Pinewood char templated mordenite/carbon honeycomb composite

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Biotemplating with carbonized wood is a novel way of zeolite adsorbent and catalyst production, with uniform, hierarchically ordered macro- and micropore structure, having low diffusional resistances against mass transport of adsorptives, reactants and products around the zeolite crystallites. Pinewood (*Picea abies*) cubes of 1-cm size edges were carbonized at 700 °C in nitrogen flow. The obtained charcoal cubes contain parallel channels of 20–30 μm diameter, separated by about 1–3 μm thick carbon walls. The hydrophobic character of the channel walls was effectively reduced using oxidative treatment with nitric acid. Following saturation with zeolite synthesis solution the carbon cubes were exposed to hydrothermal conditions. Mordenite/carbon composite materials were formed where Na-mordenite microcrystals coated the walls of the carbon macropores. The thickness and density of the zeolite layer was controlled by varying the synthesis conditions. Owing to reduced diffusional resistance, the preparations are favourable adsorbents and catalysts.

Introduction

In chemical industries, adsorbents and catalysts, among others zeolites, with bidisperse pore structure are extensively used. The accessibility of the adsorbing sites, located inside the zeolite crystals strongly determines the effectiveness of a zeolite molecular sieve type material.[1] Although the zeolite crystal structure is most essential to create a good selectivity, the size of transport channels among the crystallites also plays an important role having strong influence on the activity.[2] To get the possible lowest rate-controlling intercrystalline diffusion resistance, interconnecting meso- and macropore systems must be generated. In commercial applications usually pellets of zeolite crystals are prepared. However, the hindered accessibility of the zeolite crystals within the pellets often governs the rate of adsorption and the catalytic efficiency of the zeolite. The adsorptive or reactive molecules can have much easier access to the intracrystalline sorption sites if the zeolite forms thin layer on the surface of relatively large pores. The same concept is applied, when honeycomb ceramic monoliths are used, *e.g.* for catalytic abatement of gaseous exhausts.[3]

Nowadays a wide variety of methods have been suggested for the preparation of zeolite coatings on supports of different chemical compositions and porous structures.[4] Using the procedure of hydrothermal zeolite synthesis uninterrupted thin zeolite films of uniform thickness were formed on the surface of various supports. Chemical bonds between the zeolite and the support can stabilize high zeolite dispersion. There is a great deal of interest in materials with regular porosity, having ordered, preferably uniform macropores, covered by a thin microporous zeolite layer. The macropores permit easy access to zeolite micropores, wherein active centres can participate in ion exchange, adsorption or catalytic processes. In a previous study[5] such a hierarchical macropore/micropore system was prepared by synthesizing a ferrierite layer on the inner surface of a macroporous ceramic honeycomb monolith (cordierite). The inner surface area of ceramic monolith is usually less than about 100 cm^2/cm^3.

Nature is a school for material science. Biomimetism and bioinspiration shows direction to the design of innovative materials and systems.[6] The vascular bundles of trees is a structure comprising virtually parallel ordered tubes and this cellular structure of wood provides excellent accessibility for fluids *via* the inherent vascular transportation system. Most trees can be characterized by a multimodal pore size distribution of circular vessels, having diameters up to 300 μm. In contrast, coniferous woods, *e.g.*, Norway spruce (*Picea abies*), contain close to uniform-size parallel channels of rectangular or hexagonal cross section. The mean pore diameter is about 20 μm.

The manufacture of zeolite honeycomb monoliths by use of binder materials is complicated and limited.[7] A further disadvantage is that the intracrystalline diffusional resistance in the product is similar to that in pellets. Zeolites have been supported successfully on very different materials, among them carbons were also tested with different origin, porosity, surface chemistry and conformations without conscious use of the hierarchical biological organizations.[8] The combustion of these zeolite/carbon composites often produces microtubules of pure zeolites having improved diffusivity of gases compared with zeolite powders and pellets. However the need for fast adsorbents and catalyst particles in industrially useful amounts is not satisfied yet.

