

STUDY OF NANOCOMPOSITES OBTAINED BY CARBONIZATION OF DIFFERENT ORGANIC PRECURSORS WITHIN TAENIOLITE MATRICES

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Abstract—The lithium form of taeniolite served as the molecular template for carbon nanocomposites. It was intercalated with hydroxyaluminum and hydroxyaluminum-zirconium cations. Aliquots of the inorganic matrices were saturated by furfuryl alcohol followed by its interlayer polymerization. The structures were heated at 973 K in nitrogen to carbonize the polymeric precursor. Additional materials were mixed with polypropylene glycol which was then carbonized within the mineral layers. The surface properties of the nanocomposites were studied by X-ray diffraction (XRD), DTA, SEM and sorption experiments (sorption of nitrogen). The results showed that structural properties of the derived materials depend on the inorganic matrix and organic precursor. The carbon-taeniolite nanocomposites derived from polyfurfuryl alcohol as a precursor were characterized by high carbon content and a high percentage of its surface area in micropores. A broad spectrum of surface characteristics of the final products were found, depending on the history of the sample.

Key Words—Furfuryl Alcohol, Polypropylene Glycol, Taeniolite Intercalation, Taeniolite-carbon Nanocomposites.

INTRODUCTION

The need for microporous materials with unique separation and storage properties has resulted in a search for new methods of modification of sorbents or creation of new sources of such materials. One method that leads to production of porous materials (nanocomposites or carbons) has been developed recently using intracrystalline spaces of layered minerals for in-situ carbonization (Bandosz et al. 1992; Bandosz et al. 1993; Bandosz et al. 1994a, 1994b). The idea is based on the template carbonization method (Oya et al. 1986; Oya et al. 1990; Seron et al. 1993; Sonobe et al. 1990; Kyotani et al. 1994; Bandosz et al. 1995). In this method, the properties of mineral matrices, as well as the nature of the organic precursor, are factors that determine the properties of the final products. Using different inorganic matrices with different layer composition, different cation exchange capacity and different interlayer space can influence the microstructure of the materials. Water, which is a natural component of minerals, acts as a pore former during in-situ carbonization/activation of organic material/carbonaceous deposit. In all of these cases, the limited thickness of carbon layers incorporated into the structures of the template prevents the creation of pores larger than the intercrystalline size. These properties afford the opportunity of creating materials by the template carbonization method (nanocomposites and carbons) for sep-

aration/storage systems where the size of pores is a critical factor.

This paper is a continuation of an ongoing study of the surface properties of materials obtained within mineral matrices. It was shown elsewhere, carbonization of polyfurfuryl alcohol within the structure of intercalated montmorillonites leads to the creation of microporous carbon and nanocomposites that possess sieving properties (Bandosz et al. 1994a, 1994b). The objective of this present study is to use a synthetic mineral with a layered framework, for example, taeniolite, as a molecular container to obtain microporous materials. Taeniolite is characterized by a different chemical composition than smectite because it lacks hydroxyls within its structure. Thus, the influence of the inorganic matrix and the use of different organic precursors on the final properties of the sorbent obtained can be studied.

EXPERIMENTAL

Materials

A set of nanocomposites and carbon samples were prepared using the synthetic mineral, taeniolite, provided by Topy Ind. Co. (Japan). The lithium form of this mineral (TL-0) has the following chemical formula: $\text{Li}(\text{Mg}_2\text{Li})(\text{Si}_4)\text{O}_{10}\text{F}_2 \cdot n\text{H}_2\text{O}$. The sample obtained from the manufacturer was intercalated with hydroxyaluminum cations from a solution of Chlorhydrol® (TL-1) and Rezal® (TL-2). Samples (TL-0, TL-1 and TL-2) were saturated with an 80% solution of furfuryl alcohol (FA) in benzene for 3 d. Polymerization was carried out by heating the samples under an N_2 flow at 343 K for 24 h and then at 423 K for 6 h. The

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Table 1. X-ray diffraction results and carbon content.

