Formation of a combined micro- and mesoporous material using zeolite Beta nanoparticles

C.J. Van Oers,*, W.J.J. Stevens, E. Bruijn, M. Mertens, O.I. Lebedev, G. Van Tendeloo, V. Meynen

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A B S T R A C T
Composite micro- and mesoporous materials are synthesized using zeolite Beta nanoparticles without the need for a structure directing agent to form the mesopores. This leads to important ecological and economical advantages. The influence of the way of cooling the aged nanoparticles solution on the formation of the composite materials has been studied. The materials have been characterized towards porosity by N2-sorption, towards zeolitic properties by TGA, DRIFT, XRD and TEM, towards aluminium content by EPMA. All prepared structures possess zeolitic properties. However, the method of cooling down of the aged seeds leads to differences in the porosity and intensity of the zeolitic characteristics.

1. Introduction
Zeolites are widespread in the industrial world for catalysis, sorption and separation applications. Their popularity results from a good activity, selectivity and stability. Nevertheless, these microporous materials possess a limited use towards large bulky molecules and viscous liquids as found in the pharmaceutical, biological and fine chemical industry due to their narrow pore size distribution and small pores (< 2 nm). This major drawback resulted in the beginning of a still expanding research for the synthesis of ordered mesoporous materials (2 × < 50 nm) [1,2].

The first generation of ordered mesoporous materials (MCM-41 [3,4], SBA-15 [5], etc.) is still inferior to zeolites when it comes to application in industry. The most important disadvantages of these mesoporous materials are the low hydrothermal and mechanical stability as a result of their amorphous pore walls and the difficulty to build in heteroelements. To overcome these problems, several new materials have been developed. On the one hand the original synthesis for mesoporous materials was adapted. The PHTS-structures (Plugged Hexagonal Templated Silicas) are comparable to SBA-15-materials except that they possess an improved stability because of their thicker pore walls and the pillaring effect of the plugs [6–8]. PHTS resembling, activated materials were obtained by the deposition of active heteroelements, in the form of zeolitic precursor particles, in amorphous siliceous materials in order to improve their activity [9,10]. On the other hand, the research was focussed on the development of various synthesis approaches for the preparation of structures that combine the properties of mesoporous materials with those of zeolites [1]. One of the first techniques applied was the post-synthesis dealumination process using steaming or acid leaching on full-grown zeolites [11,12]. Unfortunately, these structures only possess a minor improvement in mass transfer. This can be explained by assuming that either the mesoporous network is not connected [13] or the mesopores are not linked to the outer surface of the particle or the mesopores are not sufficiently wide. Recently, a procedure for the controlled desilication of zeolites by an alkaline treatment was obtained whereby the mesopores would be interconnected [14,15]. Both methods destruct part of the zeolite to form the mesopores, which can be a problem towards reproducibility. Recrystallisation of mesoporous structures was performed by impregnating the amorphous silica walls with a directing agent for the micropores. After a hydrothermal treatment, a semi-zeolitic material is formed [16,17]. Another approach is the carbon based synthesis. Carbon nanofibers or carbon black aggregates can serve as a template in the zeolite synthesis. A post-synthesis calcination procedure to remove the carbon, gives rise to mesopores in the zeolite structure [2,11,18–20]. The same procedure can be used with carbon replica’s or inversed replica’s as a template, whereby the carbons have
the reversed or inverted structure of a mesoporous amorphous material [21–23].

The last couple of years several syntheses were developed using zeolite nanoparticles, zeolite seeds, as silica source [1]. There is a discussion going on about the typical characteristics of those seeds. Some attribute zeolitic properties to the nanoparticles [24,25], while others suggest an evolution over seeds to intermediate particles ending in zeolite crystals [26,27]. The addition of a mesopore directing template to a solution of zeolite nanoparticles results in the formation of a combined micro- and mesoporous material. Some examples of materials obtained in such a way are MAS-7 [28,29], MTS-9 [30,31], MSU-S [32,33], zeogrid [34], zeolite [35], etc.

More recently new synthesis routes are developed whereby the micropore and mesopore directing agents are added at the same time, instead of adding a mesopore directing template to a zeolite seeds solution. In that case organic-inorganic hybrid surfactants or polymers are added as mesopore directing agents to the synthesis mixture, resulting in combined micro- and mesoporous materials [36–40].