Sieber *et al.*[9] prepared microcellular ceramic materials by the reproduction of wood morphologies by biotemplating, where the structural features of the native wood are maintained in the ceramic product (Al_2O_3, SiC, ZrO_2). Biomorphic

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ceramics were manufactured *via* the sol–gel route by repeated infiltration of a low viscous sol into a wood disk followed by sintering in air at high temperature. Wood tissue in its original form has been also utilized and the seed-growth strategy was used for the preparation of zeolite molecular sieve (silicalite-1) having an hierarchical porous system.[10] Organic components were removed by combustion in air at 600 °C. This high combustion temperature is the main disadvantage of the method, because it can not be applied for most zeolites. To elude this problem Sieber's group applied another method for the manufacturing of SiSiC-zeolite structured cellular composites.[11] The process consists of fabricating the SiSiC composite ceramic monolith from carbonized cylindrical cardboard specimens. This support was functionalised with zeolite coating thorough a hydrothermal treatment of the SiSiC carrier in an alkaline solution containing the template, while the Si was provided from the ceramic substrate. The great problem is that they could carry out this procedure only with a corrugated cardboard monolith, having channel diameters from 1 to 8 mm and not with wood tissue containing high inner surface area.

In a previous study, a carbon honeycomb was obtained by controlled carbonizing of pine wood xylem (Norway spruce) and used as support, having low diffusional resistance, to develop a thin, uninterrupted Na-X zeolite layer, synthesized under hydrothermal conditions inside the channels.[12]

However, the synthesis conditions of different zeolites are quite different depending on the framework. Na-X has a three-dimensional pore structure, low Si/Al ratio and cubic crystals. Na-mordenite contains a one-dimensional pore system and much lower aluminium content. The crystal morphology is orthorhombic, that is often synthesized or occurs in minerals with the shape of long needles. The charcoal obtained from pine wood earlier,[12] containing nearly uniform ordered tubular macropores, was aimed to be used again as a special natural bio-template support for synthesizing a microporous Na-mordenite zeolite–macroporous carbon composite.

Experimental

A log of Norway spruce (*Picea abies*) was cut to cubes of $10 \times 10 \times 10$ mm^3 size. These were heated up to 700 °C in N_2 flow and calcined for 1 h to empty the vascular bundles and carbonize the xylem.[13] The obtained char cubes, from here on referred to as parent charcoal cubes, contain long parallel channels of rectangular cross section. Oxygen-containing polar groups were generated on the surface of the carbon channels, having a size of 20–30 μm, by soaking the cubes at room temperature in 5 mol dm^{-3} nitric acid solution. Further samples were prepared by soaking HNO_3-treated char cubes in 2 mol dm^{-3} NaOH solution or in diluted water-glass solution (the water to water-glass volume ratio was 5) at room temperature for 4 h. The soaked cubes were filtered off, flushed with distilled water and dried at 150 °C. The water-glass-treated sample was then put into 2 mol dm^{-3} H_2SO_4 solution for 1 h, flushed again with water, and dried as before. The objective of this treatment was to reduce the hydrophobic character of the carbon surface and promote its interaction with aqueous solutions. The hydrophilic property of the preparations was characterized by the rate and amount of water uptake.

Air removal from the macropores of char cubes by evacuation increased the amount and rate of water uptake and also the penetration rate of the solution, used for zeolite synthesis *in situ* in the carbon channels.

Zeolite Na-mordenite was obtained from a solution, having the molar composition of $6\,Na_2O : 20\,SiO_2 : Al_2O_3 : 780\,H_2O$ under hydrothermal conditions.[14] Transparent synthesis solutions were obtained by mixing aqueous solutions of sodium hydroxide (Reanal, Hungary), sodium aluminate (Wako Pure Chemical Industries LTD, Japan) and Ludox HS-30 colloidal silica (Aldrich, Germany). After having been aged, the solution was contacted with various pre-treated char cubes for a period up to 61 days. The synthesis in the gel/charcoal system was accomplished by raising the temperature to 150 °C for 48 h. Then, the charcoal cubes and the zeolite suspension was separated, both fractions were washed in distilled water and dried at 50 °C overnight.

The X-ray diffraction pattern of the product zeolite powder was determined using a Philips PW1200 type X-ray diffractometer, which was equipped with a graphite monochromator and Cu-Kα X-ray source.

