

THERMAL BEHAVIOR OF MULTIWALL CARBON NANOTUBE/ZEOLITE NANOCOMPOSITES

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In this study we report the synthesis and thermal characterization of multiwall carbon nanotubes containing zeolite based nanocomposites. Three different zeolites (LTA, FAU and MFI) were used in this study and it was observed that the morphologies of the synthesized nanocomposites were significantly different. For FAU zeolite nanocrystals with a few nm in diameter were nucleated on the nanotubes covering their surface, however, for LTA and MFI zeolites bulky crystals with nanotubes crossing them were observed by transmission electron microscopy. One of the most important results of our study was the generation of secondary mesoporosity in the zeolites after removing the carbon nanotubes.

Keywords: nanocomposites, secondary mesoporosity, TEM, zeolites

Introduction

The carbon – silicate nanocomposites show increasing interest in the laboratories working on the nanosized materials. The reason of the exploration of research is the potential production of novel matter with peculiar behavior. There are several papers published on the synthesis of various carbon nanotube/polymer [1] and carbon/silicate nanocomposites [2]. By our knowledge zeolites as silicate components were used only in some cases [3]. There are only two papers in the literature dealing with the synthesis and characterization of zeolite/carbon nanotube composites [4]. The short communication from the Topsoe laboratory describes the synthesis and the characterization of MFI – Multiwall Carbon Nanotube (MWNT) composites from the catalytic point of view, i.e. the mesopores in the zeolite crystal enhance the rate of diffusion of molecules into the center of the crystals assuring more effective catalytic actions. The work from Jacobsen's group reports a novel synthesis to prepare zeolite crystal coating on carbon fibers or nanotubes [5].

We performed experiments to synthesize zeolites in presence of carbon nanotube in the reactive gel. Such syntheses of three zeolite types – LTA [6], FAU [7] and MFI [6] – were investigated. After studying the hydrophobic/hydrophilic properties of carbon nanotubes [8] and their modification by heat treatment at high temperatures [9], we were able to optimize the synthesis method from the carbon nanotube side. We found that MWNTs should be heat treated at 873 K in order to have clean outer surface. The composites were prepared with three different

zeolite/MWNT ratios. The products were characterized by several physical and chemical methods from which the thermal behavior of the composite will be discussed in this paper.

Experimental

The multiwall carbon nanotubes were prepared in our laboratory using CCVD synthesis technique [10]. The purified nanotubes [11] were heated at 873 K for 3 h in nitrogen atmosphere, where the adsorbed water, the loosely bond water, the weakly bond OH groups and the thermally instable functional groups were released from the surface. MWNT samples treated in this way were applied in the zeolite synthesis.

MWNT/LTA composites were synthesized using the recipe published by Thompson and Huber [12]. The composition of the synthesis gel was as follows: 1 SiO₂:1.643 Na₂O:0.519 Al₂O₃:66.5 H₂O. For synthesis of MWNT/FAU composite the synthesis description of the zeolite faujasite published by Kühn [13] was applied. The gel compositions were: 1 SiO₂:2.5 Na₂O:0.45 Al₂O₃:0.75 K₂O:55.5 H₂O. Prior to the synthesis of the MWNT/LTA and MWNT/FAU composites, the MWNT sample was mixed with the sodium silicate solution. We used 1:5, 1:10 and 1:50 MWNT/zeolite ratios. The pure zeolite, as reference material, was also synthesized. The synthesis recipe for preparation of MFI type zeolite was published by Barrer [14]. The gel composition was: 1 SiO₂:0.01 Al₂O₃:0.64 Na₂O:0.1 TPABr:0.18 H₂SO₄:14.0 H₂O. In the synthesis gel the MWNT/zeolite ratios were 1:5, 1:10 and 1:50. In this case besides the

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MWNTs, the original template tetrapropylammonium bromide (TPABr) was also present in the as synthesized sample. This fact might influence the thermal behavior of the composite.

