Structural and Textural Properties of Pyrolytic Carbon Formed within a Microporous Zeolite Template

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A new class of pyrolytic carbon materials has been prepared by chemical vapor infiltration of a microporous zeolite powder followed by removal of the zeolitic substrate. A wide-pore Y zeolite was used as the substrate for the pyrolytic carbon, and propylene was used as the carbon precursor. The structure and porous texture of the resulting carbons were examined by X-ray diffraction, scanning and transmission electron microscopy, and by adsorption of N_2 at 77 K and CO_2 at 273 K. Carbon reactivity studies were performed by both nonisothermal and isothermal thermogravimetric analysis. Under the present conditions of chemical vapor infiltration (800−850 °C, 2.5 vol % C_3H_6, 1 atm of N_2), high-surface-area microporous carbons, with wide microporosity, well-developed mesoporosity and high adsorption capacity were obtained. The carbon yield and the apparent surface area of the carbon increased with increasing propylene pyrolysis temperature. The morphology of the carbons was very similar to that of the zeolite template. Their O_2-reactivity profiles exhibited a two-stage behavior, with the inflection point between the two stages occurring at different conversion levels depending on the deposition temperature. Such oxidation behavior suggests that the carbons consist of two different structures with different reactivities, the oxidation of the more reactive carbon taking place first and the remaining more ordered carbon being consumed in the second stage. These carbons do not exhibit molecular sieving properties for small adsorbate/reactant species.

1. Introduction

Zeolites are highly crystalline aluminosilicates with a uniform pore structure; Their channel apertures are in the range 0.3−1.0 nm, depending on the type of zeolite and its preparation history (e.g., calcination, leaching, or various chemical treatments). They have been of considerable commercial importance not only as catalysts but also as molecular sieves, due to their ability to separate linear from branched hydrocarbons. This separation ability is associated with the extremely fine pore structure, which permits only certain molecules to penetrate into the interior cages of the zeolite particles.[1] The stability of carbon materials at high temperatures and in acidic media and their lower affinity for water offer unique advantages over inorganic molecular sieves and make the development of such materials very attractive. For example, carbon molecular sieves (CMS) for the separation of O_2 from air has become of great commercial interest. More generally, the design of microporous carbons with a predetermined pore size distribution (e.g., for methane storage) continues to be of great fundamental interest and has increasing practical importance.

Studies of molecular sieve properties of carbons derived from polyvinylidene chloride (PVDC)[2,3] and from Saran (copolymer of vinylidene chloride and vinyl chloride in a mole ratio of about 9:1)[4,5] have shown that heat treatment of these polymers results in amorphous carbons which do not have a regular crystalline structure, but they do present a system of cavities connected by slit-shaped pore constrictions and adsorption capacities comparable to those of the zeolites.[6]

More recently, Foley and co-workers,[7−9] using a similar approach, prepared CMS by controlled pyrolysis of poly(furfuryl alcohol). Their results show that the chemical and physical properties of the CMS, especially porosity and pore size, can be systematically modified by varying the temperature and time of pyrolysis. Higher synthesis temperatures and longer soak times leaded to CMS with narrower pores, when compared to CMS prepared at lower temperatures and soak times. The decrease of micropore diameter with heating tem-

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[1] Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; Wiley: New York, 1974.

[2] Dacey, J. R.; Thomas, D. G. *Trans. Faraday Soc.* **1954**, *50*, 647.

[3] Kipling, J. J.; Wilson, R. B. *Trans. Faraday Soc.* **1960**, *56*, 557.

[4] Culver, R. V.; Heath, N. S. *Trans Faraday Soc.* **1955**, *51*, 1569.

[5] Heath, N. S.; Culver, R. V. *Trans. Faraday Soc.* **1955**, *51*, 1575.

[6] Lamond, T. G.; Metcalfe, J. E.; Walker, P. L., Jr. *Carbon* **1965**, *3*, 59.

[7] Lafyatis, D. S., Tung, J.; Foley, H. C. *Ind. Eng. Chem. Res.* **1991**, *30*, 865.

[8] Mariwala, R. K.; Foley, H. C. *Ind. Eng. Chem. Res.* **1994**, *33*, 607.

[9] Kane, M. S.; Goellner, J. F.; Foley, H. C.; DiFrancesco, R.; Billinge, S. J. L.; Allard, L. F. *Chem. Mater.* **1996**, *8*, 2159.

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perature affected the effective diffusivities of different gases tested, modifying the molecular sieving properties of the carbons. Mariwala and Foley[8] attributed the effect of time and temperature on the CMS properties to an annealing of the glassy microstructure, leading to larger aromatic microdomains with better alignment and order and less free volume for gas adsorption and diffusion. Addition of high molecular weight (MW > 2000 amu) poly(ethylene glycol) to the PFA prior to pyrolysis developed a meso- and macropore structure (i.e., transport pores) in the resultant CMS,[7] which provides for more efficient internal mass-transport processes in the sorption of gases into the narrow micropores.

Activated carbons (ACs) have been used as precursors in the production of carbon molecular sieves. Their pore structure, with a wide micropore size distribution, provides high surface area and extensive adsorption capacity. The access to the narrow micropores of the AC can be modified to generate constrictions similar in size to an adsorbing species, allowing its selective adsorption. Thus, CMS can be produced by altering the size of pore constriction of ACs to match the size of the desired adsorbate. Walker et al.[10] reported that coating a granular AC with a thermosetting polymer, followed by curing and carbonization of the polymer layer can create molecular-size constrictions in its pore structure, thus generating CMS. Using a similar approach, preparation of CMS was carried out by carbon deposition from pyrolysis of propylene on microporous carbons.[11,12] This technique has been shown to be only partial successful for separation of gases. Because of their typically wide micropore size distribution, ACs showed no useful development of molecular sieving characteristics. Only carbon precursors possessing narrow micropore size distribution achieved considerable adsorption selectivity in the separation of gases whose molecular size falls within a narrow range. Conditions of chemisorption and pyrolysis of pyrolytic carbon precursor have to be selected very carefully to satisfy the conflicting requirements of maximum adsorption selectivity and minimum pore blocking (i.e., uniform deposition over the entire pore surface), with its least detrimental effect on adsorption capacity.[13]

Verma and Walker[14] reported that the preparation of CMS by depositing carbon from pyrolysis of propylene in an AC is made viable by adding a hydrocarbon cracking catalyst to the AC. In this study, Ni, used as the hydrocarbon cracking catalyst, was included in AC by the incipient-wetness technique. The preferential cracking of propylene at the Ni sites within the pores of the AC particles and/or at the particle external surface, generating constrictions of the size required for gas separation, was suggested by the authors as a possible explanation for the formation of CMS.

A new approach in the preparation of carbon molecular sieves from activated carbons was presented by Nguyen and Do.[15] Coke deposition via benzene thermal cracking on an AC was allowed to proceed until all micropores became nearly closed, followed by an activation step necessary to refine the opening of the pore mouth to provide to the carbon molecular sieve characteristics.

Toda et al.[16] studied the change produced in the microporous structure and the micropore size distribution of an AC made from coal by steam activation after heat treatment at high temperature. They suggested that preparation of CMSs from ACs may be achieved by heat treatment only. However, the micropore volumes of the heat-treated carbons decreased rapidly with temperature, without producing appreciable molecular sieve properties to make them useful as CMS.

