity of N_2 and weight loss after heat treatment.

aration history. The AC sample was prepared from a precursor containing hydroxylaluminum pillars. We propose that water released as a result of the dehydroxylation of pillars *during* the carbonization process created a micropore structure within the carbonaceous deposit. Such an effect would be similar to the heat treatment of activated carbons in steam, which is known to increase their microporosity (Gergova *et al.*, 1992). This would not occur in the case of AHC sample whose precursor (AH) already contained aluminum oxide pillars.

Heat pretreatment plays a very important role in the case of hydrotalcite-based composite materials. The nitrogen adsorption isotherms presented in Figure 2 show a significant increase in adsorption capacity with the temperature of pretreatment of these samples after exposure to the atmosphere; the apparent N_2 BET area increased from 50 to $325 \text{ m}^2/\text{g}$ for H2C and from 105 to $277 \text{ m}^2/\text{g}$ for H3C. It is interesting to note that the hydration–dehydration process is reversible and the initially rehydrated H3C has almost twice the adsorption capacity of the H2C sample. As the treatment temperature increases, the difference between adsorption isotherms for these two samples vanishes. To establish a uniform index of comparison, the effect of heat treatment on adsorption capacity is expressed by the nitrogen amount adsorbed at 700 mmHg for all samples under study. This index is shown in Figure 3 as a function of treatment temperature. The heat treatment of rehydrated samples causes their dehydration and/or dehydroxylation accompanied by weight loss. The index is plotted in Figure 4 as a function of weight loss. Montmorillonite-based samples show a small weight loss, which is consistent with the insignificant changes observed in their adsorption properties as a function of treatment temperature (Figure 3). On the other hand, weight loss due to heat treatment of the rehydrated hydrotalcite-based materials is more significant; concomitantly, these “dehydration” processes result in an increase in adsorption capacity.

The relationship between adsorption properties and water content of carbon-mineral composite materials is complex. This is particularly true for the calcined hydrotalcite-based materials and is probably due to the charge imbalance on the layers. Exposure of such systems to atmospheric moisture may cause their rehydration and stabilization but at the expense of N₂ adsorption space. The rehydrated H2C and H3C samples treated at 423 K show a significant difference in nitrogen adsorption capacity (factor of 3). This difference disappears after heat treatment exceeding 573 K, where presumably some dehydroxylation occurs (Figure 3). Thermal processes may be responsible for uniformly opening the structure of these materials, thus resulting in an increase of adsorption space. The state of hydration appears to be the dominant factor controlling adsorption in the hydrotalcite composites because practically the same adsorption capacity of dry (623 K treated) H2C and H3C samples indicates that the carbon content and layer charge are not key factors in adsorption.

Additional information related to the microporosity of our samples is obtained from gas chromatographic results which are collected in Table 1. These results refer to dry materials since the samples were conditioned at 623 K. The two quantities, free energy of adsorption of CH₂ group, ΔG_{CH_2} , and adsorption enthalpy, ΔH , of hexane are related to nonspecific gas-solid interactions. These quantities are sensitive to the micropore structure of the solid. It was shown theoretically (Everett and Powl, 1976) and experimentally (Carrott and Sing, 1987; Jagiełło *et al.*, 1992) in the case of carbonaceous materials that molecular interactions with fine micropores enhance significantly ΔH and ΔG_{CH_2} values.

Initially H2 and H3 hydrotalcite samples are characterized by low ΔG_{CH_2} values compared to those for the final carbon-mineral composites. We propose that in these cases the hydrotalcite materials' ΔG_{CH_2} values correspond to alkane interaction with the outer surface of the minerals because their interlayer space is inaccessible to alkane molecules. The higher values of this parameter for carbon-mineral composites and montmorillonite precursors are undoubtedly related to alkane interactions with pores created within the interlayer spaces of these materials. Accessibility of these pores for alkane molecules is consistent with the measured interlayer distances (Table 1). The values of the ΔG_{CH_2} parameter and also hexane adsorption enthalpies, ΔH , are similar for all carbon-mineral composites where the minor differences seen in these values may be attributed to differences in pore structures. For instance, higher values of ΔG_{CH_2} and ΔH for AC compared to AHC samples indicate the existence of smaller pores in the former sample. This additional adsorption space, we have proposed earlier, develops as water released during the carbonization process acts as an ac-

tivation agent by creating a finer pore structure in the carbonaceous material.

