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In situ surfactant removal from MCM-type mesostructures by ozone treatment

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Surfactant removal from MCM-41 mesostructures using ozone produced by an ozone generator is reported. Traces of water are needed to start the degradation of the mesostructure. Ozone treatment of the mesostructure powder, containing traces of water, results in a highly exothermic reaction that cannot be controlled. Suspending the mesostructure in water and treating it with ozone results in mesoporous MCM-41 after 14 h. In addition, *in situ* ozone treatment of the as-prepared MCM-41 mesostructure in its mother liquor also results in mesoporous MCM-41. Ozone-treated samples have larger pores than traditionally calcined samples.

Introduction

Since its discovery in 1992, MCM-41 has become the most popular member of the M41S family of mesoporous silicate and aluminosilicate materials.[1] MCM-41 consists of a regular pore system, hexagonally arranged, with a narrow pore size distribution. Its pore diameter can be varied between 2 and 10 nm. A high specific surface area of up to $1500\ \mathrm{m^2\ g^{-1}}$, a specific pore volume of up to $1.3\ \mathrm{mL\ g^{-1}}$ and a high thermal stability make the material potentially suitable for a great number of applications, *e.g.* catalysis,[2] membrane separation,[3,4] selective adsorption of gases and liquids[5] and electronic applications.[6] Several metals have been incorporated into the siliceous framework, such as titanium,[7] vanadium[8] and zirconium.[9] Many publications report on the formation mechanism of the MCM mesostructure. A summary of the state of the art can be found in recently published reviews by Ying *et al.*[2] and Lindén *et al.*[10] However, there are only a limited number of studies specifically dealing with the removal of the organic material from the as-synthesised mesostructure.[11–15] Thermal methods are commonly used to transform the organosilica composite material into mesoporous MCM-41. This involves heating the dry mesostructure under a flow of air or oxygen with a ramp of $1\ \mathrm{K\ min^{-1}}$ to 550 °C and holding it at this temperature for several hours.[2,3] In addition, solvent, plasma and supercritical fluid extraction have also been used to remove the organic surfactant from the mesostructure.[11]

Ozone is commonly used in environmental technology, *e.g.* ozone treatment of water[16] for purification, in physics for cleaning polished flat surfaces or in organic syntheses for preparing special carbonyl compounds.[17] It has been also used to test the stability of ODS-modified silica surfaces.[18] Recently, we reported on surfactant removal to form MCM-41 type materials by use of ozone.[19] In this study, the dry silica mesostructure was treated by ozone using a UV lamp whose wavelength was known to produce ozone from atmospheric oxygen. After ozone treatment, the pore size of the ozone-treated sample was larger, the pore size distribution narrower, and the hexagonal ordered pore system showed a much higher long-range order in the XRD spectra compared to ordinary calcined MCM-41. However, the amount of ozone produced could not be adjusted and the reaction took quite a long time due to the low ozone concentration. To speed up the reaction by increasing the amount of ozone produced, an ozone generator was used in the present study, where structure, surface area and pore size distribution are followed as a function of the duration of the ozone treatment.

Experimental

Preparation of the MCM-41 mesostructure

The MCM-41 mesostructure was prepared according to the procedure of Grün *et al.*[20] The quaternary ammonium salt, 2.40 g of cetyltrimethylammonium bromide (CTABr) $[\mathrm{CH_3(CH_2)_{15}N(CH_3)_3Br}]$ (Aldrich) was dissolved in 120 ml of distilled water. Once the surfactant was dissolved, 8 ml of aqueous ammonia (32%, Merck) followed by 10 ml of tetraethyl orthosilicate (TEOS) (98%, Aldrich) was added. The solution was stirred for 60 min during which time a white precipitate was formed. The precipitate was recovered by suction filtration and washed using distilled water until a pH of 7 was obtained for the filtered liquid. The mesostructure was dried in a vacuum oven at 90 °C for 12 h. The batch was divided into two parts and stored in a closed container (mesostructure 1) or in an open beaker (mesostructure 2) for several weeks.