The cubes were split into halves and the *in situ* synthesized mordenite crystallites were examined along the coated carbonized channels by scanning electron microscopy (SEM). A Hitachi SEM-570 type microscope was used.

Adsorption isotherms of the carbon supports and the mordenite/carbon composites were determined for nitrogen and oxygen in the 0–3 kPa pressure range at −20 °C using an all-glass volumetric sorption system.

Results and discussion

In the industrial application of zeolites the rate of adsorption and catalytic transformation is often governed by the rate of diffusion in the macropores among the crystals in large agglomerates or pellets. In such cases the efficiency of the process can be significantly improved by decreasing the intercrystalline mass transport resistance. Honeycomb ceramic monolith structures were found to be especially favourable in industrial practice, *e.g.*, cordierite, which is broadly used as a catalyst support in the catalytic abatement processes of polluted exhaust gases. Nevertheless, the specific surface area of the honeycomb monolith is low because of the relatively large channel diameters. Natural carbon honeycombs could be easily obtained with much higher surface area by carbonizing properly cut log pieces. However, until now, only a few studies have dealt with carbon "monoliths" made of wood.[13,15–17]

The pinewoods in the *Picea* family were found to have the most favourable texture for the preparation of charcoal having uniform, one-dimensional, parallel macropores with a high similarity to artificial ceramic monoliths. All the coniferous wood samples examined had water-filled parallel channels of rectangular or hexagonal cross section, oriented parallel to the trunk axis. The pyrolysis of the wood resulted in charcoal retaining the original ordered vascular texture. The weight loss of the wood was 78–86 wt%. The cubes suffered a non-isotropic shrinkage of about 25–35%. The diameter of the tracheids and the channels formed from them in the pyrolysis procedure reflect the seasonal change of the weather, however, the variance of the channel size is hardly higher than that of the ceramic honeycombs. Most of the channel diameters are in the range of 20–30 μm. Carbon walls of 1–3 μm thickness separate parallel channels (see later in Fig. 2(A)). Thus, the geometric surface area of the macropore channels must be higher than about 1000 cm^2/cm^3.

The aim of this work was to produce an uninterrupted zeolite coating over the inner surface of the carbon honeycomb. We faced the problem of filling up the macropores with the aqueous synthesis solution because of the hydrophobic property of the carbon. Another difficulty arose from the weak interaction between the zeolite and the inert carbon surface. In order to mitigate the mentioned adverse affects we increased the wetting of the carbon surface.[18–21] Thereby, we were able to increase the amount of zeolite formed within the pores and enhanced the adherence of the zeolite crystallites to the pore walls. Regarding the properties of the prepared carbon/zeolite composite, the synthesis conditions were found to be also important, which was primarily determined by the type of the target zeolite.

The water uptake was found to be significantly accelerated by exposing the parent carbon cubes to oxidative pre-treatment.[12] The mechanical stability could be preserved and favourable wetting was achieved by soaking the parent charcoal in nitric acid. Full saturation of the acid-treated degassed sample was obtained in a few minutes. The treatments by water-glass or sodium hydroxide solution reduced water uptakes relative to that of the HNO_3-treated charcoal cubes. Presumably, the latter treatments plugged some of the channels.

The zeolite Na-mordenite/carbon composite was formed by *in situ* zeolite synthesis in the honeycomb macropores. The synthesis gel could fully penetrate into the pores of the degassed charcoal cubes. The carbon cubes, immersed in the synthesis gel, was treated to produce mordenite crystals. Crystallization was initiated by increasing the temperature. The morphology of the product was modified by changing the synthesis conditions, such as, applying ageing, seeding, *etc.* XRD and SEM examinations showed that crystalline zeolite was obtained from the synthesis solution both inside and outside. By seeding and varying the aging time of the reactant mixture prior to the synthesis, the crystal and aggregate sizes, the zeolite yield and the coverage of the carbon surface could be significantly affected.