Sample	d_{001} [Å]	Spacing [Å]	Carbon content [%]
TL-0	12.1	2.1	—
TL-1	18.2	8.2	—
TL-2	18.8	8.8	—
TLC-0	11.8	1.8	15
TLCS-0	—	—	19
TLC-1	16.7	6.7	46
TLCS-1	16.6	6.6	51
TLC-2	16.5	6.5	30
TLCS-2	16.0	6.0	35
TLPC-0	—	—	20
LPC-0	—	—	31
TLPC-2	—	—	10
LPC-2	—	—	72

samples, with incorporated polymer in the interlayer space, were heated at 973 K for 3 h under N_2 flow to carbonize the organic compound. The nanocomposites were designated as TLC-0, TLC-1 and TLC-2. To assess changes in the structure with partially removed inorganic matrix, some of the samples were treated with concentrated hydrochloric acid. It was assumed that the octahedral layers were dissolved during this treatment. The samples obtained in this way were designated: TLCS-0, TLCS-1 and TLCS-2.

Another set of samples was prepared by saturation of TL-0 and TL-2 with a 20% solution of polypropylene glycol in ethanol. Suspensions were stirred for 2 d, filtered and then carbonized at 873 K under a nitrogen flow for 2 h. The nanocomposites were designated as: TLPC-0 and TLPC-2. After partial removal of inorganic matrices with concentrated HCl and HF the samples were designated as: LPC-0 and LPC-2.

Methods

X-RAY DIFFRACTION ANALYSIS. All taeniolite and nanocomposite mounts were rehydrated at humidity below 50%. X-ray diffractograms (XRD) were obtained with a Philips PW 1729 diffractometer using filtered $CuK\alpha$ radiation.

THERMAL ANALYSIS. Thermal analysis was carried out using a Perkin Elmer Data 1700 Differential Thermal Analyzer. The instrument settings were: heating rate 10°C/min and nitrogen atmosphere with 10 ml/min flow rate.

SCANNING ELECTRON MICROSCOPY. Morphological observations were made with a scanning electron microscope (SEM) JEOL JSM-35G, operated at 24 kV after samples were coated in a Hummer II apparatus using Au-Pd electrodes.

CARBON CONTENT. The carbon content was estimated by burning the organic deposit in the oven at 1273K and measuring the weight loss.

SORPTION EXPERIMENTS. Nitrogen isotherms were mea-

sured by a GEMINI III 2375 Surface Area Analyzer (Micromeritics) at 77K. Before the experiment, the samples were heated for 10 h at 473 K and then out-gassed at this temperature under a vacuum of 10^{-2} mmHg. The isotherms were used to calculate the specific surface area, micropore volume and micropore area (t-method) (Lippens et al. 1964) and mesopore size distributions (Barrett-Joyner-Halenda method) (Barrett et al. 1951).

RESULTS AND DISCUSSION

The results of the (XRD) study show significant increase in d_{001} of taeniolite after its intercalation with inorganic polycations (Table 1). Introduction of bulky polycations into the structure of the mineral resulted in the increase of its interlayer distances similar to the intercalated montmorillonites (Occelli and Tindwa 1983; Pinnavaia 1983; Zyla and Bandosz 1987; Bandosz et al. 1992; Baksh and Yang 1992; Gil and Montes 1994).

It has been previously reported (Bandosz et al. 1994a, 1994b), that not only the size of the interlayer spacing in the inorganic host, but also the chemical composition and thermal behavior of the host-guest system can influence the mechanism of in-situ carbonization. These factors may determine the adsorption properties of the resulting carbon-mineral nanocomposites and/or template carbons. To study the influence of the above factors, we have chosen two different polycations and two different organic precursors to cover a wider variability of conditions that can influence the final adsorption properties of the materials. One of the most important factors in the template carbonization method is the thermal stability of the host-guest precursor system. It is important to note that nanocomposites prepared in this study are characterized by different thermal stabilities. The intercalated taeniolites saturated with polyfurfuryl alcohol withstood heat treatment at 973 K without the collapse of their layered framework and well defined d_{001} peaks were observed (Figure 1). Their interlayer spacing decreased from 8.2–8.8 Å to about 6.5 Å after heat treatment, which is probably limited by the thickness of the carbon deposit present between the layers. Similar values were also observed for smectites used as the mineral host for template carbonization (Bandosz et al. 1993; Bandosz et al. 1994a, 1994b). On the other hand, taeniolite saturated with polypropylene glycol has lower thermal stability, and does not show a crystalline structure after heat treatment.