CONCLUSION

Montmorillonites intercalated with hydroxyaluminum polycations and hydrotalcites were used to obtain carbon-mineral composites. The sorption properties of these materials and pore structure depend on the history of the samples. Montmorillonites with hydroxyaluminum pillars are characterized by higher nitrogen sorption capacity than the sample with dehydroxylated pillars. We proposed that water released during calcination (carbonization of polyfurfuryl alcohol) is an activation agent that can create small pores in the carbonaceous deposit. The water content has a significant influence on the sorption properties of hydrotalcite-based samples. The state of hydration of the hydrotalcite composites appears to be the dominant factor controlling their adsorption.

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REFERENCES

- Barrer, R. M. (1978) *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*: Academic Press, London.
- Bandosz, T. J., Jagiełło, J., Andersen, B., and Schwarz, J. A. (1992) Inverse gas chromatography study of modified smectite surface: *Clays & Clay Minerals* **40**, 306–310.
- Bandosz, T. J., Jagiełło, J., Amankwah, K. A. G., and Schwarz, J. A. (1992) Chemical and structural properties of clay minerals modified by inorganic and organic material: *Clay Miner.* **27**, 435–444.
- Bandosz, T. J., Putyera, K., Jagiełło, J., and Schwarz, J. A. (1993) Application of inverse gas chromatography to the study of the surface properties of modified layered materials: *Microporous Mat.* **1**, 73–79.
- Carrott, P. J. M. and Sing, K. S. W. (1987) Gas chromatographic study of microporous carbons: *J. of Chromatography* **406**, 139–144.
- Dimotakis, E. D. and Pinnavaia, T. J. (1990) New route to layered double hydroxides intercalated by organic anions: Precursors to polyoxometalate-pillared derivatives: *Inorg. Chem.* **29**, 2393–2394.
- Everett, D. H. and Powl, L. C. (1976) Adsorption in slit-like and cylindrical micropores in the Henry's Law region: *J. Chem. Soc., Faraday Trans. 1* **72**, 619–639.
- Gaffney, T. R., Farris, T. S., Cabrera, A. L., and Armor, J. N. (1992) Modified carbon molecular sieves for gas adsorption: *U.S. Pat.* **5,098,880**.
- Geismar, G., Lewandowski, J., and de Boer, E. (1991) Anion-exchange and reactions in Mg-Al oxide hydrates with hydrotalcite structure. II. Intercalated anion-exchange in organic solvents and chemical reactions: *Chemiker-Zeitung* **115**, 335–339.
- Gergova, K., Galushko, A., Petrov, N., and Minkova, V. (1992) Investigation of the porous structure of activated carbons prepared by pyrolysis of agricultural by-products in a stream of water vapor: *Carbon* **30**, 721–727.
- Jagiełło, J., Bandosz, T. J., and Schwarz, J. A. (1992) Inverse gas chromatography study of activated carbons: The effect

- of controlled oxidation on microstructure and surface chemical functionality: *J. of Coll. Inter. Sci.* **151**, 433–445.
- Kiselev, A. V. and Yashin, Y. I. (1969) *Gas Adsorption Chromatography*: Plenum Press, New York, p. 23.
- Occelli, M. L. and Tindwa, P. M. (1983) Physicochemical properties of montmorillonite interlayered with cationic oxyaluminium pillars: *Clays & Clay Minerals* **31**, 22–28.
- Pinnavaia, T. J. (1983) Intercalated clay catalysts: *Science* **220**, 365–371.
- Putyera, K. (1991) Molecular oxygen activation with Co(II) complexes intercalated into intracrystalline spaces of inorganic matrices: Ph.D. thesis, Slovak Academy of Sciences, Bratislava, CSFR.
- Sonobe, N., Kyotani, T., and Tomita, A. (1990) Carbonization of polyfurfuryl alcohol and polyvinyl acetate between the lamellae of montmorillonite: *Carbon* **28**, 483–488.
- Verma, S. K. and Walker Jr., P. L. (1992) Preparation of carbon molecular sieves by propylene pyrolysis over microporous carbons: *Carbon* **30**, 829–836.

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