XRD profiles were recorded and compared after each modification step, i.e. the pure zeolites, the zeolites containing MWNTs in different concentration and the samples after burning the carbon nanotube off were monitored. XRD patterns were registered using a Russian made Dron 3 diffractometer working under computer control. Each diffractogram was taken in the 4–50 2θ angle range covering both the characteristic reflections of zeolites and also the graphitic carbon structures (including carbon nanotubes).

TEM images were taken using a Phillips CM10 type electron microscope. The preparation of the grids was as follows. The prepared samples were dispersed in ethanol using sonication. A drop of this suspension was put on the grid and after drying the samples were analyzed.

Thermal behavior of the composites was investigated by taking the TG-DTG-DTA (TG: thermogravimetry, DTG: differential thermogravimetry, DTA: differential thermal analysis) profiles using a Hungarian made Derivatograph-Q instrument. 100 mg of sample was weight into the ceramic crucible and the temperature was increased from room to 1273 K using 5 K min^{-1} heating rate in air.

Results and discussion

In Fig. 1 the TEM images of the pure zeolites and the MWNTs used in the synthesis of MWNT/LTA, MWNT/FAU and MWNT/MFI composites are seen. The average outer diameter of MWNTs was around 10 nm as determined from TEM images. TEM images

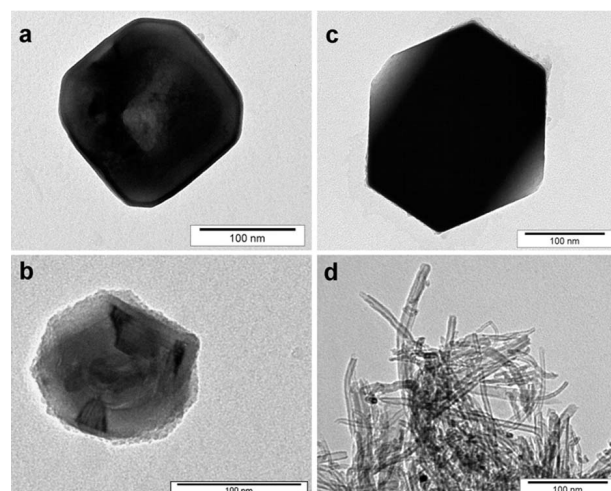


Fig. 1 TEM images of pure zeolites; a – LTA, b – FAU, c – MFI and d – multiwall carbon nanotubes

of the zeolites show that LTA and FAU have cubic, while MFI has monocline symmetry. The average particle sizes of the zeolites are: ~ 210 nm, ~ 90 nm, and ~ 150 nm for LTA, FAU and MFI samples, respectively.

Figure 2 shows TEM images of the composite samples. There are similarities and differences between them depending on the type of the zeolite. The MWNT/LTA sample contains two kinds of composite particles. In one of them the tubes are surrounded by the crystals since the tubes are much longer than the zeolite crystal (see part a of the Fig.). The second characteristic particles are seen in the b part of the Fig. 2. Here the short tubes are surrounded by very small zeolite crystal particles. There is no bulk zeolite crystal grown around the carbon nanotube.

In Fig. 2c and d the TEM images of MWNT/FAU are shown. Here the nanotubes connect the zeolite crystals. The tubes get into the crystal that can be clearly seen. In part d of the Fig. the image shows that the nanotubes act as crystal seeds, the crystal just starting to grow on them.

Figure 2e and f show two images taken on the MWNT/MFI composite. In this composite the MWNTs generally go through the crystals, i.e. the zeolite crystals were nucleated and grown on the surface of the nanotubes.