The X-ray diffraction (XRD) patterns of the powder samples obtained from the synthesis gels contacting the pre-treated support char cubes (Fig. 1) confirmed the formation of Na-mordenite. Because of the low concentration, the zeolite crystals inside the char channels could not be analysed. Therefore, it was supposed that zeolite, formed inside the pores, had nearly the same composition as that which was formed outside the carbon cubes. The time of ageing influenced the purity of the zeolite product. A commercial Na-mordenite, obtained from Süd-chemie AG, Germany, was used as reference material. XRD patterns of samples containing mordenite, obtained in the presence of the nitric acid treated, *i.e.*, oxidatively functionalized charcoal cubes, are compared in Fig. 1. The zeolite product, obtained immediately after contacting the synthesis gel components, contained by-product beside mordenite. This was assigned as gismondite on basis of its XRD reflections. In general, gismondite, analcime and quartz as competing phases can often appear during mordenite synthesis.[14] If the same gel was aged for three days the quantity of gismondite phase decreased substantially, while some analcime crystals appeared. Addition of seeds (Na-mordenite from Süd-chemie AG) is also advantageous to increase the crystallinity and to obtain almost pure mordenite product only with traces of gismondite or analcime. Much longer ageing results in gismondite as the main product, consequently there is an optimum regarding the ageing time. The mordenite, added as seeding agent directs the synthesis towards mordenite formation. The initial generation of an abundant amount of new

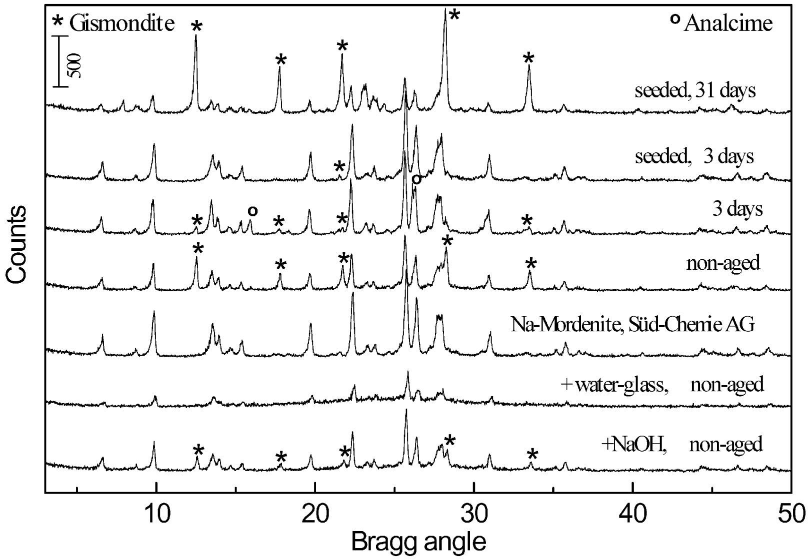

Fig. 1 X-Ray diffraction patterns of products containing Na-mordenite obtained in the presence of carbon honeycombs oxidized by nitric acid, after different periods of ageing with or without zeolite seeds.