In similar studies to that of Toda et al.,[16] Verma,[11] and Verma and Walker[17] came to the conclusion that the thermal treatment of an AC produced no useful molecular sieving properties for the separation of gases of close molecular size. They suggested that the fine sieving pores generated initially by heat treatment at moderate temperature, due to elimination of some surface oxygen functional groups, are reduced in size due to pore sintering at higher temperatures.

In recent years there has been quite a bit of interest in designing novel materials by exploiting the variations of both zeolites (or other inorganic solids) and carbons. For example, Leboda[18,19] studied the chemical structure and morphology of carbon deposits contained in complex carbon/mineral adsorbents prepared by pyrolysis of different carbonaceous substances on the surface of mineral sorbents such as silica gels, Al_2O_3, aluminosilicates, etc. Foley[20] prepared composite structures of CMS and inorganic oxides and supported metals in order to combine the surface chemical properties of the inorganic oxides with the molecular sieving properties of the carbon (i.e., adding functionality to the carbon molecular sieves). Model results suggested that these carbon molecular sieve composites could be tailored to produce catalysts with improved selectivity for synthesis gas conversion in the Fischer–Tropsch reaction.[21] More recently, the group of Foley[22] prepared noncrystalline composite catalysts, consisting of silica–alumina and amorphous carbon molecular sieves, which were able to produce mono- and dimethylamines from methanol and ammonia with higher selectivity than the silica–alumina catalysts used in the commercial practice. Schwarz and co-workers[23–26] have investigated the pore structure of carbon/mineral nanocomposites prepared by using the intracrystalline space of layered minerals for in situ carbonization. Kyotani et al.[27,28] found that high-surface-area carbons can be obtained by carboniza-

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(10) Walker, P. L., Jr.; Lamond, T. G.; Metcafe, J. E., III *Proc. 2nd Conf. on Industrial Carbon and Graphite*; Society for Chemical Industry: London, 1966; p 7.

(11) Verma, S. K. *Carbon* **1991**, *29*, 793.

(12) Verma, S. K.; Walker, P. L., Jr. *Carbon* **1992**, *30*, 829.

(13) Moore, S. V.; Trimm, D. L. *Carbon* **1977**, *15*, 177.

(14) Verma, S. K.; Walker, P. L., Jr. *Carbon* **1993**, *31*, 1203.

(15) Nguyen, C.; Do, D. D. *Carbon* **1995**, *33*, 1717.

(16) Toda, Y., Yuki, N.; Toyoda, S. *Carbon* **1972**, *10*, 13.

(17) Verma, S. K.; Walker, P. L., Jr. *Carbon* **1990**, *28*, 175.

(18) Leboda, R. *Mater. Chem. Phys.* **1992**, *31*, 243.

(19) Leboda, R. *Mater. Chem. Phys.* **1993**, *34*, 123.

(20) Foley, H. C. *ACS Symp. Ser.* **1988**, *368*, 355.

(21) Lafyatis, D. S.; Foley, H. C. *Chem. Eng. Sci.* **1990**, *45*, 2567.

(22) Foley, H. C.; Lafyatis, D. S.; Mariwala, R. K.; Sonnichsen, G. D.; Brake, L. D. *Chem. Eng. Sci.* **1994**, *49*, 4771.

(23) Bandosz, T. J.; Putyera, K.; Jagiello, J.; Schwarz, J. A. *Microporous Mater.* **1993**, *1*, 73.

(24) Bandosz, T. J.; Gómez-Salazar, S.; Putyera, K.; Schwarz, J. A. *Microporous Mater.* **1994**, *3*, 177.

(25) Bandosz, T. J.; Jagiello, J.; Putyera, K.; Schwarz, J. A. *Carbon* **1994**, *32*, 659.

(26) Bandosz, T. J.; Jagiello, J.; Putyera, K.; Schwarz, J. A. *Chem. Mater.* **1996**, *8*, 2023.

tion of poly(furfuryl alcohol) (PFA) in a zeolite template, thus avoiding the conventional activation process. They also reported that carbons obtained in this way retain their high surface area even after treatment at high temperature. Hernadi et al.[29] have even been successful in preparing carbon nanotubes by decomposing acetylene on the surface of a Y zeolite impregnated with cobalt.

In the present work, an alternative approach was pursued. Microporous carbons prepared by infiltration of a widepore zeolite with pyrolytic carbon from pyrolysis of propylene has been studied. Zeolite, a molecular sieve, is used as template for the pyrolytic carbon deposition. If the carbon deposition is assumed to take place on the surface of the internal channel of the zeolite during the pyrolysis of propylene, once the zeolite is removed, i.e., by acid washing, the remaining carbon should have acquired a porous structure similar to that of the zeolite, i.e., a porous structure of a CMS. This approach, is used in this study to tailor the physical surface properties of the carbon materials obtained by this technique.

2. Experimental Section

2.1. Materials and Carbons Preparation. Zeolite/carbon composites have been prepared by chemical vapor infiltration of zeolite powder with pyrolytic carbon at 800−850 °C. A wide-pore microporous Y zeolite (Z-14 US, Davison Chemical Co.), widely used as a hydrocarbon cracking catalyst, was used as the substrate for pyrolytic carbon deposition. The experiments were carried out in a conventional horizontal tubular furnace (5 cm i.d.). Propylene (2.5 vol %), in a stream of nitrogen at atmospheric pressure, was used as the pyrolytic carbon precursor. In a typical experiment, the zeolite powder was placed in a ceramic boat inside the isothermal zone of the furnace. The temperature was increased from room temperature to the reaction temperature at a heating rate of 10 °C/min in N_2 atmosphere. Once the reaction temperature was reached, the inlet gas was changed from N_2 to the propylene/N_2 mixture, and the reaction was carried out for ca. 24 h. The temperature was maintained within ±1 °C. The composites were denoted by the name of the zeolite followed by CVD and the deposition temperature in °C (e.g., Z14US/CVD800). The amount of pyrolytic carbon accumulated on the zeolite was calculated by weighting the zeolite sample before and after the deposition experiments.

Pure carbon samples were obtained by recovering the pyrolytic carbon after demineralizing the zeolite/carbon composite. A standard demineralization procedure, involving HCl and HF, was used.[30] The carbons thus obtained were denoted by ZCVD followed by the deposition temperature (e.g., ZCVD800). Carbons ZCVD850LT and ZCVD850HT were prepared by carbonization of carbon ZCVD850 (10 °C/min) in N_2 at 1000 °C for 2 h (LT) and by further heat treatment in a graphite induction furnace (∼100 °C/min) at 2900 °C in Ar for 5 min (HT).

2.2. Carbon Characterization. The structure of the carbons was studied by XRD (40 kV, 20 mA, Cu Kα radiation, Rigaku), scanning and transmission electron microscopy (SEM and TEM), and N_2 (77 K, Omnisorp 100 CX, Coulter) and CO_2 (273 K, Autosorb, Quantachrome) adsorption. Reactivity studies (1 atm of O_2, 60 cm^3(STP)/min) were performed by both nonisothermal (5 °C/min) and isothermal thermogravimetric analysis (Cahn microbalance, Model 113X). The reactivity profiles, $1 - X$ vs temperature and R vs X (where X represents carbon conversion or burnoff (BO) and $R = [1/(1 - X)]\mathrm{d}X/\mathrm{d}t$) were obtained from the noisothermal and isothermal experiments, respectively.