As far as the mechanical stability of the composites is concerned, we observed no separation of the components of composites. The strongest confirmation of this finding is the preparation of TEM grids,

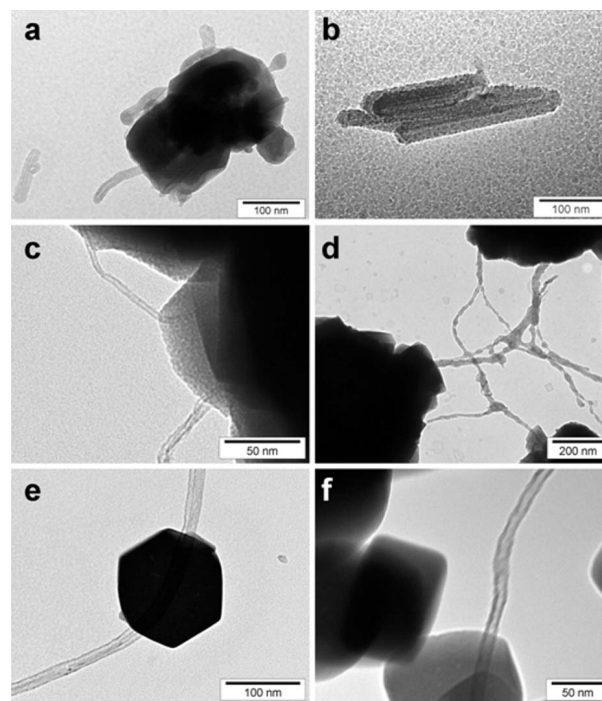


Fig. 2 TEM images of a,b – MWNT/LTA, c,d – MWNT/FAU and e,f – MWNT/MFI composites

since we applied sonication for the preparation of perfectly dispersed suspensions. Even after applying 1 h high power ultrasound treatment the nanotube/zeolite composites were not separated into their components.

The XRD profiles proved that each sample preserved the crystallinity, since the profiles were identical to that published in Zeolite Atlas [15].

TG-DTG-DTA measurements were performed to study the thermal behavior of composites, e.g. the temperature of dehydration for the composites compared to the pure zeolite components.

In Fig. 3 TG curves of the pure components are depicted. For LTA and FAU zeolites (curve ■ and ●, respectively) only one mass loss step can be observed due to the removal of adsorbed and loosely bond water. The temperature of maximal mass decrease was somewhat lower for LTA than FAU. However, the mass loss due to the dehydration was a bit higher for LTA than for FAU. This can be explained by the higher hydrophilic character of LTA which is due to its lower Si/Al ratio, i.e. its higher aluminum content. It is noteworthy that for LTA zeolite a second mass loss step appeared in the range of 500–700 K, which can be attributed to dehydroxylation of the –OH groups which might be generated in the washing step at the synthesis.

Completely different feature was found for MFI sample (Fig. 3 curve ▲). It is worth mentioning that this material was synthesized in presence of organic template that incorporated into the channels of the zeolite. The first step centered at around 390 K is due to dehydration (i.e. desorption of the adsorbed water); where about 3 w% of the mass was released. Since the MFI zeolite has much higher Si/Al ratio (1:0.005 Si/Al ratio means 200 Si atoms for one Al), therefore much less aluminum is in the unit cell, consequently it is much less hydrophilic than the zeolites discussed above.

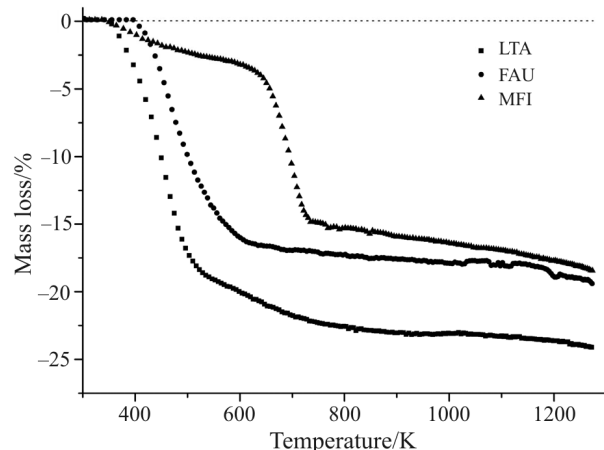


Fig. 3 TG curves of pure zeolite components

The second step is due to removal of the template molecules. This second very exothermic mass loss step appeared at around 690 K is due to burning off the organic matter in the sample, as well known in the literature [16]. The height of this mass loss is about 14 w%. This is the amount of organic compound built in into the zeolite channels. This value is in excellent correlation with that of calculated from the gel composition.