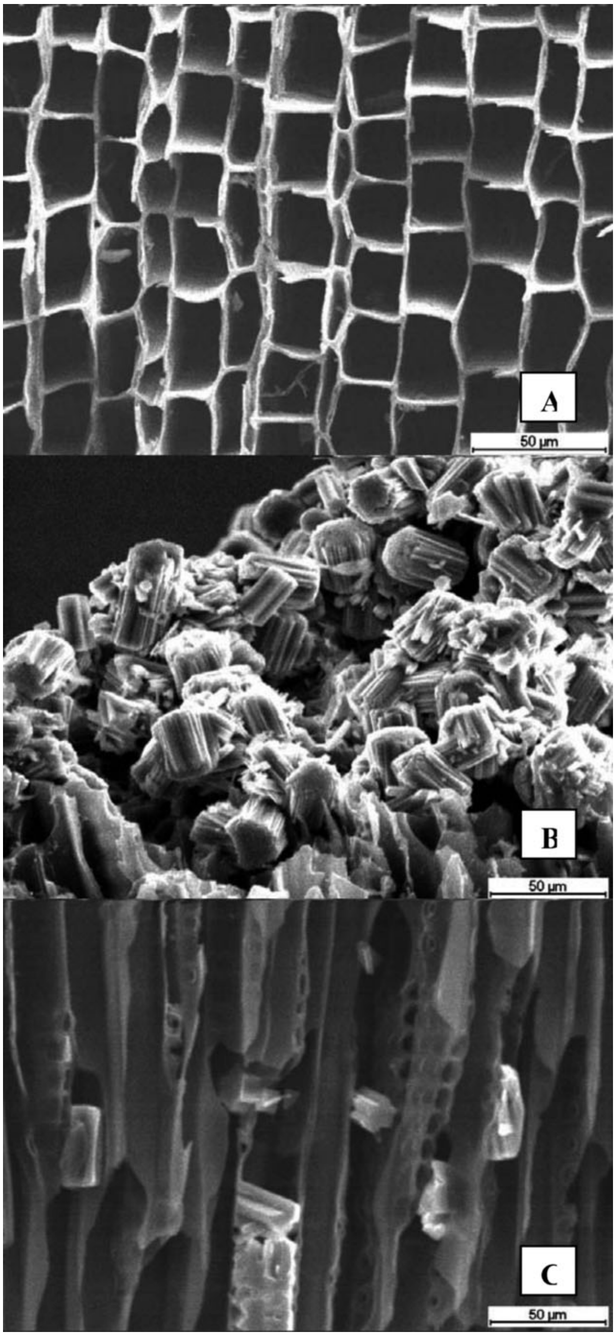

Fig. 2 SEM micrographs of the cross section of the Norway spruce (*Picea abies*) cubes (A); macropore entrances with as-synthesized mordenite crystals on the outer surface of a char cube (B); and mordenite crystals inside the channels of a split char cube (C).

mordenite seeds ensures the preferential formation of mordenite relative to that of gismondite. However, if the seeded synthesis solution is aged for a longer time the mordenite seeds can get completely dissolved. Impregnation of the carbon cubes with NaOH solution decreased the gismondite by-product formation to some extent, but other advantages, *e.g.*, higher coverage, thicker mordenite layers inside the cubes, *etc.*, could not be observed (Fig. 1, bottom curve). The pre-treatment of the cubes with water-glass resulted in low production of mordenite phase and in formation of round shape particles with low crystallinity. The introduction of excess silica with the carbon cubes seems to lead to changes of the composition of the synthesis gel. The water-glass pre-treatment of the cubes resulted in amorphous products and crystallites of poorly defined shapes. The crystalline and amorphous products obtained outside and inside the cubes, were very similar.

Without seeding and ageing, regular aggregations of quite large zeolite crystals could be obtained under the applied conditions (see Fig. 2). Nice, well-shaped, almost uniform crystals were formed both outside (Fig. 2(B)) and inside (Fig. 2(C)) the carbon honeycomb cubes. The crystal size is commensurable with the channel dimensions of the charcoal (Fig. 2(A)). On the SEM images large zeolite aggregates were observed that completely plugged some of the channels. Mordenite and gismondite, members of two different zeolite families, have quite different microporous structure. Mordenite has orthorhombic crystals and a one-dimensional system of large pores. The crystal morphology can be generally described as needles or fibres with *c*-elongation. The crystals can form spherical or prismatic aggregates that can be loosely bound or compact. On the contrary, gismondite has monoclinic crystals and a three-dimensional system of small pores. In natural mineral the gismondite crystals appear in the form of as "pseudo-octahedra" or "pseudo-tetragonal bipyramids". The latter morphology can not be visualised on our SEM images if mordenite and gismondite are formed together. At low gismondite content long mordenite needles can be often observed (Fig. 3(B)) and loose aggregates of large and thin platelets also can be seen (Fig. 3(A)). Probably such platelets are the building units of the compact, uniform, well-ordered aggregates of zeolite crystals where mordenite and gismondite were synthesised in comparable concentration forming crystals together with uniform size and a special shape (Fig. 2(B) and (C)). Regarding the final aim of the present study, namely, to prepare zeolite/carbon composites, having low diffusion resistance in the main transport channels, this experiment was not successful, although it is an important progress that zeolite crystals could be generated thorough the full volume of the carbon cube. It is interesting to see that aggregations of needle type crystals or platelets were obtained and not ordered solid particles. The length of the intergrown needles, or rather platelets, is almost the same. It is to be noted that gismondite formed in comparable quantity with the target product mordenite, therefore, the crystal morphology could be significantly affected also by the phase composition.