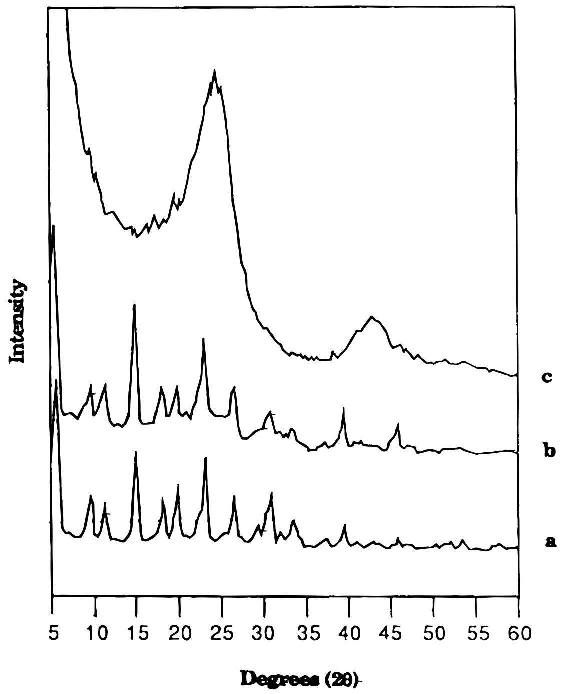

Figure 1. X-ray diffraction patterns for the zeolitic substrate, Z14US (a), the composite, Z14US/CVD800 (b), and the recovered matrix material, ZCVD800 (c).

3. Results and Discussion

3.1. Porous Structure and Morphology. Figure 1 shows the X-ray diffraction (XRD) patterns of the substrate, Z14US, the composite, Z14US/CVD800, and the recovered matrix material, ZCVD800. Clearly, the disappearance of all zeolite peaks and the appearance of broad C(002) and C(10) peaks for ZCVD800 indicate that the procedure of removing the zeolite by acid leaching was successful. Selected area electron diffraction and elemental analyses of the carbon samples further supported the complete removal of the zeolite from the carbons. The average crystallographic parameters d_{002} and L_c for ZCVD800 were 0.363 and 1.7 nm, respectively. Similar results were found for ZCVD850 carbon, with corresponding values for d_{002} and L_c being 0.356 and 1.3 nm, respectively. These values indicate that an increase in the propylene pyrolysis temperature tends to result in carbon with lower interplanar distance and lower average thickness of parallel pseudographitic layer.

Figure 2 shows the N_2 adsorption isotherms of the zeolite and the carbons. Table 1 summarizes the weight percentages of carbon in the composites, the effective micropore volume values, obtained from the application of the t method to the N_2 adsorption isotherm data[31] and from the application of the Dubinin−Radushkevich (DR) equation[32] to both the CO_2 and N_2 adsorption isotherm data, and the apparent BET and DR surface

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[27] Kyotani, T.; Natty, T.; Tomita, T. *Extended Abstracts of Carbon '92*, Essen, 1992; p 437.

[28] Kyotani, T.; Inoue, S.; Nagai, T.; Tomita, A. *Chem. Mater.* **1997**, *9*, 609.

[29] Hernadi, K.; Fonseca, A.; Nagy, J. B.; Bernaerts, D.; Fudala, A.; Lucas, A. A. *Zeolites* **1996**, *17*, 416.

[30] Radovic, L. R.; Walker, P. L., Jr.; Jenkins, R. G. *Fuel* **1983**, *62*, 849.

[31] Lippens, B. C.; de Boer, J. H. *J. Catal.* **1965**, *4*, 319.

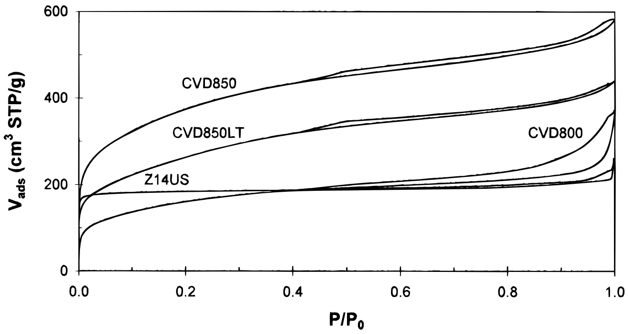

Figure 2. N_2 adsorption–desorption isotherms for the zeolite and carbons.

area values (derived from the data of the N_2 and CO_2 isotherms, respectively) for the zeolite, composites and carbons. The characteristic type I isotherm of the Y zeolite (Z14US) confirms its relatively high surface area and narrow microporosity. The fact that its S_{BET} value is lower than S_{DR} can be attributed to the lack of achievement of true N_2 adsorption equilibrium due to restricted diffusion through the pores at the low temperature of 77 K;[33] it also further supports the existence of very narrow micropores in the structure of the zeolite. Infiltration of the zeolite with pyrolytic carbon at 800 °C (Z14US/CVD800) yielded 45% of carbon matrix and reduced its BET surface area from 720 to ~4 m^2/g, most probably due to both partial filling of the pores and blockage of the pore entrance by the pyrolytic carbon. When the infiltration temperature was 850 °C, a 57% matrix yield was achieved (Table 1); pyrolytic carbon deposition also resulted in a decrease of the surface area of the zeolite. Thus, under the experimental conditions used in this study, the higher the deposition temperature, the higher the pyrolytic carbon yield. Once the zeolitic material was leached out, the isolated carbon products exhibited a relatively high BET surface area, 590 and 1380 m^2/g for ZCVD800 and ZCVD850, respectively. Further heat treatment of ZCVD850 at 1000 °C (ZCVD850LT) and 2900 °C (ZCVD850HT) reduced the apparent surface area to 963 and 39 m^2/g, respectively.

The N_2 adsorption isothermal profiles for ZCVD800, ZCVD850, and ZCVD850LT are quite similar to each other (Figure 2). They are all type I isotherms and exhibit a more rounded "knee" at low relative pressures and more pronounced slope at higher relative pressure than the zeolite. The apparent surface area and the micropore volume of these carbons, derived from the N_2 isotherms, are larger than those obtained from CO_2 isotherms (Table 1). These two observations indicate that these carbons possess a much wider microporosity than the zeolitic substrate. The relatively high CO_2 apparent surface area and micropore volume of the zeolite-derived carbons (Table 1) indicate that, even though these carbons have developed a wide micropore size distribution, they maintain a considerable volume of narrow micropores, which represents more than 50% of the total micropore volume for all the carbons. This feature may be important for the sieving properties of the carbons that, under certain conditions, could be used to separate small gas molecules.[26] The presence of narrow micropores in these carbons is supported by the results shown in Figure 3, which represents the DR plots for the zeolite and carbons, based on the N_2 adsorption isotherm data. The DR plots exhibit deviation from linearity at low relative pressure values, as it is frequently observed for coals, carbonized materials and carbons with very narrow micropores.[34] This behavior has been attributed to activated diffusion in the narrow micropores of the carbons.[35] Such deviations can be linearized to some extent by using the Dubinin–Astakhov equation[36] with values of the *n* parameter being ~3, ~4, and ~5 for ZCVD800, ZCVD850, and ZCVD850LT, respectively. A value of *n* higher than 2 has been associated to molecular sieve carbons with a system of relatively narrow micropores.[37]

The presence of a type H3 hysteresis loop in the desorption branch of the isotherms, including that of Z14US, at relative pressures above 0.4, which exhibits no limiting adsorption at $P/P_0 \sim 1$, is indicative of the presence of slit-shaped pores.[38]

The morphology of the Z14US/CVD800 composite and ZCVD800 carbon is not different from that of the parent zeolite, as can be concluded from the scanning electron micrographs shown in Figure 4. Similar results were obtained for samples Z14US/CVD850 and ZCVD850. This suggests that chemical vapor infiltration of zeolite by pyrolysis of propylene, followed by removal of the zeolite produces a pyrolytic carbon that acquires a morphology quite similar to that of the zeolite, with a fine microporosity and a relatively high surface area.