Ozonation

Ozone was produced using an ozone generator (OZONEUR OZAT®, Type CFS-1; Ozonia, France). Oxygen ($>98\%$) was introduced into the generator at a pressure of 1 bar, a gas flow of $6\ \mathrm{l\ h^{-1}}$and energy of 250 W.

Ozonation of the dried samples

Ozone was introduced into an ampoule containing the dried mesostructure *via* a glass tube to around 1 cm from the sample. Around 4.0 g of sample was used for these experiments. The samples were either completely dried (mesostructure 1) or left with traces (*ca.* 2%) of water prior to ozone treatment (mesostructure 2).

Ozonation of the resuspended MCM-41 mesostructure

100 mL of deionized water was added to 1.0 g of the MCM-41 mesostructure (mesostructure 2) and the mixture agitated with

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a magnetic stirrer. The hydrophobic mesostructure floated on the surface of the water. Ozone was introduced into the mesostructure suspension by bubbling the gas through the liquid *via* a glass tube. After approximately 30 min, the hydrophobic mesostructure became hydrophilic and the material became totally suspended in the water. For further characterisation, *ca.* 50 mL aliquots of the suspension were taken after 2, 4, 10, 14 and 26 h, filtered through a glass frit (G4) and the solid obtained washed with water. The samples were then dried for 12 h at 50 °C in a vacuum oven.

In situ ozonation of the MCM-41 reaction suspension

For the *in situ* ozone treatment, the as-prepared mesostructure was used in its reaction suspension without further pre-treatment (mesostructure 3). Ozone was produced as described above and added to the reaction suspension under agitation with a magnetic stirrer. For further characterisation, approx. 50 mL aliquots of the suspension were taken after 8, 17.5, and 27.5 h, filtrated through a glass frit (G4) and the solid obtained washed with water. The samples were dried for 12 h at 50 °C in a vacuum oven.

Thermal calcination of the MCM-41 mesostructure

From each batch, about 1.0 g of the mesostructure was calcined under an airflow (heating rate: 1 K min^{-1}, heating ramp: 5 h at 550 °C) for comparison with the ozone-treated samples (calcined 2 and calcined 3).

Further characterisation

Nitrogen sorption measurements were performed on a Quantachrome Autosorb 6B instrument (Quantachrome Corporation, Boynton Beach, FL, USA). Before measurement, all samples were evacuated at 323 K for at least 12 h under a residual pressure lower than 2.6 Pa. Surface areas were determined by using the BET equation. The BJH method was used to compare the pore size distributions of the various samples.

X-Ray diffraction patterns were recorded on a STOE STADI P transmission XRD using Cu-Kα_1 radiation of wavelength 0.154 nm. Diffraction data were recorded between 1.000 and 10.990° (2θ) at intervals of 0.010°. A scanning speed of 360 s step^{-1} was used.

Elemental analyses were performed using a Heraeus CHN-rapid analyser (Heraeus, Hanau, Germany) at a combustion temperature of 1273 K.

The organic content of the samples was determined by thermogravimetry (TG and DTA) using a Linseis L81 thermal analyser (Linseis, Selb, Germany). The samples were heated under atmospheric conditions at a rate of 10 K min^{-1}, from room temperature up to 1273 K. The mass loss was calculated between 473 and 1273 K. All calculations were done using the Sta 1.1. software package (*Linseis Datenauswertung für Windows*, version 2.18, Linseis GmbH, Selb, Germany, 1991–1993).

Results and discussion

Treatment of dried samples

It was impossible to transform the dry mesostructure 1 into mesoporous MCM-41, even after two weeks of ozonation. Nitrogen sorption isotherms (not shown) gave a type II isotherm, typical of a nonporous material, showing that no porosity was created. Treating the mesostructure that contained traces of water (mesostructure 2) resulted in a highly exothermic reaction ('uncontrolled ozonation'). After a few moments of ozone treatment, the sample turned bright red due to the high reaction temperature. From this coloration, a sample temperature of 800 °C can be estimated at this point. The sample thus prepared showed a specific surface area of 332 $\mathrm{m}^2\ \mathrm{g}^{-1}$ which corresponds to about 30% of the porosity of traditionally calcined MCM-41 (Fig. 1 and Table 1). The only difference between the treatments is the water content of the mesostructure. This leads to the conclusion that water seems to play a key role in the degradation of the mesostructure by using ozone.