The TG curve of MWNT measured in air shows one mass loss (not shown) which can be attributed to the burning of the nanotubes themselves. The temperature of this burning is higher than that of the template removal; therefore, we had some chance to separate the two processes.

In Fig. 4 the TG curves for MWNT/LTA composites are shown. Compared to the TG profile of NaA-LTA, the most obvious change in the TG curves of composites is the appearance of the second mass loss steps around 780 K. The height of these highly exothermic steps is regarded as the experimental measure of the MWNT content of samples. Thus, the higher the MWNT/LTA ratio calculated from the gel composition,

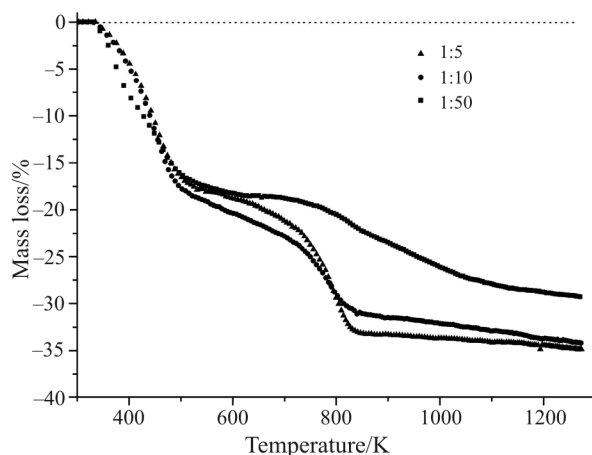


Fig. 4 TG curves of MWNT/LTA composites

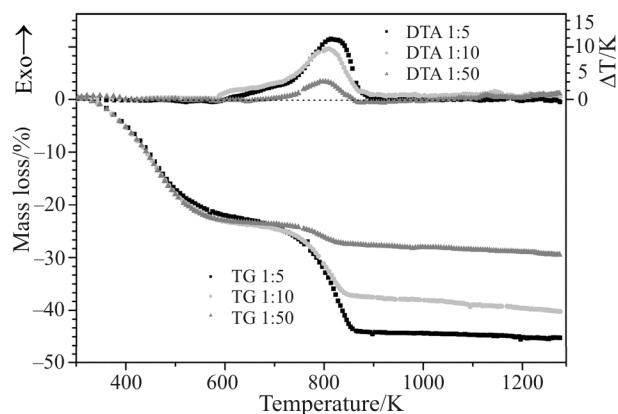


Fig. 5 TG and DTA curves of MWNT/FAU composites

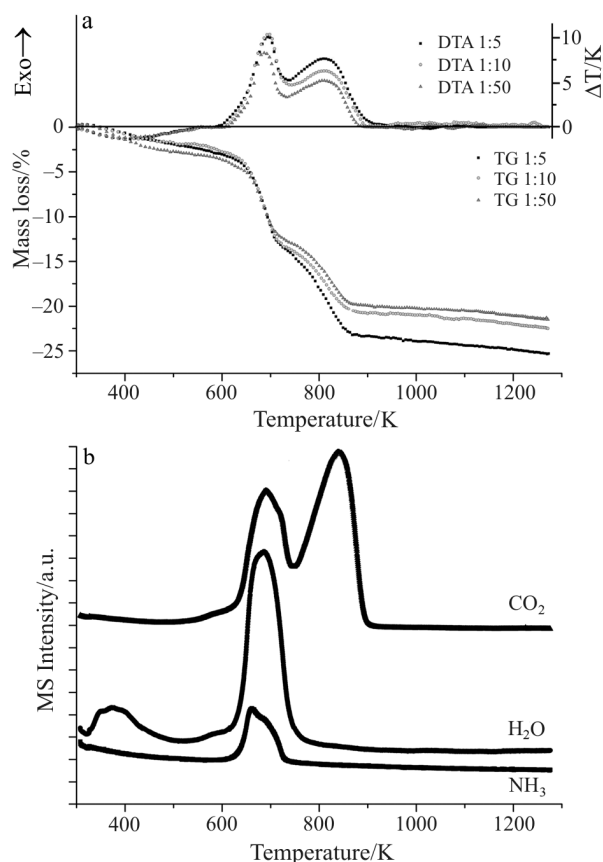


Fig. 6 a – TG and DTA curves of MWNT/MFI composites.
b – MS signal of the liberated gaseous products during the TG measurement of 1:10 MWNT/MFI composite

the higher is the mass lost in the second step. It was found that the temperature of the second mass loss shifts to higher values with decreasing the nanotube content of the composite. It is noteworthy, that we have some discrepancy between the starting compositions and the mass losses measured. It seems that some nanotubes are not covered with zeolite crystals and these nanotubes can be easily washed out during the synthesis.

Figure 5 shows the TG and DTA curves for the MWNT/FAU composites. The temperatures and the MWNT contents determined from the TG curves are summarized in Table 1.