Nowadays it is already well known[22] that the size of zeolite crystallites can be reduced simply by ageing of the synthesis solution to obtain crystal seeds in a great number before the synthesis is initiated. Using the same charcoal cubes and synthesis solution as above, the synthesis was repeated, permitting long periods of aging for the synthesis mixture. SEM micrographs of the obtained zeolite Na-mordenite/carbon composite are shown in Fig. 3. The images suggest that ageing resulted in much smaller crystallites, less ordered aggregates and a wide variety of morphologies. Although islands, spots of continuous zeolite layer (see left side of Fig. 3(A)) cover a great part of the inner surface of the carbon channels, though the walls does not seem to be fully covered by a zeolite layer.

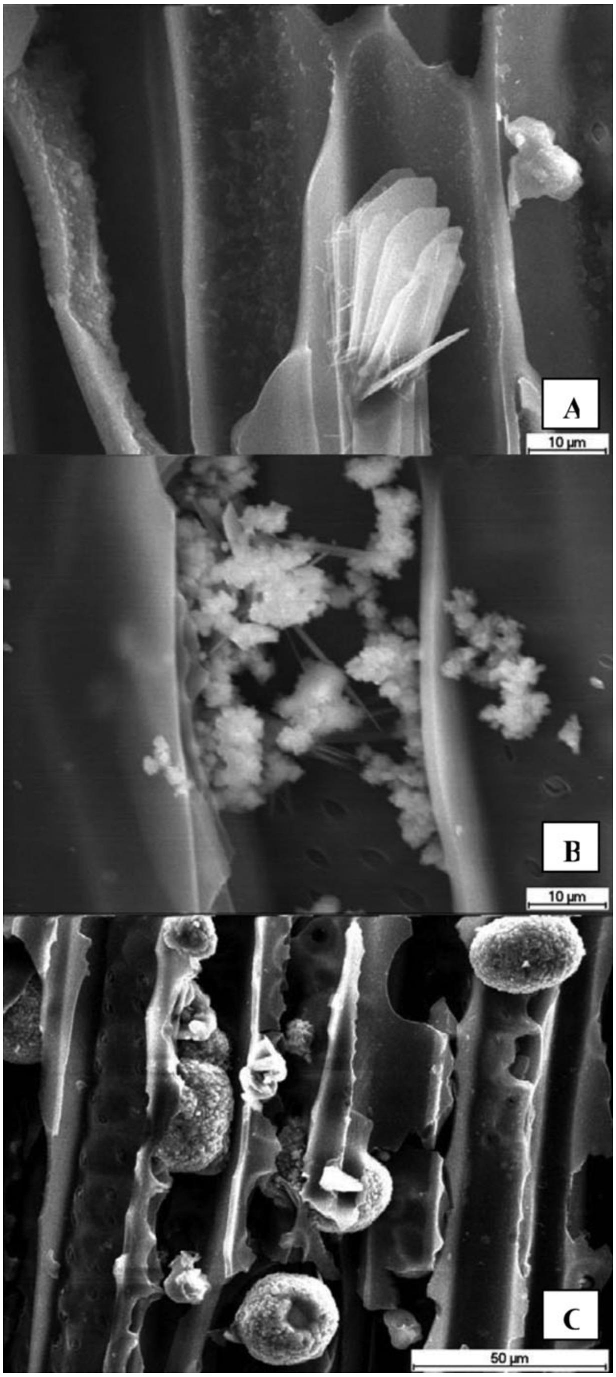

Fig. 3 SEM images showing the mordenite crystals formed after ageing for three days along the channels of the charcoal cube with different morphologies. Magnifications: 1000× (A); 1000× (B) and 500× (C).

Large platelets, long needles and small aggregates of tiny needle crystals can be also observed (Fig. 3(B)). Large aggregates of cauliflower-like morphology were also formed (Fig. 3(C)), not present in the preparations obtained without ageing (Fig. 2(C)). The different morphologies can be associated with the various phase compositions of the samples. It can be concluded that ageing is beneficial for producing much smaller crystallites with higher purity, however, the product showed very heterogeneous morphology. For most applications this composite material would be disadvantageous because of the wide size distribution of the zeolite crystals and aggregates.