Thermal processes that take place within the taeniolite matrices were studied by differential thermal analyses (DTA). Figure 2 shows that the initial lithium form of the mineral is thermally very stable (Oya et al. 1990). We only observed the release of physically adsorbed water at temperatures below 500 K and then a nearly featureless thermogram exists in the

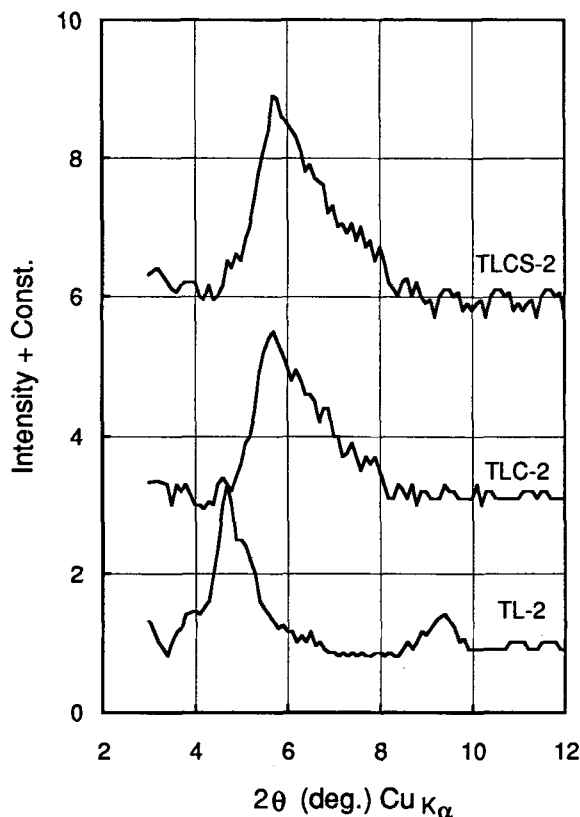


Figure 1. X-ray diffraction curves for nanocomposites obtained on the basis of polyfurfuryl alcohol as a carbon precursor and TL-2 matrix.

high temperature range. The DTA spectrum for taeniolite suggests a higher thermal stability than found in the related smectites, probably due to structural fluorine anions replacing the less stable OH groups. After introduction of hydroxyaluminum and hydroxyaluminum-zirconium pillars into the taeniolite framework, no peaks were observed at temperatures below 300 K. In the high temperature range, only a broad endothermic peak appeared between 600 and 1100 K for both intercalated samples (TL-1 and TL-2). This endotherm is due to dehydroxylation of pillars. The temperature range of its appearance agreed with results obtained for smectite intercalated with hydroxyaluminum and hydroxyaluminum-zirconium cations where the dehydroxylation of pillars was observed (Bandosz et al. 1994a, 1994b, 1995).

DTA curves for taeniolite matrices after saturation with furfuryl alcohol provide some information about the complex mechanism of the interlayer polymerization, polycondensation and carbonization. On the thermograms of the TL-1(FA) and TL-2(FA) samples (Figure 2) we observed an endothermic peak in the range between 500 and 900 K, where the above mentioned changes of the organic precursor can occur. The carbonization temperature, chosen to be 973 K, is in the