3.2. Oxidation Behavior.

Figure 5 shows the weight loss vs temperature curve obtained upon gasification of the Z14US/CVD850 composite in O_2. The pyrolytic carbon starts to oxidize at ~500 °C (no weight loss was observed in blank experiments, when only zeolite was used). The rate of weight loss is very low within the temperature range 500–600 °C and increases significantly at 600 °C. Above 700 °C the remaining weight stays constant at a value that corresponds to ~44% of the initial weight of the composite, indicating that the carbon matrix of the composite has been completely consumed. (This weight loss agrees very well with the percentage of carbon matrix in Z14US/CVD850 given in Table 1.) Figure 6 compares the nonisothermal reactivity profiles of the pyrolytic carbon in the presence (Z14US/CVD800) and absence (ZCVD800) of the zeolite substrate. The free-standing pyrolitic carbon (ZCVD800) is seen to be more reactive than the corresponding carbon in the composite (Z14US/CVD800), in agreement with its higher apparent and reactive surface area.[39] It is important to note that it also clearly exhibits a two-stage reactivity behavior, with the inflection point between the two stages occurring at a conversion level of ~25%. This behavior suggests the

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(32) Dubinin, M. M.; Radushkevich, L. V. *Proc. Acad. Sci., SSSR* **1947**, *55*, 331.

(33) Rodríguez-Reinoso, F., In *Carbon and Coal Gasification*; Figueiredo, J. L., Moulijn, J. A., Eds.; Martinus Nijhoff Publishers: Dordrecht, 1986; pp 601–642.

(34) Marsh, H.; Rand, B. *J. Colloid Interface Sci.* **1970**, *33*, 101.

(35) McEnany, B.; Master, K. J. *Thermochim. Acta* **1984**, *82*, 81.

(36) Dubinin, M. M., *Surface and Membrane Science*; Cadenhead, D. A., Ed.; Academic Press: New York, 1975; Vol. 9, pp 1–70.

(37) Kraehenbuehl, F.; Stoeckli, H. F.; Addoun, A.; Ehrburger, P.; Donnet, J. B. *Carbon* **1986**, *24*, 483.

(38) Linares-Solano, A. In *Carbon and Coal Gasification*; Figueiredo, J. L., Moulijn, J. A., Eds.; Martinus Nijhoff Publishers: Dordrecht, 1986; pp 137–178.

(39) Lizzio, A. A.; Jiang, H.; Radovic, L. R. *Carbon* **1990**, *28*, 7.

Table 1. Percentage of the Matrix in the Composite and Porous Structure Characteristics of Zeolite, Composites, and Carbons

sample	$V_t^{N_2}$ (cm^3/g)	$V_{DR}^{N_2}$ (cm^3/g)	S_{BET} (m^2/g)	$V_{DR}^{CO_2}$ (cm^3/g)	$S_{DR}^{CO_2}$ (m^2/g)	% matrix
Z14US	0.277	0.282	720	0.379	1052	
Z14US/CVD800			~4			45
Z14US/CVD850			~3			57
ZCVD800	0.250	0.206	590	0.137	374	
ZCVD850	0.601	0.493	1380	0.322	920	
ZCVD850LT	0.436	0.318	963	0.235	641	

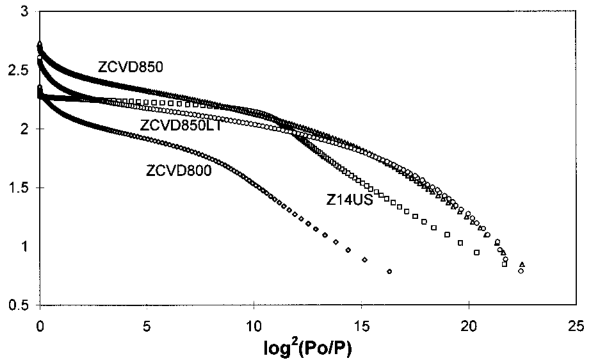

Figure 3. N_2 DR plots for the zeolite and carbons.

presence of two different structures with different reactivities in this carbon.[40] The oxidation of the more reactive one (25% of the carbon) takes place first while the remaining less reactive carbon (75%) is consumed in the second stage, at higher temperatures. The fact that the carbon in the Z14US/CVD800 composite, which, in principle, is expected to have similar structure to that of ZCVD800, shows a lower reactivity than ZCVD800, and does not exhibit a two-stage behavior, suggests that only a small fraction of the total surface area of this carbon is available to the oxidant gas. Most of the surface area of the carbon in the composite must be blocked and becomes available to the gas only as oxidation proceeds.

Figure 7 shows the reactivity profiles for ZCVD850 carbon. Those for ZCVD850LT and ZCVD850HT are also included and will be discussed later. Sample ZCVD850, even though prepared at higher temperature, is seen to be more reactive than ZCVD800 (Figure 6), in agreement with its higher surface area. Oxidation of ZCVD850 also shows a two-step reactivity profile, but the inflection point for this carbon (~50% burnoff) suggests that, under the experimental conditions used in this study, as the deposition temperature increases, the percentage of the more reactive structure in the carbon also increases. However, for both ZCVD800 and ZCVD850 the more reactive carbon and the less reactive carbon are oxidized within the same temperature range, ~500 to ~550 °C and ~575 to ~675 °C, respectively. The existence of two distinct structures[40] is also suggested by the isothermal reactivity profiles at different temperatures, illustrated in Figure 8 (with the transition burnoff value for ZCVD850 being ~50%).