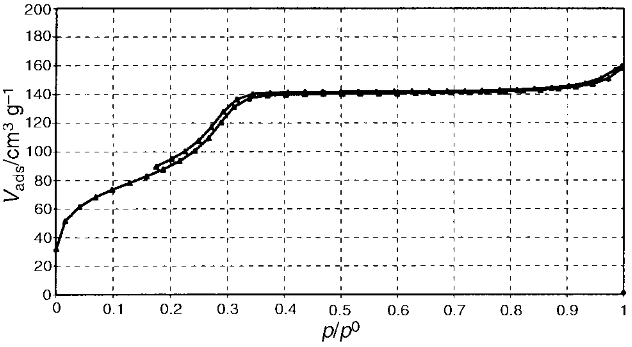

Fig. 1 Nitrogen sorption isotherms at 77 K of the partly porous MCM-41 which was subjected to uncontrolled ozonation (mesostructure 2).

Treatment of dried samples resuspended in water

In order to both provide water and control the exothermic character of the reaction, the mesostructure was suspended in water before being treated with ozone. The MCM-41 mesostructure powder (mesostructure 2) was added to water in a round-bottomed flask and stirred with a magnetic stirrer. The powder floated on the surface due to its hydrophobic character. After approximately 30 min of ozonation, the mesostructure started to become suspendable, which indicated the loss of the hydrophobic carbon chains on the external surface of the mesostructure particles. Ozonation was continued for several hours and portions of the sample were extracted after 2, 4, 10, 14, and 26 h for further characterisation. Fig. 2 shows the nitrogen sorption isotherms at 77 K for

Table 1 Nitrogen sorption at 77 K

Sample	Specific surface area, BET/$\mathrm{m}^2\ \mathrm{g}^{-1}$	Specific pore volume, Gurwich/$\mathrm{cm}^3\ \mathrm{g}^{-1}$	Average pore diameter, BJH desorption/ nm
Mesostructures 1 and 2	—	—	—
Uncontrolled ozonation	332	0.234	2.5
Calcined 2	894	0.615	2.4
Re-suspended, 2 h	106	0.101	1.8
Re-suspended, 4 h	63	0.061	2.2
Re-suspended, 10 h	929	0.679	2.4
Re-suspended, 14 h	1019	0.823	2.7
Re-suspended, 26 h	642	0.367	1.3
Mesostructure 3	—	—	—
Calcined 3	969	0.758	2.5
Reaction suspension, 8 h	234	0.222	2.5
Reaction suspension, 17.5 h	642	0.474	2.3
Reaction suspension, 27.5 h	1101	0.916	2.5

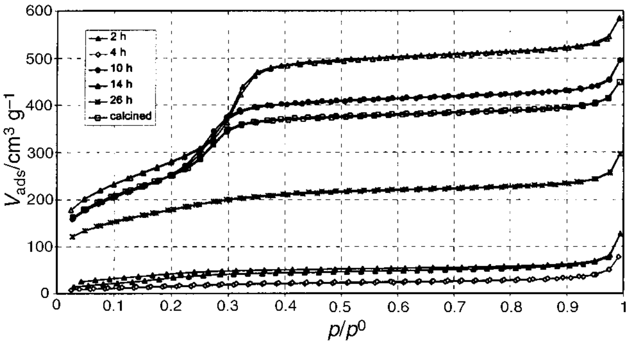

Fig. 2 Nitrogen sorption isotherms at 77 K of the calcined (calcined 2) and resuspended MCM-41 mesostructure 2 after ozonation.

the various ozonated samples and for a sample calcined under a flow of air at 550 °C.