We focus our research on the synthesis of combined micro- and mesoporous materials with zeolitic properties. The major difference with the previous methods lies in the fact that in this case no structure directing agent for the formation of the mesopores is added. This leads to important ecological and economical advantages in comparison to the syntheses using templates to direct the formation of the mesopores. There is a growing interest in this specific field of research. Recently, a synthesis method is developed with a great analogy to the method discussed in this article, the TUD-M and TUD-C materials [41,42]. The resemblance between the synthesis of TUD-M and TUD-C and the reported synthesis here, is the absence of a mesopore directing agent. Nevertheless there are some substantial differences such as the acidity of the synthesis environment and the second hydrothermal treatment of the synthesis method discussed in this article. The synthesis of TUD-M is performed in alkaline environment, while in the method reported in this manuscript, the zeolite seeds are acidified after ageing. Moreover, the method mentioned in this article makes use of a second hydrothermal treatment at 150 °C during 3 days after the ageing of the seeds. The TUD-M synthesis on the other hand involves a more delicate treatment at a temperature of 50 °C for 10 days. The hydrothermal treatment not only results in a remarkable shortening of the synthesis time, but can also contribute more to the formation of a zeolites phase. The method discussed in this article has already been described in a recent contribution [43], however in that case a silicalite-1 precursor solution is used as silica source.

2. Experimental

2.1. Synthesis

The zeolite Beta nanoparticles solution with a molar composition of SiO2: 0.02 Al2O3: 0.028 Na2O: 0.6 TEAOH: 0.2 HCl: 20 H2O was synthesized according to the slightly modified procedure described by Huang et al. [44]. The only difference lies in the prolonged hydrothermal treatment, namely 24 h instead of 20 h. After ageing at an elevated temperature of 140 °C, this precursor solution underwent a fast cooling by quenching or a slow stepwise cooling. The resulting nanoparticles solution was acidified using a 12 M HCl solution until a pH lower than zero was obtained. For this purpose 18 mL of the Beta seeds solution was added to 5 mL of concentrated HCl under vigorous stirring. Next, the solution was transferred into an autoclave for a second hydrothermal treatment at a temperature of 150 °C during 72 h. After filtrating, washing and drying of the product, a calcination procedure was carried out. The materials were calcined in ambient atmosphere at 550 °C for 6 h with a heating rate of 1 °C/min. The obtained structures are named according to the cooling treatment of the aged nanoparticles solution: MB-Q for the structure grown from the quenched seeds and MB-S for the material grown from the slowly cooled seeds.

A full-grown zeolite was made as a reference. The zeolite was grown from the nanoparticles solution before acidification by a hydrothermal crystallisation period of 7 days at 150 °C. The characteristics of the prepared zeolite fully confirm those as described in the Atlas of Zeolite Frameworks Types and in the Collection of Simulated XRD Powder Patterns for Zeolites of the International Zeolite Association [45,46].

2.2. Characterization techniques

The N2-sorption measurements at –196 °C were determined using a Quantachrome Autosorb-1-MP automated gas sorption system. The samples were outgassed prior to measurements under vacuum during 16 h at a temperature of 200 °C. The Barret–Joyner–Halenda (BJH) method applied on the desorption branch of the isotherm was used to achieve the pore size distribution. The t-plot method was used to determine the micropore volume, while the Brunauer–Emmet–Teller (BET) method was applied to calculate the specific surface area. The total pore volume was determined at P/P0 of 0.98.

Electron probe microanalysis (EPMA) was utilized for the determination of the aluminium concentration in the samples. The EPMA analyses were preformed on a JEOL JXA 733 apparatus.

Thermogravimetric analysis results were recorded on a Mettler Toledo TGA/SDTA851. The analyses were performed in an oxygen atmosphere, whereby the samples were heated from 30 °C to 700 °C with a heating rate of 5 °C/min.

Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy measurements were recorded on a Nicolet 20 DXB Fourier Transform IR spectrometer equipped with a DTG detector. The samples were mixed with KBr (2% sample, 98% KBr). The resolution was set to 4 cm−1 and 200 scans were averaged. All measurements were performed under a flow of dry air.

X-ray diffraction (XRD) measurements were carried out on a Pananalytical XPERT PRO MPD diffractometer with filtered Cu Kα-radiation. The measurements were performed in the 2θ mode using a bracket sample holder with a scanning speed of 0.04°/4s continuous mode.

The combined materials were further characterized by transmission electron microscopy (TEM) and EDX analysis using a Philips CM20 microscope equipped with an Inca X-ray microanalysis unit, operating at 200 kV and having point resolution of 0.27 nm. The TEM samples were prepared by crushing the material in methanol in an agate mortar and dropping this dispersion of finely ground material onto a holey carbon film supported on a Cu grid. Low electron beam intensities and low magnification were applied in order to minimize the e-beam damage of the material. Fourier transformation (FT) of high resolution TEM (HRTEM) images was performed using the Digital Micrograph 3.3 software.