Seeding and three days of ageing results in pure Na-mordenite (see Fig. 1). This improvement in the phase purity occurred together with production of nanosized crystals and complete coverage of the carbon walls (100%) in the carbon transport channels (Fig. 4(A)). Reduction of the water content of the gel by 35 wt% did not induce a great increase of the layer thickness (Fig. 4(B)). The average thickness of the continuous layer can be estimated as several times the size of a single microcrystal. The non-carbon content of this composite was 10.2 wt%, as determined by TG analysis. From the mass of Na-mordenite the thickness of a solid zeolite layer was calculated as approximately 120 nm. This value is comparable to the value estimated by SEM. Most of the channel cross-section remained empty. To increase the thickness of the zeolite coating the synthesis procedure was repeated subsequently two and three times, however these efforts failed. Significantly thicker zeolite layer on the channel walls could not be obtained. Presumably the existing zeolite layer was always dissolved in the fresh gel before a new zeolite layer could form. Consequently the mass and the thickness of the zeolite coating did not increase. In some experiments after repeated synthesis steps very loose aggregates of small mordenite crystallites were formed, which were not anchored to the wall surface but filled up quite long sections of the channels (Fig. 4(C)). This type of mordenite/carbon composite, containing higher zeolite mass inside the channels might be membrane like. However, we can fill up only short sections of the macropores with mordenite crystals at present.

Both zeolites and carbon molecular sieves are often used as pressure-swing adsorbents for air separation. When nitrogen is the desired useful product, carbon adsorbents are more favourable than zeolites. In contrast, zeolite molecular sieves are the preferred adsorbents for oxygen generation. The selectivity of the adsorbent resides in the difference of either the sorption equilibrium or the sorption dynamics of the main air components. The samples were characterized by low-temperature (-20 °C) adsorption isotherms for nitrogen and oxygen. Equilibrium N_2 and O_2 adsorption isotherms of the charcoal support and the zeolite/carbon composite are compared in Fig. 5. The isotherms show increased N_2 adsorption capacity with increasing mordenite content of the composite material. This change results in higher selectivity of the Na-mordenite zeolite/carbon composite for nitrogen compared to that of the parent carbon support based on differences in the sorption equilibrium. Comparison of samples shown in Fig. 4(A) and (B) demonstrate that latter sample has double the nitrogen uptake of the first sample. This finding suggests that using a more concentrated synthesis gel a Na-mordenite layer of double thickness was attained on the walls of the carbon macropores. In the channel system of the carbon honeycomb the zeolite sorption sites must be reached more rapidly by the adsorptive molecules than the sites of conventional adsorbent granules. This infers that the zeolite/carbon composite can be more efficient than the known pressure swing adsorbents. Preparation of such composites with various types of zeolites, having different structures and zeolites modified with cation