The infiltration of Y zeolite with pyrolytic carbon, followed by removal of the zeolitic substrate, is thus concluded to produce carbons whose surface area is higher than that of the zeolite itself. A striking feature of these carbons is that they also exhibit two different

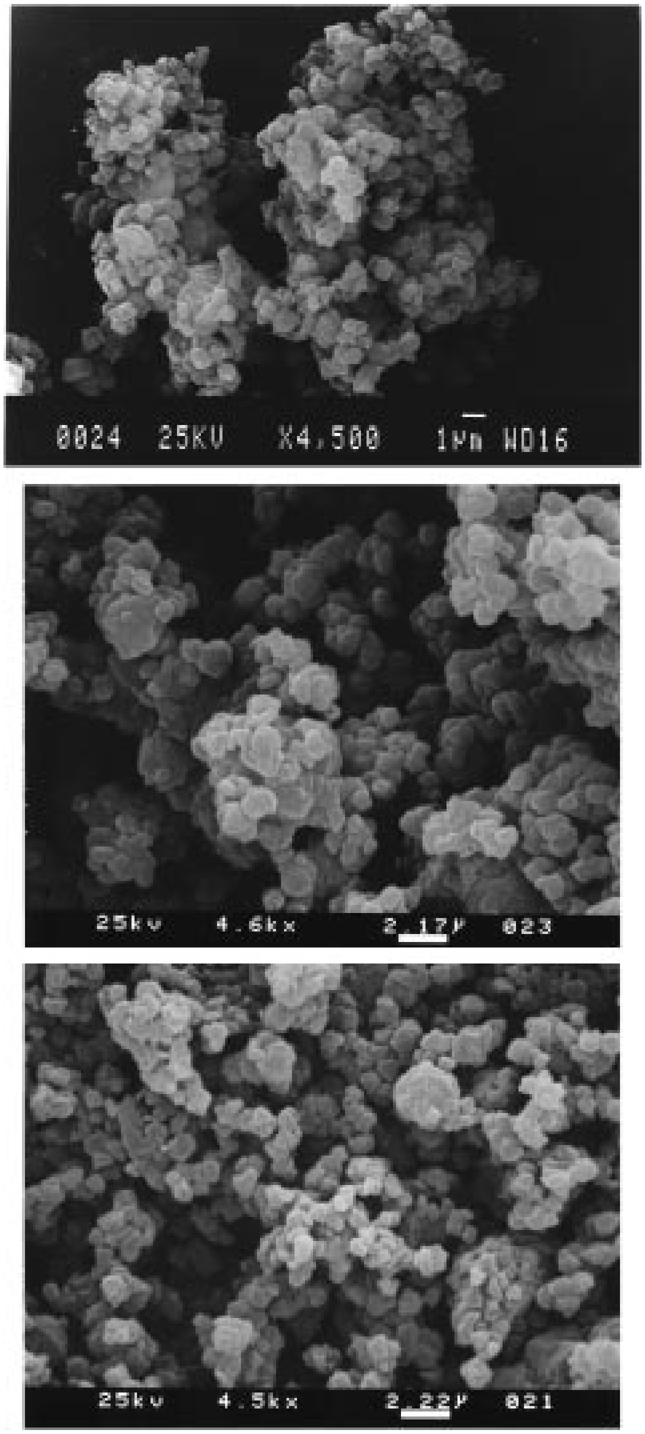

Figure 4. Scanning electron micrographs for Z14US zeolite (top), Z14US/CVD800 composite (middle), and ZCVD800 carbon (bottom).

regions in their oxidation behavior. This finding is in agreement with our earlier reports on the behavior of C/C composites made with fiber and matrix materials

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[40] Cordero, T.; Thrower, P. A.; Radovic, L. R. *Carbon* **1992**, *30*, 365.

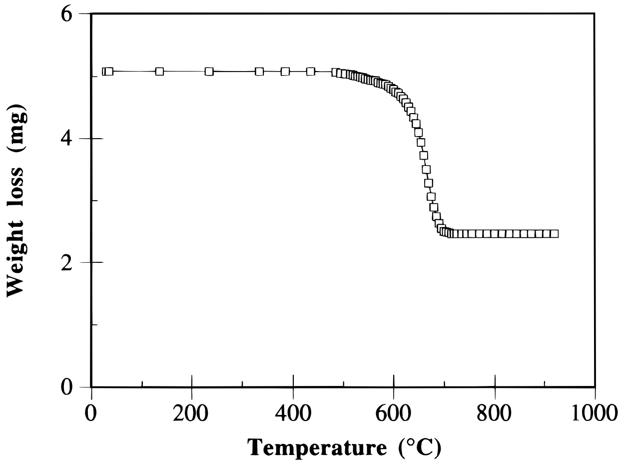

Figure 5. Nonisothermal weight-loss vs temperature profile for the oxidation of Z14US/CVD800 composite, at a heating rate of 5 °C/min.

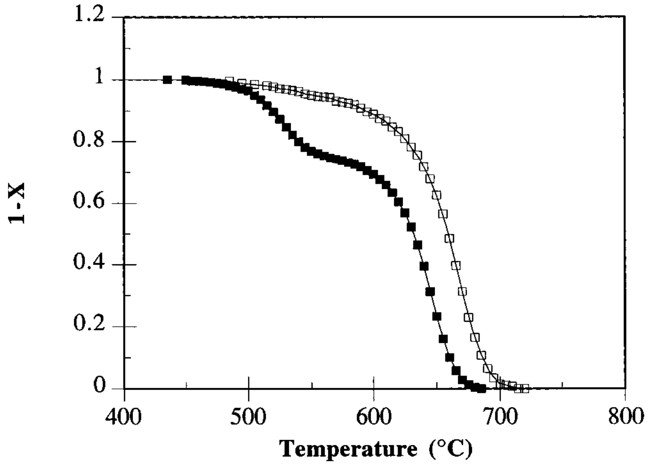

Figure 6. Nonisothermal reactivity profiles for (□) Z14US/CVD800 (calculated only for the carbon material) and (■) ZCVD800 at a heating rate of 5 °C/min.

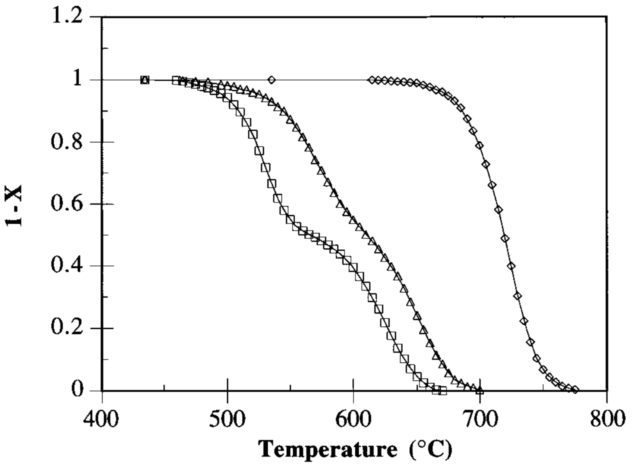

Figure 7. Nonisothermal reactivity profiles for (□) ZCVD850, (△) ZCVD850LT and (◇) ZCVD850HT carbons, at a heating rate of 5 °C/min.

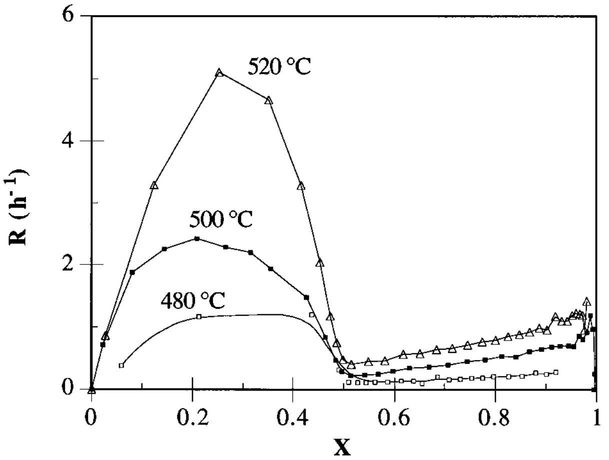

Figure 8. Isothermal reactivity profiles for ZCVD850 carbon at different temperatures.