3. Results and discussion

Nitrogen sorption measurements were done in order to evaluate the influence of the Beta nanoparticles properties on the obtained materials. The N2-sorption isotherms are shown in Fig. 1. Depending on the treatment of the nanoparticles during preparation, slow cooling or quenching, different isotherms were obtained. Both materials possess a type IV isotherm according to the IUPAC
classification, pointing out the presence of a mesoporous system. The hysteresis is of the H1 type indicating a narrow pore size distribution [47]. Clear differences in the N2-sorption isotherms of both mesoporous materials can be observed. MB-Q shows much larger pore diameters and volumes in comparison to MB-S. Nevertheless, the mesoporous structure of MB-S is more uniformly built, as can be deduced from the pore size distribution in Fig. 1 (inset) which is narrower for MB-S. Table 1 gives an overview of the N2-sorption results. Both MB-Q and MB-S materials exhibit micro- and mesopores. However, MB-S has a remarkably higher micropore volume than MB-Q.

The presence of incorporated active heteroelements is of great importance towards future applications of this type of materials with bimodal porosity, which aim at combining the characteristics of mesoporous materials and zeolites. In this case aluminium is incorporated in the structure. The results of element analysis are given in Table 1. Although the aluminium concentration is lower than in the full-grown zeolite, both MB-Q and MB-S show relatively high aluminium contents, despite a severe acidification step in their synthesis procedure. This suggests a strong framework incorporation of the aluminium in the zeolite precursor nanoparticles. MB-S shows higher aluminium content compared to MB-Q, suggesting a stronger incorporation of the aluminium in this material.

To study the presence of zeolite characteristics, TGA and DRIFT measurements were performed. In this way, small structural characteristics specific to zeolite Beta that occur on short range order can be determined. On the other hand, XRD measurements are used to indicate the presence of long range ordering zeolite characteristics of the materials found by the crystalline repetition of the Beta unit cells. The thermal analysis results (DTG and TGA (inset)) are shown in Fig. 2. The DTG curve can be divided into four regions. The first part, up to 150 °C, is the result of the decomposition of TEAOH ions which serve as counterions for connectivity defects in the silica structure [50,51]. In literature, this weight loss is also described as the result of the decomposition of adsorbed TEAOH [48,49]. The removal of the TEA+ counterions of Al(OSi)4 is an exothermic process leading to a third weight loss in the area 350–500 °C. The fourth region is situated above 500 °C. This exothermic process is caused by the removal of residual organic material confined in the zeolitic pores [50,51]. Although both combined micro- and mesoporous materials (MB-Q and MB-S) show these four different regions, there is still an important difference between the two structures. The loss for MB-Q in the third and fourth region is relatively low in comparison with the weight loss in region two, in contrast to the weight losses in MB-S. This implies that the template has a stronger affinity with MB-S than with MB-Q. A possible explanation can be that the zeolitic properties are more abundant in MB-S compared to MB-Q. However, both materials differ from the pure zeolite.

DRIFT is used to study the different types of bonds in the combined micro- and mesoporous structures. Fig. 3 shows the DRIFT spectra of a full-grown zeolite Beta and of the two mesoporous materials. All spectra exhibit a clear difference in bonding between the various structures. The absorption bands at 525 cm−1 and 575 cm−1 are typical for a full-grown zeolite Beta since they present the five and six membered rings in the zeolite structure [44–46]. In the spectrum of MB-Q only one signal at a wave number of 575 cm−1 can be observed. Therefore no true zeolitic characteristics are present since only one of the two typical zeolite Beta signals is present. This was confirmed by TGA measurements that already indicated that the zeolitic properties in MB-Q are less pronounced. On the other hand, when the zeolite seeds were slowly cooled (MB-S), both bands at 525 and 575 cm−1 can be observed in the DRIFT spectrum (Fig. 3c). Also TGA results indicate, to some extent, the presence of zeolitic characteristics in this sample. The absorption band at 1230 cm−1 is the result of the asymmetric stretching of strained siloxane bridges at the surface of the pore walls. The sharpness of this signal can be related to the presence of a particular siloxane bridge having the same bond length all over

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**Table 1**

Porosity data derived from N2-sorption measurements at 77 K and aluminium contents determined by EPMA.