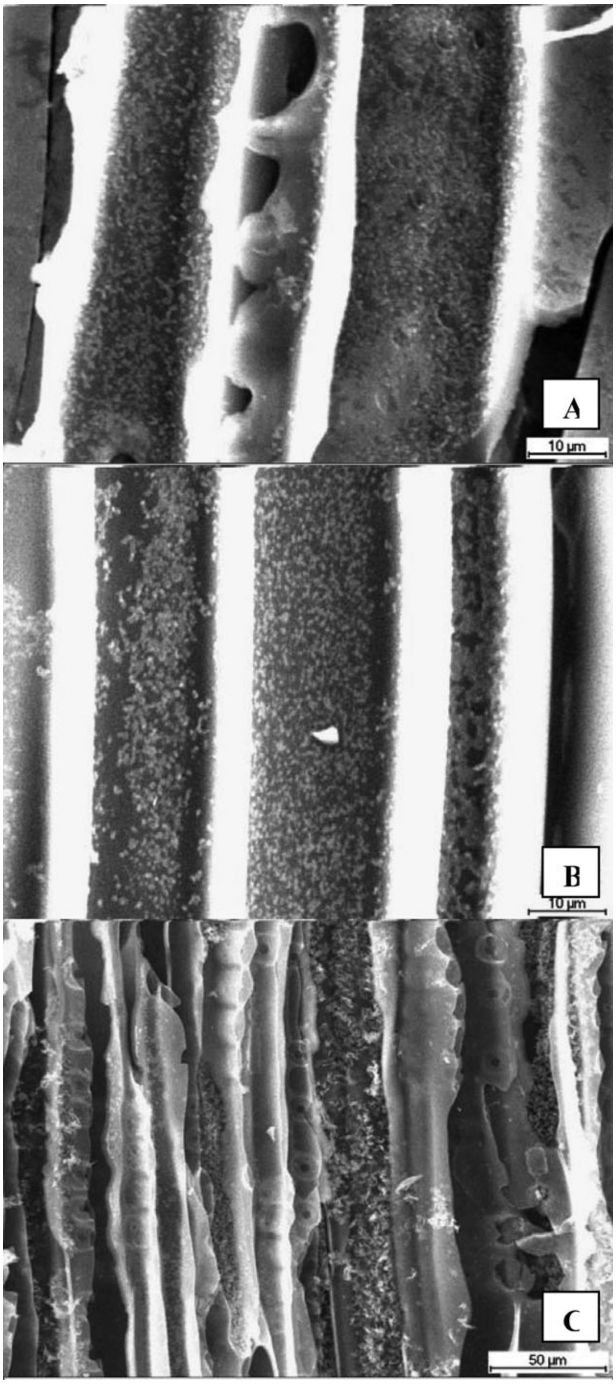

Fig. 4 SEM pictures of the inner surface of zeolite Na-mordenite/charcoal composite prepared after seeding and ageing for three days of the synthesis gel (A); using gel with less water (B); and after the synthesis procedure, repeated twice (C).

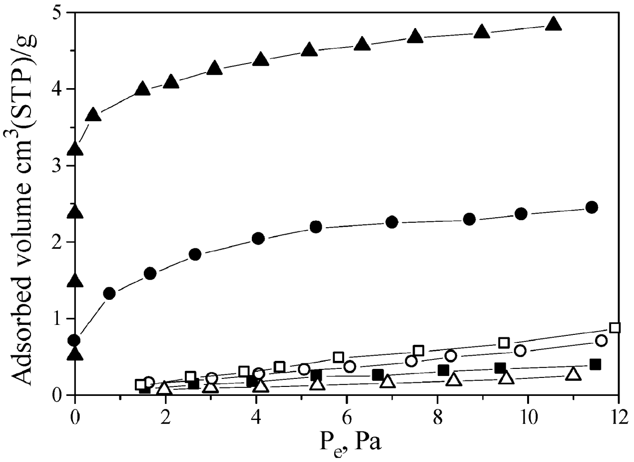

Fig. 5 Nitrogen (solid symbols) and oxygen (open symbols) adsorption isotherms of the parent carbon honeycomb (■,□); and the mordenite/carbon composites shown in Fig. 4(A) (○,●) and Fig. 4(b) (△,▲) at −20 °C.

exchange, results in a wide variety of quick adsorbents, providing solutions for numerous gas separation problems. A further potential field of application for these composite materials is catalysis, where mass transfer resistances can often limit the efficiency, result in reduced activity and disadvantageous selectivity. The thin zeolite layer on the carbon walls can be favourable regarding both the catalytic activity and selectivity. For a number of reactions the preferential location of the active sites is at the mouths of the zeolite pores. In this respect the tiny zeolite crystallites, characteristic of our composite material, have definite advantages. In this direction catalytic studies are urgently needed.

Conclusions

On the basis of the present work it can be concluded that, small zeolite Na-mordenite crystallites can be synthesized to form a continuous layer, coating the inner surfaces of a carbon honeycomb, made from pinewood. To obtain such coating layer the concentration of polar functional groups has to be increased on the surface of the virtually uniform macropores of the carbon and the right conditions of zeolite synthesis has to be selected. The phase purity and the morphology of the mordenite coating can be controlled by ageing and seeding the synthesis gel. The microcrystals, fully covering the surface of the macropores in the charcoal, leave the channels open for rapid mass transport forming advantageous zeolite/carbon material for the purpose of applications such as fast adsorbents and catalysts.

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