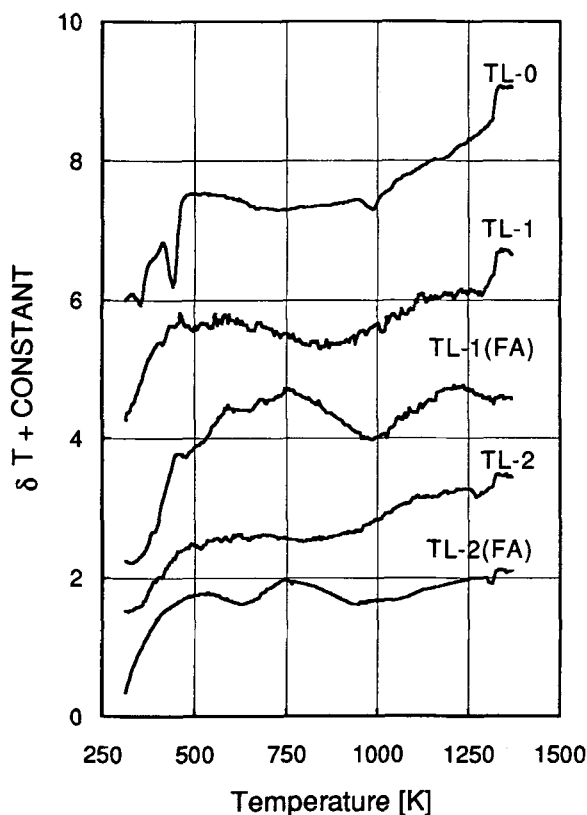


Figure 2. DTA curves for inorganic matrices and matrices saturated with furfuryl alcohol.

temperature range where the simultaneous dehydroxylation of the intercalated polycations is also occurring. This coincidence of dehydroxylation and carbonization mechanisms during template carbonization can be significant in the process of pore formation (Bandosz et al. 1994a, 1994b; Kyotani et al. 1994).

In the case of samples with incorporated polypropylene glycol (PPG), the DTA curves are very similar to each other. In the low temperature range when the release of water from the structure of polypropylene glycol (PPG) can occur (Figure 3), we observed an endotherm. The second broad endotherm, centered at about 900 K, is related to the complex carbonization mechanism. The curves differ in the temperature range higher than 900 K due to the release of water introduced to the structure of the matrix in the form of hydroxy-aluminum-zirconium pillars (TLP-2). This phenomenon has already been observed for TL-1, TL-2, TL-1(FA) and TL-2(FA) samples (Figure 2).

Analysis of nitrogen adsorption isotherms provides basic information about the pore structure of all samples. As an example, isotherms of intercalated taeniolite/carbon nanocomposites derived from polyfurfuryl alcohol are shown in Figure 4. The observed typical Langmuir shape (monolayer adsorption) indi-

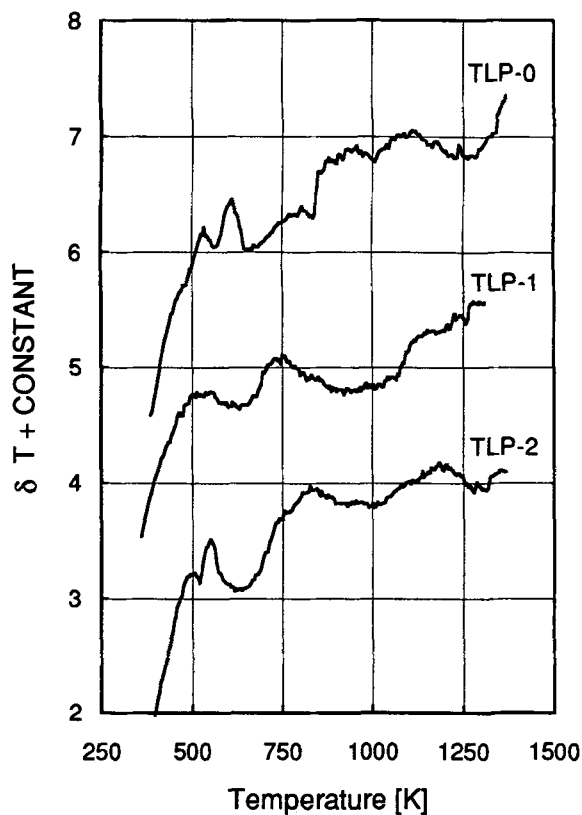


Figure 3. DTA curves for samples saturated with polypropylene glycol.

icates that the pores in these materials are mainly in the micropore range. The calculated adsorption parameters such as specific surface area, micropore volume, micropore area and total sorption capacity, are collected in Table 2. Materials with the highest surface areas are obtained from intercalated taeniolite saturated with furfuryl alcohol. The surface areas for this set of samples decrease in the following order: TLC-1,

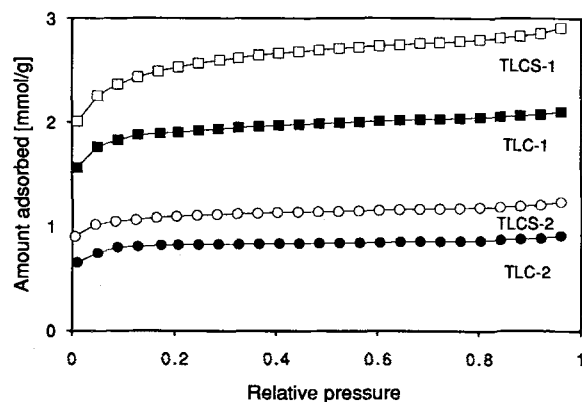


Figure 4. Nitrogen adsorption isotherms on nanocomposites obtained from intercalated taeniolite matrices.