In Fig. 6a we plotted the TG-DTA results obtained for MWNT/MFI composites. Here three well resolved mass loss steps were identified. The first is due to the removal of water from the outer and inner surfaces. As can be seen in Fig. 6b there is only one MS signal (H_2O) at this temperature. The second step appearing much higher temperature, around 670 K, was attributed to burning of the organic template off. In this temperature range CO_2 , NH_3 and H_2O was detected by MS revealing the complex chemistry of template removal. While the first mass loss step was slightly endothermic, the second one is strongly exothermic. The third step is related to the burning of MWNT off. At this temperature only CO_2 was detected by MS as gaseous product what can be easily understood since the MWNTs contains only carbon. This procedure is also rather exothermic as the DTA profiles show. Above 1000 K there is no further mass change was found.

It was an exciting question whether the structure of zeolites was or was not influenced by the burning procedure. By the XRD measurements each type of zeolite showed the characteristic profiles, although in some cases the intensities were somewhat smaller. Figure 7 shows the XRD pattern of LTA zeolite.

TEM investigations revealed that the samples obtained by burning the MWNTs from the zeolite crystals off, had holes of nanometer diameter (Fig. 8). These holes might serve as secondary pore systems assisting the easier diffusion of the guest molecules.

Characterization of the adsorption-desorption properties both of the composites and of the final product which has bimodal pore system is in progress. The bimodal pore system, one is characteristic of zeolite phase and a second one formed upon burning the MWNTs off, renders peculiar properties of these basically microporous solids.

Table 1 Mass losses calculated from the TG-DTG measurements, at temperatures characteristic of the MWNTs burning

Composites	Temperatures/K	Mass loss/%
MWNT/LTA (1:5)	799	14
MWNT/LTA (1:10)	785	12
MWNT/LTA (1:50)	820	5
MWNT/FAU (1:5)	808	21
MWNT/FAU (1:10)	804	14
MWNT/FAU (1:50)	804	4
MWNT/MFI (1:5)	808	10
MWNT/MFI (1:10)	808	8
MWNT/MFI (1:50)	814	7