Nitrogen sorption measurements for samples treated for up to 14 h give type IV isotherms according to IUPAC nomenclature.[21] At the outset of the ozone treatment (2 and 4 h), the adsorption and desorption branches of the nitrogen sorption isotherm do not meet. This is may be due to an insufficient equilibrium time during the measurement, however, this phenomenon seems to be characteristic of the presence of chains inside the pore structure.[15] After 14 h of ozonation, most of the organic content was removed, which is reflected by the carbon content of 5.52%, compared to 29.26% in the mesostructure and 0.41% in the ordinary calcined sample. The specific surface area (BET) and the specific pore volume at $p/p^0 = 0.95$ (applying the Gurvich rule) reach their maxima after 14 h (Table 1), while further ozonation (up to 26 h) leads to a collapse in the pore structure. This collapse is demonstrated by nitrogen sorption measurements at 77 K, which show that the specific surface area and the pore volume decrease drastically. In addition, the XRD pattern of the sample ozonated for 26 h shows a loss in the long-range order of the pore system (Fig. 3). The nitrogen sorption properties of this latter sample are mainly characterised by a type I isotherm, typical of microporous materials. The mesostructure calcined at 550 °C under a flow of dry air gives a type IV isotherm, typical of mesoporous materials. However, the adsorbed volume at $p/p^0 = 0.95$ and the specific surface area, BET, are lower compared to the ozone-treated sample. In addition, the steep increase in the adsorbed volume due to the pore filling of the ozonated sample is shifted to higher values compared to the ordinary calcined sample (inflection point at $p/p^0 = 0.33$ instead of $p/p^0 = 0.28$).

The average pore diameter (calculated according to the BJH method from the desorption branch) increases from 1.8 nm after 2 h to 2.7 nm after 14 h, which indicates that in the initial stages of the ozone treatment some of the organic alkyl chains may still remain in the pore system and thus decrease its diameter. The mass loss, determined by thermogravimetry between 200 and 1000 °C, and the elemental analysis show that, even after 26 h of ozonation, some of the organics are still present in the silica framework [mass loss: $\Delta m = 9.3\%$ (ozonated), $\Delta m = 4.4\%$ (calcined); carbon content 1.45% (ozonated) *vs.* 0.41% (calcined), see Table 2]. The increase in the mass loss from 6.0% (14 h) to 9.3% (26 h) can be explained by a higher OH-group density in the latter sample, which is reflected by a decrease in the carbon content (5.52 *vs.* 1.45%) and an increase in the hydrogen content (1.53 *vs.* 1.63%). Compared to the ordinary calcined sample, the ozone-treated sample shows a larger average pore diameter after 14 h (2.7 instead of 2.4 nm; BJH, desorption branch). It seems that the pore system of the mesoporous MCM-41 does not shrink as much when treated with ozone as it does for ordinary calcined samples. This is also reflected in the XRD patterns (Fig. 3 and Table 3) of the samples, where the (100) reflection decreases from 4.07 nm for the mesostructure to 3.68 nm after calcination and 3.89 nm after ozonation for 14 h. This corresponds to the pore size distribution calculated from the nitrogen sorption isotherms at 77 K. As seen from the nitrogen sorption isotherms, ozonation in an aqueous suspension leads to a MCM-41 material with a higher surface area pore volume and pore diameter than ordinary calcined MCM-41. However, the long-range order of the pore system does not appear to be improved by this treatment, contrary to what was observed for the UV-generated ozone-treated sample.[18]

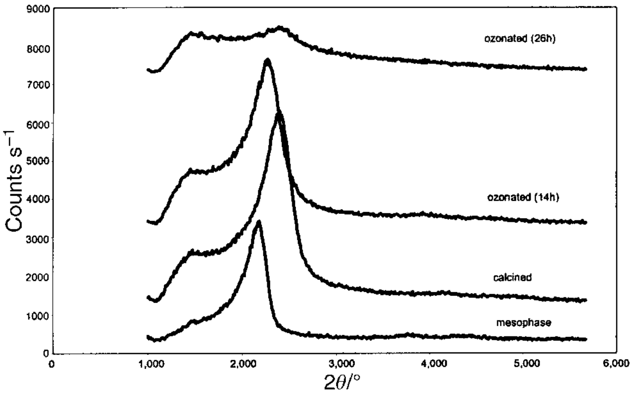

Fig. 3 X-Ray diffraction patterns of the resuspended MCM-41 mesostructure 2, the traditionally calcined sample (calcined 2) and the ozonated sample.