Table 2. Parameters calculated from nitrogen adsorption isotherms.

Sample	S_{sp} [m^2/g]	V_{mic} [cm^3/g]	V_{total} [cm^3/g]	S_{mic} [%]
TLC-0	2	—	—	—
TLCS-0	26	—	0.074	—
TLC-1	193	0.054	0.073	88
TLCS-1	263	0.061	0.101	66
TLC-2	83	0.025	0.031	86
TLCS-2	120	0.034	0.043	77
LPC-0	133	0.014	0.282	26
LPC-2	158	0.016	0.170	21

TLC-2, TLC-0. The dependence obtained was fully expected and agrees with the decreasing water content in the samples studied. In the case of TLC-1 and TLC-2 nanocomposites the additional water, as a pore former, was introduced during the process of intercalation to form pillars. In these cases, similar to that of smectites (Bandosz et al. 1994a, 1994b), samples obtained from the matrix intercalated with Chlorhydrol have higher surface area because larger pores could be created and more water was released. In the case of samples derived from lithium taeniolite as a host (TLC-0), a nonporous surface of nanocomposite was obtained due to the lack of any pore former.

Conversely, samples obtained by carbonization of PPG within the taeniolite interlayer space, with inorganic pillars or without, have similar sorption characteristics (Table 2). The surface areas of the TLPC series are very low. The nitrogen isotherms were almost undetectable similar to the TLC-0 sample. The partial removal of the inorganic matrix results in an increase in the surface area. However, we attribute this increase to the development of meso- and macroporosity since the micropores occupy only approximately 20% of the total surface area of these materials.

The mesopore size distributions collected in Figures 5–7 show significant differences in the pore structure of the samples. In the case of nanocomposites where

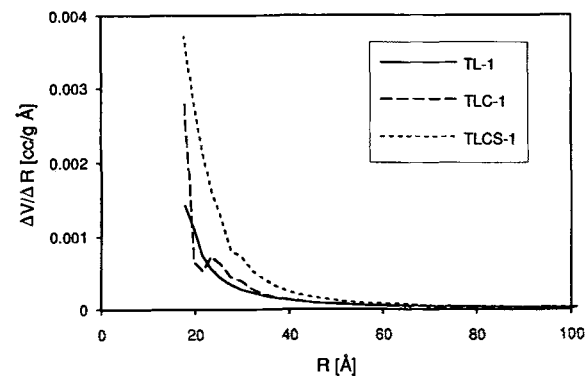


Figure 5. Mesopore size distribution on nanocomposites obtained on the basis of TL-1 sample and polyfurfuryl alcohol.

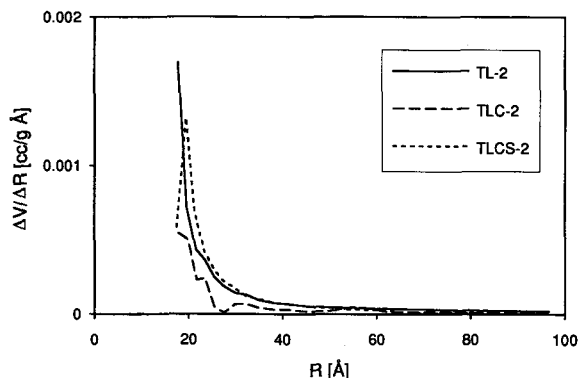


Figure 6. Mesopore size distribution on nanocomposites obtained on the basis of TL-2 sample and polyfurfuryl alcohol.