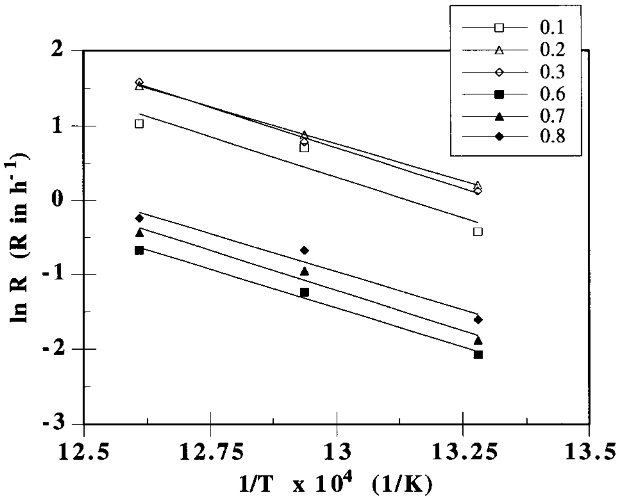

Figure 9. Arrhenius plots for ZCVD850 oxidation at different carbon conversion.

with similar structure but possessing different surface area.[40-42] Additional polarized light microscopy studies revealed that formation of only laminar structure in ZCVD800 and ZCVD850 carbons, which is in turn consistent with the finding that at relatively low temperatures, intermediate hydrocarbon concentration and large bed surface areas, laminar carbon can form on the substrate surface.[43,44]

Figure 9 shows the Arrhenius plots for ZCVD850 oxidation at different carbon burnoff levels. Higher carbon reactivity is again clearly seen below 50% burnoff (see also Figures 7 and 8). Nevertheless, parallel straight lines are observed, indicating similar apparent activation energy values in the entire range of carbon conversion. Table 2 summarizes the apparent activation energies at different conversion levels for oxidation of ZCVD850. The average value of 175 kJ/mol agrees reasonably well with the values reported in the literature for the carbon−oxygen reaction.[45-48] The large

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(41) Rodríguez-Mirasol, J.; Thrower, P. A.; Radovic, L. R. *Carbon* **1993**, *31*, 789.

(42) Rodríguez-Mirasol, J.; Thrower, P. A.; Radovic, L. R. *Carbon* **1992**, *33*, 545.

(43) Bokros, J. C. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1969; Vol. 5, pp 1−118.

(44) McAllister, P.; Hendricks, J. F.; Wolf, E. E. *Carbon* **1990**, *28*, 579.

(45) Lizzio, A. A.; Piotrowski, A.; Radovic, L. R. *Fuel* **1988**, 67, 1691.

(46) Miura, K.; Hashimoto, K.; Silveston, P. L. *Fuel* **1989**, *68*, 1461.

(47) Miura, K.; Nakamura, K.; Hashimoto, K. *Energy Fuels* **1991**, *5*, 47.

(48) Rodríguez-Mirasol, J.; Cordero, T.; Rodríguez, J. J. *Carbon* **1996**, *34*, 43.

Table 2. Apparent Activation Energies for ZCVD850 Oxidation at Different Conversion Levels

conversion level (%)	apparent activation energy (kJ/mol)	conversion level (%)	apparent activation energy (kJ/mol)
10	175	60	174
20	166	70	180
30	186	80	171

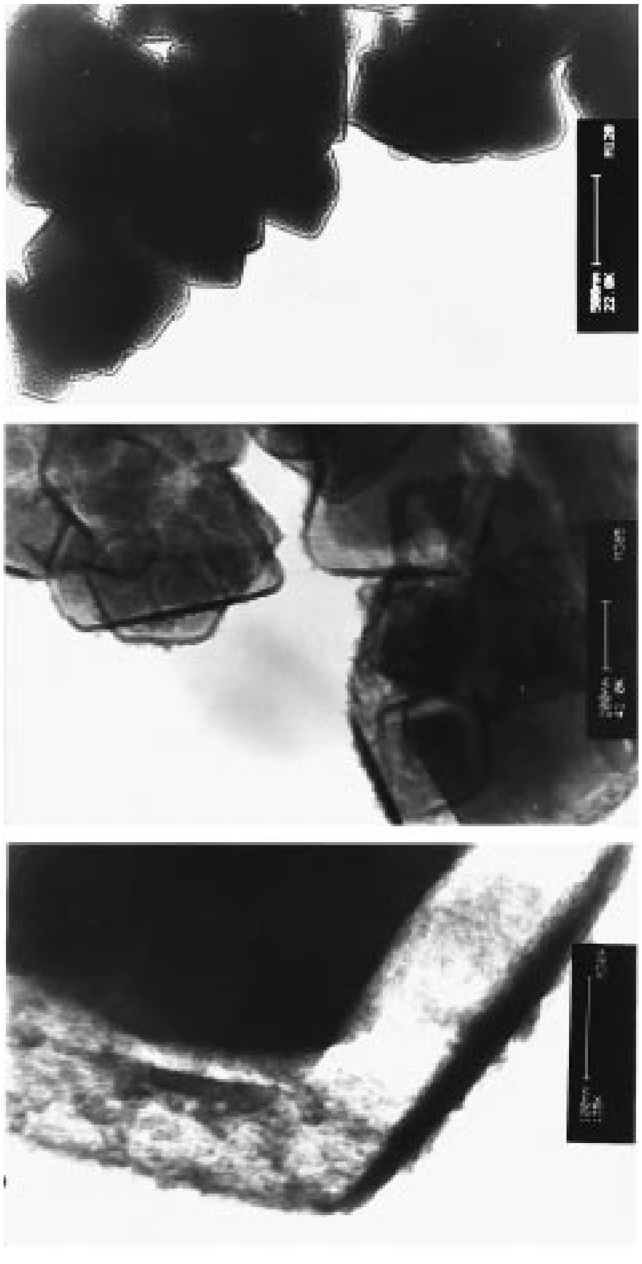

Figure 10. Transmission electron micrographs for Z14US (top), ZCVD850 (middle), and ZCVD850 at higher magnification (bottom).

differences in reactivity at low and high conversion levels may be attributed to different surface area (and thus, most probably, different reactive surface area[39]) available to the gas at low and high conversion levels.

3.3. Structural Features. Transmission electron micrographs of samples Z14US and ZCVD850 (Figure 10) reveal that the appearance of the ZCVD850 carbon is quite similar to that of the Z14US zeolite, supporting the results obtained by SEM (Figure 4). Two structures can be clearly differentiated in the skeleton of the pyrolytic carbon particles (Figure 10, middle and bottom panels): a dense and compact structure forming the external boundary and a less dense and less ordered structure constituting the interior. Qualitatively similar results were obtained for the ZCVD800 carbon. It appears convincing, therefore, that the interior less ordered structure provides a greater contribution of surface area to the carbon and that the more dense external structure represents only a small percentage of the total surface area of the carbon.

