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Synthesis and characterization of large-pore vinyl-functionalized mesoporous silica SBA-15†

Yanqin Wang, Bodo Zibrowius, Chia-min Yang, Bernd Spliethoff and Ferdi Schüth*
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany.
E-mail: schueth@mpi-muelheim.mpg.de

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Ordered mesoporous silicas SBA-15 with high loadings of pendant vinyl groups have been synthesized *via* co-condensation of tetraethoxysilane (TEOS) and triethoxyvinylsilane (TEVS) templated with a triblock copolymer.

Shortly after the discovery of ordered mesoporous silica, a quest for ordered mesoporous organic–inorganic composites with a high content of organic groups uniformly distributed over the ordered structure started.[1–4] A good way to prepare ordered silicas with high loadings of pendant organic groups is based on the surfactant-templated co-condensation of organotrialkoxysilane with another silica source, such as a tetraalkoxysilane.[5–8] Vinyl-functionalized mesoporous silica was synthesized in the presence of cetyltrimethylammonium surfactant by this route.[7,8] However, the pore sizes of these materials are relatively small (less than 3 nm) and it would be desirable to have access to vinyl-silica with larger pores.

The aim of this work was to synthesize vinyl-functionalized mesoporous silica SBA-15, using Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as template. Synthesis was done under true liquid crystal templating (TLCT) conditions, as had been used for the preparation of mesoporous silica[9] and ethanesilica[10] using triblock copolymer templates. The effect of the addition of inorganic salts, which is known to improve the order of the materials,[11] on the formation of mesostructure was also studied.

In a typical synthesis, the pre-mixed TEVS and TEOS were added to an aqueous HCl solution under stirring before P123 was added to the mixture. The ethanol resulting from the hydrolysis of TEOS and TEVS was removed under vacuum (rotary evaporator). The resulting viscous mixture was hydrothermally treated at 98 °C for 24 h. The molar ratio was x TEVS : $(1 - x)$ TEOS : 0.11 P123 : (0.009–0.9) HCl : 44.4 H_2O, where x was 0.2 or 0.4 for V20/SBA-15 and V40/SBA-15, respectively. P123 was removed by treatment with 48 wt% H_2SO_4. For the investigation of the influence of inorganic salts on the mesostructure, the calculated amount of the aqueous solution of inorganic salt was added to the mixture of HCl and silica precursors before the addition of P123.‡

Solid-state ^{29}Si NMR spectroscopy was used to monitor the condensation in initial experiments, showing that well condensed samples are obtained at HCl concentrations of 0.1 and 1 M, but not for 0.01 M HCl. The following experiments were all carried out using 0.1 M HCl. Whereas the XRD pattern (see Fig. 1s†) of V20/SBA-15 shows one sharp and one broad peak corresponding to a periodicity of 9.1 nm and 4.6 nm, respectively, only one peak corresponding to 9.0 nm is observed for V40/SBA-15. These diffraction patterns indicate a regular pore size, but do not necessarily correspond to a pronounced hexagonal ordering of the pores. TEM analysis (Fig. 1a) further confirms the suggestion of uniformly sized pores in the structure, and it also shows a rather disordered structure for the V20/SBA-15 sample.

However, addition of $MgCl_2$ to the synthesis mixture leads to the development of a well-ordered hexagonal structure (molar ratio of $MgCl_2/P123 = 0.5$). The XRD pattern (see Fig. 1s†) exhibits three well-resolved reflections, which can be indexed as (100), (110) and (200) in a *P*6*m* structure. The TEM image (Fig. 1b) clearly shows the ordered channels of this sample. The unit cell parameter calculated from the (100) reflection of the XRD pattern is *ca.* 10.4 nm. For V40/SBA-15, a sharper (100) reflection is obtained in the presence of $MgCl_2$, but higher order reflections are still absent. The molar ratio of $MgCl_2/P123$ was varied from 0.25 to 1.0, and the ordered structure was obtained when the ratio exceeded 0.5. Other inorganic salts, such as $Ni(CH_3COO)_2$ and $Co(CH_3COO)_2$ were also tested. They showed a similar effect on the mesostructure. This suggests that it is not the action of a specific ion which favors the formation of an ordered structure, but rather an ionic strength effect. The formation of liquid crystalline phases is known to be dependent on ionic strength. Our syntheses in the absence of additional salts were performed at relatively low total ionic strength due to the rather diluted hydrochloric acid. Hence, it is not surprising that increasing the ionic strength by the addition of an inert salt to the synthesis mixture induces a higher degree of order. Previous work has already demonstrated the effect of inorganic salts on the formation of an ordered structure by increasing the interaction of silica precursor (or transition metal precursor) with polymer.[11] However, in our case, under conditions of relatively low ionic strength in the pure system, the salt may just assist in the formation of the mesophase by a salting out effect.