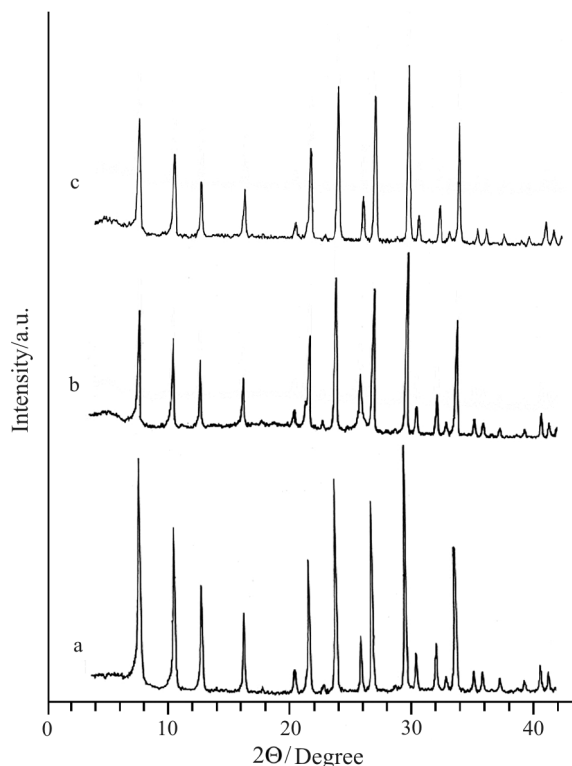


Fig. 7 a – XRD spectra of LTA zeolite synthesized without MWNTs as reference, b – MWNT/LTA composite with 1:5 ratio before template removal and c – MWNT/LTA composite with 1:5 ratio after template removal

Conclusions

In this study we reported the synthesis of nanocomposites formed from MWNT and zeolites. Three zeolite types were synthesized in presence of MWNTs. We observed that the zeolites grew around the carbon nanotubes. The morphology of the synthesis products was different. In some cases, particularly for LTA type small nanocrystals were formed around the tubes, however, bulky zeolite crystals with nanotubes crossing them was also identified by TEM. By our experiences the bonding between carbon nanotubes and zeolite crystals is strong enough; it can be attributed to the appropriate surface treatment of MWNTs.

The question arises whether chemical reactions are also involved in the composite formation, or the composite is a simple mechanical mixture. In order to add some details concerning the ratio and quantity of the components in the reacting mixture and in the final product, thermal analysis was performed. The TG-DTA results revealed that the amount or the concentration of carbon nanotubes in the nanocomposite can be determined from the TG curve even for zeolites synthesized using organic templates. In this latter case the template burns off from the zeolite at significantly lower temperature than the nano-

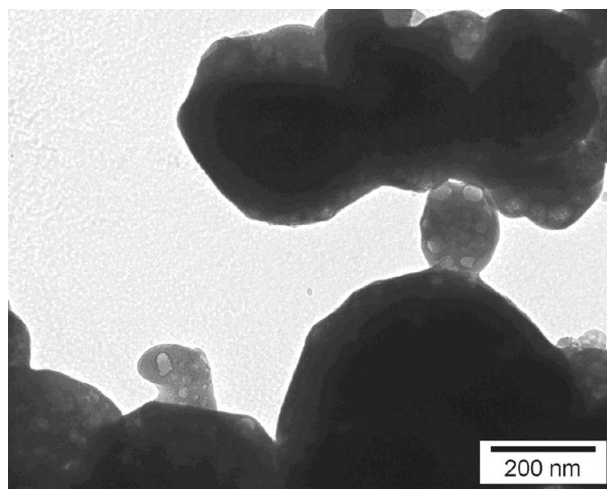


Fig. 8 TEM image of LTA zeolite after heat treatment at 873 K. The secondary pore structure generated by burning off the MWNTs can be nicely seen

tubes. This result makes the synthesis of nanocomposites based on second generation zeolites (such as MFI) possible.

One of the most important results of our study was the generation of secondary mesoporosity in the zeolites after removing the carbon nanotubes. These materials might be used as adsorbents and/or catalysts because of their peculiar new properties.

Acknowledgements

The authors thank the financial support of the Hungarian Ministry of Education (OTKA T-037952, F-038249). ZK acknowledges the support of the Bolyai Janos Research fellowship.

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