The zeolite infiltration process by pyrolytic carbon can thus be described as a catalytic cracking of the propylene on the internal surface of the zeolite particles, i.e., on the walls of the micropores. Once a first layer of pyrolytic carbon has covered the zeolite surface, the deposition continues on the surface of the pyrolytic carbon already deposited, which provides new active sites for carbon deposition.[49] Simultaneously with this catalyzed heterogeneous gas−solid reaction, homogeneous gas-phase pyrolysis reactions can occur too, as suggested by McAllister et al.,[44] producing pyrolytic carbon that grows both on the external surface of the zeolite and at pore mouths. As reaction proceeds, accumulation of gas-phase-nucleated pyrolytic carbon reduces pore accessibility and leads to slower diffusion of propylene into the pores. In the second deposition stage, when the entrance of the pores has been completely closed, deposition continues only on the external surface of the zeolite, increasing the thickness of the deposited layer. If the pyrolytic carbon is deposited uniformly on the surface of the micropores and does not fill them, once the zeolitic substrate has been removed, carbon with a channeled structure similar to that of the zeolite, but even with higher surface area, can be formed. On the other hand, the pyrolytic carbon deposited on the external surface of the zeolite gives rise to low surface area carbon with a dense and compact structure. Figure 11 shows a scheme of pyrolytic carbon infiltration of zeolite, followed by removal of zeolitic substrate. These two different structures would explain not only the high apparent surface areas found for ZCVD800 and ZCVD850, but also the two-stage O_2-reactivity profiles that these carbons exhibit.

Figure 12 shows the transmission electron micrographs of ZCVD800 and ZCVD850 samples and compares the structure of these two carbons. It is clearly observed that ZCVD800 carbon presents a thicker particle external boundary than ZCVD850, in agreement with the L_c values obtained for these carbons. This seems to indicate that more pyrolytic carbon has been deposited on the external surface of the zeolite when pyrolysis of propylene was carried out at 800 °C instead of 850 °C. On the other hand, the fact that ZCVD850 presents a higher apparent surface area than ZCVD800 (Table 1) suggests that at higher deposition temperatures more surface of the micropores of the zeolite is covered by pyrolytic carbon before the pore entrance is blocked. Higher pyrolysis temperatures result in a faster heterogeneous gas−solid reaction, with more pyrolytic carbon being deposited inside the fine microstructure of the zeolite. The blockage of the pore mouth seems to take place in a shorter time at lower temper-

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(49) Hoffman, W. P.; Vastola, F. J.; Walker, P. L., Jr. *Carbon* **1985**, *23*, 151.

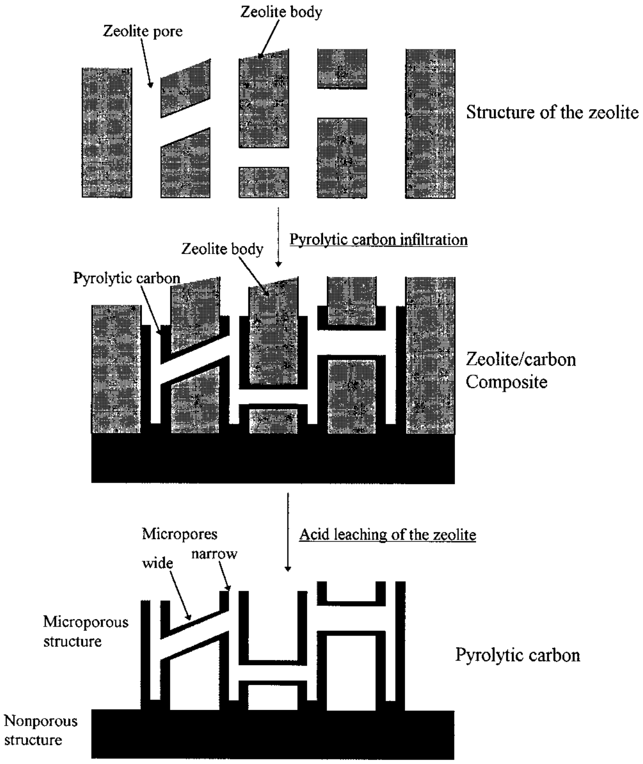

Figure 11. Scheme of pyrolytic carbon infiltration of zeolite, followed by removal of the zeolitic substrate.

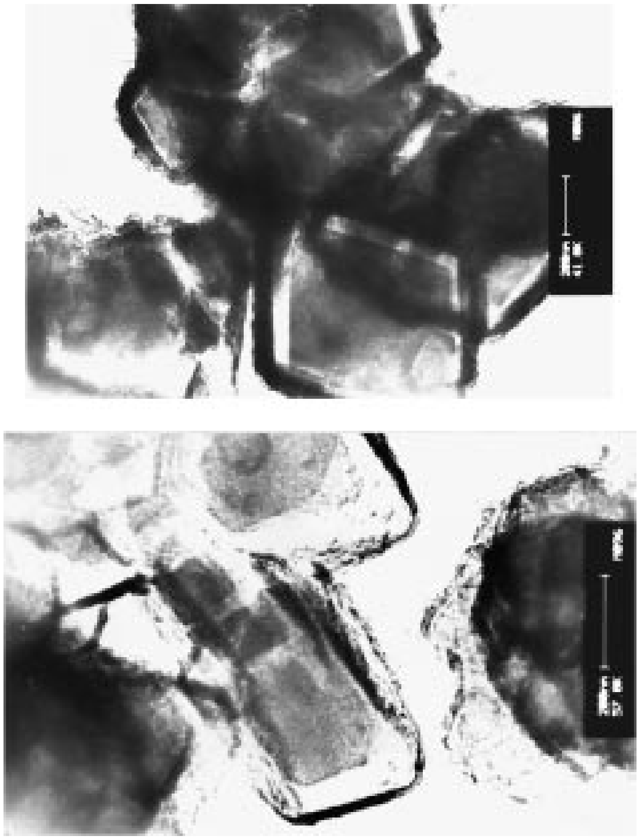

Figure 12. Transmission electron micrographs for ZCVD800 (top) and ZCVD850 (bottom).

ature and more pyrolytic carbon is deposited on the external surface of the zeolite at 800 °C than at 850 °C.

To support experimentally our hypothesis on the structure and oxidation behavior of the zeolite-derived carbons, ZCVD850 carbon was partially oxidized up to 50% burnoff. This carbon conversion corresponds to the inflection point in the reactivity profile for this carbon. A significant reduction of the surface area of CVD850 carbon, from 1380 to 122 m^2/g, after partial oxidation (50% burnoff) was observed. This result suggests that the more reactive structure of the CVD850 carbon, that containing the higher contribution to the total surface area of the carbon, has been consumed, having the other structure, more dense and compact, without being consumed. The transmission electron micrographs of CVD850 carbon oxidized at 50% burnoff (Figure 13) reveals that the interior of the particles has almost disappeared after the partial gasification of the carbon, whereas the structure forming the external boundary of the particles remains almost intact. It is important to remark that the morphology and particle size of the ZCVD850 carbon oxidized at 50% burnoff (Figure 14) are quite similar to those of the starting unoxidized ZCVD850 carbon.