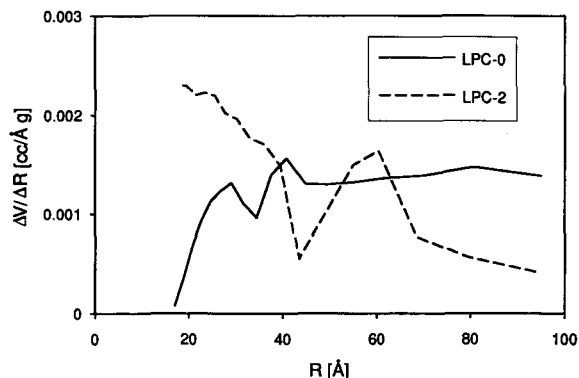


Figure 7. Mesopore size distribution on nanocomposite carbons derived from taeniolite matrices and polypropylene glycol.

polyfurfuryl alcohol was a carbon precursor, almost all pores are smaller than 30 Å and the distributions are relatively homogenous. The incorporation of carbon and acid treatment resulted in a higher contribution of small pores to mesopores. Nanocomposites with PPG as a carbon precursor have a high content of larger mesopores and almost no microporosity (LPC-0).

The differences in the adsorption behavior of nanocomposites and carbons derived from these materials can be explained by different mechanisms and structural changes that take place during subsequent intercalation, saturation and carbonization processes. In order to obtain a more comprehensive view of the various structural and surface features of taeniolite derived nanocomposites and their fracture surfaces, we analyzed their surface topography seen by scanning electron microscopy. Figure 8a is the SEM micrograph of the initial lithium form of taeniolite (TL-0). This sample is characterized by a smooth and apparently nonporous surface constructed from tightly packed thin silicate layers. Intercalation with polycation followed by saturation with furfuryl alcohol and its interlayer polymerization and heat treatment in a nitrogen atmosphere caused significant changes in surface characteristics as seen in SEM images. For example, in the case of TLC-1 and TLCS-1 samples (Figures 8b and 8c) the layered framework of the inorganic precursor is preserved. However, the silicate layers became more separated from each other forming a more open structure. These changes resulted in increased porosity (Table 2). It is interesting to note, that after the treatment of the taeniolite/furfuryl alcohol derived carbon nanocomposites with the hydrochloric acid solution, the highly organized layered structure remained in its original form. The materials seemed to be very uniform. Thus, all carbon (~50% of sample weight) is probably incorporated within the interlayer space. Based on the above results, we assume that slit-shape

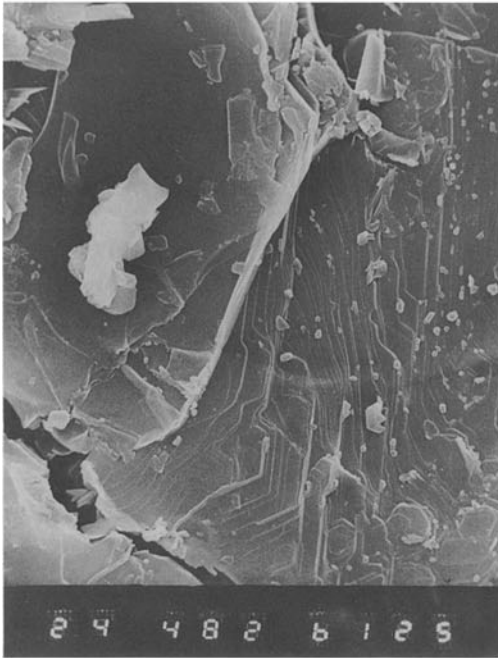
pores, seen in the range of large pores, are also present in the micropore range.

A totally different surface texture characterizes samples derived from taeniolite matrices using polypropylene glycol as an organic precursor for template carbonization. Figure 8d shows the SEM image of the LPC-2 nanocomposite, where we can clearly distinguish two separate phases. The structure of the taeniolite matrix is seen separately in the form of stacked flakes, while the small abundant dispersed grains represent the carbonized polypropylene glycol. We do not observe the organized layered structure over any large extent of the surface. The overall character of this physical mixture is amorphous.