Table 2 Mass loss TG and elemental analyses

Sample	Relative mass loss 200–1000 °C (%)	Carbon content (%)	Hydrogen content (%)	Nitrogen content (%)
Mesostructure 2	36.4	29.26	6.60	1.72
Calcined 2	4.4	0.41	0.99	<0.1
Re-suspended, 2 h	26.6	17.79	4.07	0.99
Re-suspended, 4 h	23.6	15.54	3.67	0.87
Re-suspended, 10 h	8.0	6.36	2.28	0.19
Re-suspended, 14 h	6.0	5.52	1.53	0.10
Re-suspended, 26 h	9.3	1.45	1.63	0.12
Mesostructure 3	43.9	29.6	6.56	1.80
Calcined 3	4.6	0.35	0.78	0.10
Reaction suspension, 8 h	19.4	11.13	2.81	0.92
Reaction suspension, 17.5 h	8.6	5.04	1.93	0.21
Reaction suspension, 27.5 h	7.2	5.63	1.96	0.12

Treatment of samples *in situ* (still in their mother liquor)

To avoid filtration, washing and drying of the mesostructure after its preparation, we ozonated the as-synthesized meso-

Table 3 X-Ray diffraction data

Sample	(100)/nm	(110)/nm	(200)/nm
Mesostructure 2	4.07	2.34	2.02
Calcined 2	3.68	2.12	1.80
Re-suspended, 14 h	3.89	2.24	1.91
Re-suspended, 26 h	—	—	—
Mesostructure 3	4.12	2.35	2.03
Calcined 3	3.75	2.15	1.85
Reaction suspension, 27.5 h	3.72	—	—

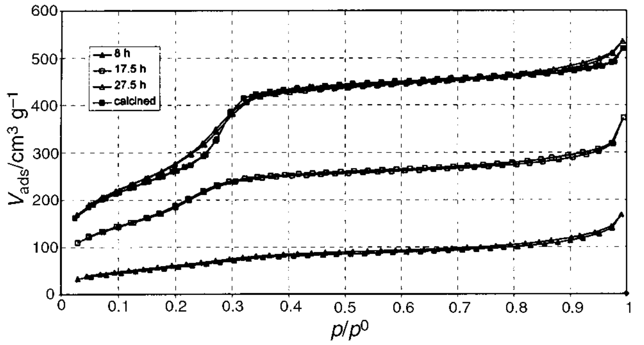

Fig. 4 Nitrogen sorption isotherms at 77 K of the MCM-41 mesostructure 3, the calcined sample (calcined 3) and the sample which was ozonated in its reaction suspension

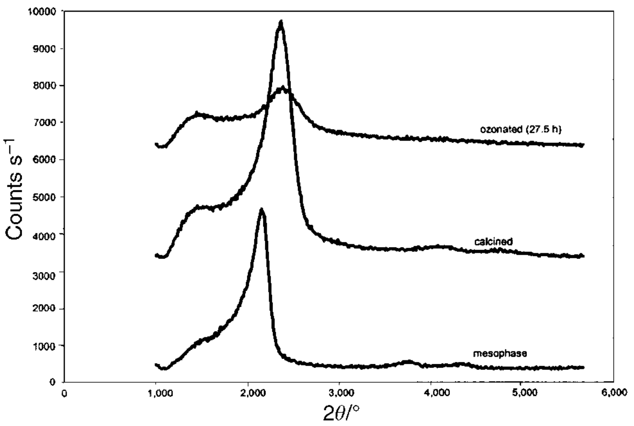

Fig. 5 X-Ray diffraction pattern of the MCM-41 mesostructure 3, calcined sample (calcined 3) and the sample which has been ozonated in its reaction suspension.

structure, still suspended in its reaction mixture, without any purification (mesostructure 3). The mesostructure was ozone-treated for 27.5 h and samples were taken after 8, 17.5, and 27.5 h for further characterisation. Nitrogen sorption measurements gave type IV isotherms for all the samples, typical of mesoporous materials, according to the BDDT classification (Fig. 4).