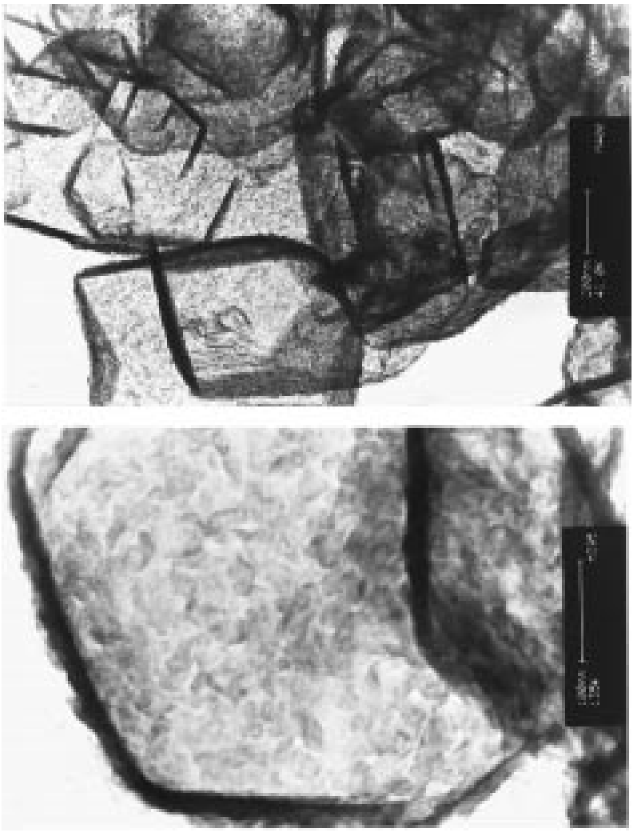

Figure 13. Transmission electron micrographs for ZCVD850 carbon oxidized at 50% burnoff at different magnification.

As already seen, ZCVD850 carbon presents a structure similar to that of the Z14US zeolite with rather high apparent surface area (almost twice the value of the zeolite, Table 1). This large surface area implies a high adsorption capacity. However, the shape of the ZCVD850 N_2 isotherm and the comparison of the surface area values obtained by N_2 and CO_2 adsorption for this carbon reveal a wide micropore size distribution, questioning the utility of these carbons as molecular sieve for separation of gases whose molecular size falls within a narrow range. In an attempt to improve the molecular sieving characteristics of this carbons, ZCVD850 was further heat-treated to higher tempera-

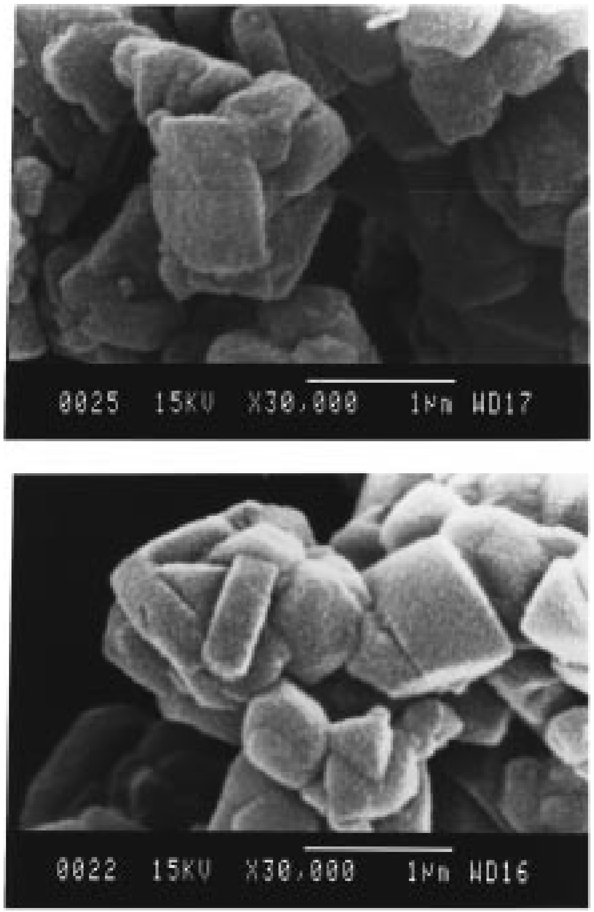

Figure 14. Scanning electron micrographs for ZCVD850 (top) and ZCVD850 oxidized at 50% burnoff (bottom).

tures. Heat treatment of ZCVD850 at 1000 °C (ZCVD850LT) reduced its surface area from 1380 to 935 m^2/g, increasing its oxidation resistance (Figure 7). ZCVD850LT still exhibits a two-stage reactivity profile, although now the difference in reactivity between the two structures present in the carbon is smaller. Heat treatment of ZCVD850 at 2900 °C (ZCVD850HT) reduced dramatically the BET surface area of the carbon to 39 m^2/g. This carbon exhibits a substantially lower O_2 reactivity than ZCVD850LT and does not exhibit a two-stage reactivity profile (Figure 7), suggesting that only one structure (the more dense and compact) is present in it. Table 1 reveals that heat treatment of ZCVD850 to higher temperatures not only decreases its BET surface area and N_2 micropore volume, but also reduces the DR CO_2 surface area and micropore volume. The $S_{(DR)}/S_{(BET)}$ ratio for ZCVD850LT shows a constant value of ~0.6, similar to that of ZCVD850, indicating that both narrow and wide microporosity have been reduced to the same extent with temperature and that useful molecular sieving properties were not developed by the thermal treatment.

The process of chemical vapor infiltration of zeolite from pyrolysis of propylene, followed by removal of the zeolitic substrate has demonstrated to produce high surface area pyrolytic carbons, which present a structure similar to that of the zeolite. The carbons thus obtained have developed a wide microporous and mesoporous structure, which confers on them a high adsorption capacity, but not useful molecular sieving properties for small adsorbate/reactant species. However, it is believed that preparation of carbon molecular sieves may be possible by means of the process described in this paper, if zeolite with an appropriate micropore size distribution and no mesoporous structure is used as substrate. Working conditions that allow pyrolytic carbon growth in the surface of the pores of the zeolite should be used. This could be acomplished by selecting a deposition temperature and a gas pressure as low as possible in practice in order to favor low rate of pyrolytic carbon deposition and low hindrance by backdiffusion of the gaseous reaction products.[50] Work is in progress to further investigate this issue using other zeolite types, temperatures, propylene partial pressures, and total pressure.

4. Summary and Conclusions

Microporous carbons with high surface area have been prepared by pyrolytic carbon infiltration of a Y zeolite from pyrolysis of propylene, followed by removal of the zeolite matrix. The pyrolytic carbon yield and the apparent surface area of the carbon increased with pyrolysis temperature. The carbons obtained present a structure very similar to that of the zeolite. Their reactivity profiles exhibit a two-stage behavior, with the inflection point between the two stages occurring at different conversion level depending on the deposition temperature. Such oxidation behavior suggests that the carbons consist of two different structures with different reactivities, the oxidation of the more reactive carbon taking place first and the remaining, more ordered carbon being consumed in the second stage.

The process of pyrolytic carbon infiltration within the microporous zeolite template produces carbons with a wide microporosity, well-developed mesoporosity, and high adsorption capacity. These carbons do not exhibit molecular sieving properties for small adsorbate/reactant species. It remains to be seen whether the pore-size distribution of the resulting carbon can be tailored by judicius selection of the template and carbon deposition conditions.

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(50) Kotlensky, W. V. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1973; Vol. 9, pp 173–262.