<table>
<thead>
<tr>
<th></th>
<th>Mesopore area (m²/g)</th>
<th>Micropore volume (mL/g)</th>
<th>Mesopore volume (mL/g)</th>
<th>Al-content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite Beta</td>
<td>99</td>
<td>0.229</td>
<td>0.167</td>
<td>3.5</td>
</tr>
<tr>
<td>MB-Q</td>
<td>331</td>
<td>0.064</td>
<td>1.065</td>
<td>1.0</td>
</tr>
<tr>
<td>MB-S</td>
<td>259</td>
<td>0.166</td>
<td>0.642</td>
<td>1.6</td>
</tr>
</tbody>
</table>
the structure. The 1100 cm\(^{-1}\) signal is a superposition of different silicate absorption bands where the major contribution is the asymmetric silicate stretching vibration\(^{[52]}\). MB-Q shows a broadening of the signal at 1100 cm\(^{-1}\) and only a weak shoulder at 1230 cm\(^{-1}\) indicating less uniform bonds in the MB-Q mesoporous structure which suggests a weak presence or the absence of crystallinity. However, the band for MB-S at 1100 cm\(^{-1}\) possesses a similar broadening as the full-grown zeolite. Moreover, also the signal at 1230 cm\(^{-1}\) can be distinguished although this has a lower intensity than in the full-grown zeolite. This implies that this structure is formed out of more uniform bonds that closely resemble that of zeolite Beta\(^{[53–55]}\).

Since zeolitic properties can be observed on a short range it is interesting to look at the crystallinity of the samples on a long range. X-ray diffraction patterns are used to investigate this ordering. The different X-ray diffractograms are given in Fig. 4. The diffraction pattern of MB-S (Fig. 4c) shows clear peaks that can be assigned to zeolite Beta characteristics. The distinct signal in the range 6.5–8.5° 2θ is an indication of a highly distorted structure due to the presence of different isomorphs in the structure\(^{[54]}\). The Beta character is less clear in the diffraction pattern of MB-Q. Only weak signals of the zeolite Beta structure can be observed around 7° and 22° 2θ. These peaks are superimposed on a broad signal between 20° and 25° 2θ associated to the presence of amorphous silica.

Results from TGA, DRIFT and XRD measurements lead to the conclusion that both materials, synthesized from zeolite Beta precursor solutions, possess zeolitic features to some extent. Nevertheless, the zeolite character is much more pronounced in the MB-S sample. Moreover, as observed with N\(_2\)-sorption, a higher zeolite character results in a higher uniformity of the pore structure, although there is a decrease in mesopore volume. The difference between both materials is caused by a variation in the cooling process after ageing of the seeds. The properties of the MB-S are the most promising in all different characterization techniques. Possibly, the properties of these materials are related to the char-
EDX measurements of different areas (within nanoparticles and outside) indicate that the aluminium is especially concentrated in the zeolite nanoparticles.

As to the size of the nanoparticles in the composite materials, there is no significant difference between both structures. Certainly, the TEM measurements indicate that the amount of zeolite seeds embedded in MB-S (Fig. 5a) is higher than in MB-Q (Fig. 5b) and the spacing between neighbouring nanoparticles is shorter for the MB-S sample. A HRTEM image of the MB-S sample (Fig. 6) shows that the zeolite nanoparticles are closely packed and that the mesoporous amorphous phase is situated in between those nanoparticles. Therefore, the increased zeolitic characteristics of MB-S with respect to MB-Q are most likely the result of a larger amount of zeolite nanoparticles embedded in the amorphous phase. Slow cooling of the precursor solution leads to the formation of more particles with similar sizes.

4. Conclusions

Composite micro- and mesoporous materials are formed using zeolite Beta nanoparticles without the use of a structure directing agent for the formation of the mesopores. A substantial difference with the previously published work using silicalite-1 nanoparticles [43] is situated in the zeolitic characteristics and the influence of the cooling process on the final characteristics. Both TGA and DRIFT measurements proved zeolitic properties on a short range, while XRD patterns gave evidence for long range ordering when slow cooling was applied. A clear effect of the cooling rate of the seeds, after the ageing at an elevated temperature, has been demonstrated. Although both quenched and slow cooled materials show zeolitic properties on a short and long range, there is still a substantial difference in their characteristics. Slow cooling instead of quenching leads to a structure with higher microporosity, higher aluminium content and better zeolitic characteristics. TEM measurements indicate that by slowly cooling the precursor solution, more zeolitic nanoparticles are formed which leads to more abundant zeolitic phases in the composite material. In this work, a synthesis method with important economical and ecological advantages has been used, leading to the formation of composite micro- and mesoporous materials with incorporated aluminium and zeolitic characteristics.

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