The isotherm for the sample after 8 hours of ozone treatment does not close for the same reasons as that quoted above. The nitrogen sorption measurements give very similar results for the calcined (calcined 3) and the ozonated (27.5 hours) sample. In contrast with the results shown with the re-suspended sample, the specific surface areas as well as the average pore diameter are almost the same for both kinds of treatment (Table 1). An insufficient ozone treatment can be excluded as a reason for this effect, since the carbon contents of these samples are similar to that of the re-suspended samples described above.

One effect might be that the ammonia, still present in the reaction mixture during its ozonation, might lead to a higher condensation rate, and thus to shrinking in the pore system. A similar technique is used to prepare spherical silica particles by emulsion-polymerisation of polyethoxysiloxanes, where the condensation rate is afterwards increased by heating the particle suspension in aqueous ammonia at 70 °C.[22] The increase of the adsorbed volume due to the pore filling in the ozonated sample is only slightly shifted to higher values ($p/p^0 = 0.26$ instead of $p/p^0 = 0.28$). The corresponding XRD pattern (Fig. 5) gives for the mesostructure a typical pattern of MCM-41 with hexagonal array of the pore system. The values of the (100), (110), (200) peaks are given in Table .

Mechanism of the ozonation

Under most conditions, the samples produced by ozone treatment have surface areas and pore volumes larger than those of ordinary calcined samples (even if the difference is small for the *in situ* treated samples). The "best" sample in terms of surface area, narrowness of pore size distribution and XRD structure was that treated with the UV lamp.[19] This could be due to the mechanism of ozone action, which can be different from one method to the next.[23] Indeed, when ozone is the sole reagent, it is not reactive toward aliphatic chains or quaternary ammonium: there is no direct reaction. This is the reason why no degradation was observed with the dry sample. The main action of ozone is through the attack of radicals produced by the decomposition of the ozone molecule. These radicals can be formed by two ways. The first is reaction of an ozone molecule with a hydroxy ion according to equation 1.

$$O_3 + OH^- \rightarrow HO_2^{\bullet} + O_2^{\bullet -} \qquad (1)$$

This reaction is indeed favoured at high pH, which is the case for the synthesis of the mesostructures, making possible the *in situ* treatment. Moreover, despite washing, hydroxy ions are probably still present inside the channels of the mesostructure, which explains the reaction observed when the samples are not dried or are resuspended in pure water.

The second way to produce the radicals is with the help of a UV lamp. UV lamps like that used in the preceding study have two main wavelengths: one around 180 nm to produce the ozone molecule, and another at 254 nm which decomposes the ozone molecule following equation 2,[24]

$$O_3 \rightarrow O + O_2\ (1\Delta g) \qquad (2)$$

where O_2 $(1\Delta g)$ is singlet oxygen, and equation 3.

$$O + H_2O \rightarrow 2HO^{\bullet} \qquad (3)$$

The first method of producing radicals leads to consumption of hydroxy ions (and also of ammonia, which is transformed to nitrates), decreasing the pH and thus accelerating the condensation rate, leading to a shrinking of the pore system. This could explain the slightly lower quality of the samples prepared using the ozone generator.

Conclusion

Ozone treatment is a useful tool for the removal of the surfactant from the MCM-41 mesostructure. By producing ozone with an ozone generator instead of a UV lamp, it is possible remove the surfactant template within only one day. As envisaged in our preceding paper, the elimination of the template is possible in the synthesis medium, which limits the number of synthesis steps. However, one must be sure not to destroy the porosity by treating the sample too long. This aspect requires further study before this method can be considered for use as a routine method.

Although the quality of the porosity is not highly affected by the type of treatment, the ozone-treated samples seem to show a higher Si–OH group density than the ordinary calcined sample. Thus, the synthesis and ozonation of spherical organosilica beads,[25,26] might lead to a porous material with a higher OH group density than ordinary calcined samples. Modification of this material with alkyl chains might lead to so-called reversed-phase silica beads with a higher carbon content, and thus a greater utility for chromatographic separations, such as high performance liquid chromatography (HPLC) and capillary electroendosmotic chromatography (CEC).

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