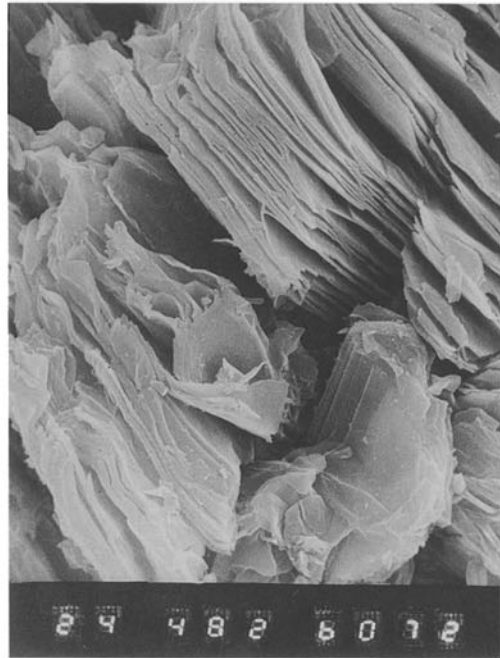
The differences in the SEM images are consistent with the different sorption behavior of our materials. In the case of furfuryl alcohol as a carbon precursor, the material obtained is very uniform with a well defined porous structure and crystalline nature. These results are also consistent with the results obtained from XRD (Figure 1) where for the nanocomposite the crystalline structure was observed even after HCl treatment. But, the incorporation of PPG inside the taeniolite layers leads to the production of an amorphous material (lack of the d_{001} peak in the diffraction pattern) with two separated phases, organic and inorganic. In this case, sorption can occur only between particles, such as meso- and macropores, and the increase in sorption capacity after partial removal of the matrix is caused by an increase in the content of nonporous amorphous carbon material.

The analysis of the carbon content (Table 1) provides us with additional information about the nature of the nanocomposites. We observed an increase in the presence of a carbonaceous deposit after acid treatment due to partial removal of inorganic matrices. The most significant changes occur in the case of the LPC-2 sample where the carbon content reaches 70%. This

A



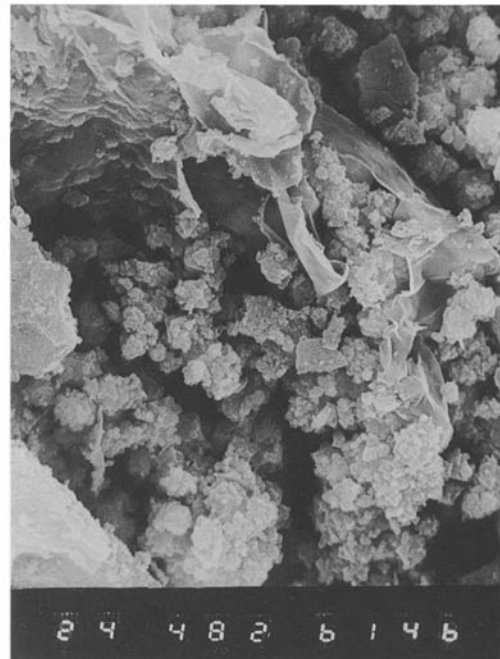
B



C



D



— 5 μm

Figure 8. SEM images of a) TL-0, b) TLC-1, c) TLCS-1 and d) LPC-2.

is also seen from the SEM micrograph (Figure 8d) where the amount of carbon significantly prevails over the amount of matrix. The dramatic change in the carbon content is reflected in the dramatic increase of sorption capacity due to the development of meso- and macroporosity. Also, the nanocomposites obtained from polyfurfuryl alcohol as a carbon precursor increased the sorption properties as the content of carbonaceous deposits increased in the order TLC-1, TLC-2, TLC-0. This factor was also related to the size of pillars and matrix water content. The small amount of carbon in the TLC-0 sample is due to the nature of the inorganic matrix in which the interlayer distance was not intentionally extended by introduction of pillaring cations.

CONCLUSION

Synthesis of materials within matrices of nanometer dimensions critically depend on the properties of the matrix and the nature of the organic precursor. Both have a significant influence on the structural and sorption properties of the derived materials. Even when the same organic precursor is used, small differences in the matrices are crucial for the micropore structure development of sorbents. We demonstrate that by in situ carbonization of organic compounds one can obtain nanocomposites with a developed pore structure and a high content of its surface area in micropores (about 80% of the total surface area). In addition, the final properties of nanocomposites can also be modified by aggressive chemical treatment as was shown for nanocomposites obtained from intercalated taeniolite/polyfurfuryl alcohol where additional pore space in the organic-inorganic material was created by the partial removal of the matrix by acid.

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