Nitrogen sorption isotherms of V20/SBA-15 samples after treatment with H_2SO_4 are shown in Fig. 2. The isotherms are of type IV with clear H_1-type hysteresis loops at high relative pressure, indicating the presence of large pores with narrow pore size distributions. Table 1 gives the textural properties of vinyl-functionalized SBA-15 materials. The BET surface area increases, but pore volume and pore size decrease with increasing concentra-

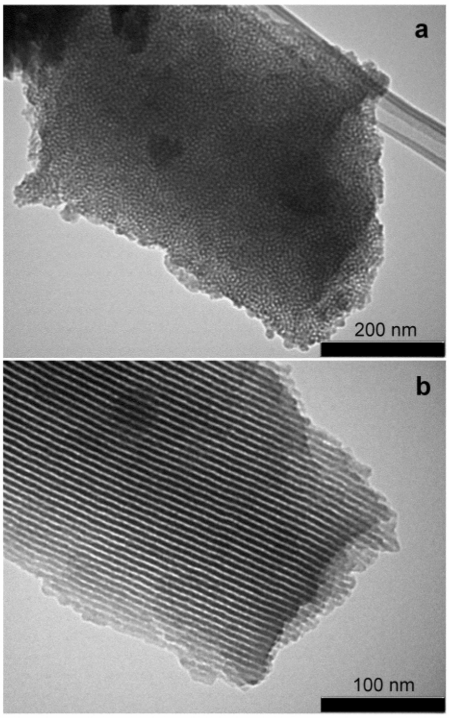

Fig. 1 TEM images of the V20/SBA-15 without (a) or with (b) $MgCl_2$.

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† Electronic supplementary information (ESI) available: Figure 1s. See http://www.rsc.org/suppdata/cc/b3/b309578a/

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tion of TEVS, independent of the addition of inorganic salt. The decrease of the pore size with increasing concentration of TEVS can not be attributed exclusively to the occupation of space inside the pore with vinyl groups. It might also be due to the co-surfactant effect of TEVS, which interacts with the template and reduces the diameter of the micelles. The samples synthesized in the presence of additional salt typically have larger pore sizes and higher pore volumes, as can be seen in Table 1 and Fig. 2.

The incorporation of vinyl groups in the mesoporous materials and the removal of P123 were confirmed by solid-state NMR spectroscopy. Fig. 3 (a and b) shows the ^{13}C CP/MAS NMR spectra of V40/SBA-15 before and after the treatment with H_2SO_4. The lines at 130 and 137 ppm are attributed to the carbons of vinyl groups, and the lines at 17, 70–76 ppm are attributed to carbons of P123. It can be inferred from the spectra that most of the P123 template is removed by sulfuric acid. Changes can also be seen in the vinyl-carbon range, which may indicate reactions during template removal, for instance, as described by Gibbons *et al.*[12] Further work is in progress to clarify this point.

Fig. 3 (c and d) shows the ^{29}Si MAS NMR spectra of the same V40/SBA-15 samples. The lines of the T groups indicate the presence of organosilane groups in the material. After the treatment with sulfuric acid, there is no obvious change of T-group lines, indicating that the Si–C bonds are not affected. The increase of the Q^4/Q^3 and T^3/T^2 ratios after the acid treatment points to a further condensation brought about by the strongly acidic conditions in 48 wt% H_2SO_4. This effect has also been observed during template removal with sulfuric acid from as-prepared CN-functionalized SBA-15.[13]

In conclusion, large-pore vinyl-functionalized SBA-15 has been prepared with high loadings of vinyl groups. By addition of inorganic salt under suitable conditions, the normally obtained disordered mesoporous structure was altered to a hexagonal structure with a high degree of order.

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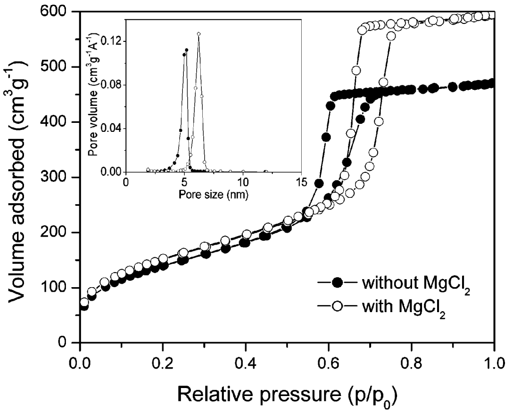

Fig. 2 N_2 sorption isotherms and the derived BJH mesopore size distributions for V20/SBA-15 samples after treatment with H_2SO_4.

Table 1 Properties of H_2SO_4-treated vinyl-functionalized silicas prepared with or without $MgCl_2$

Sample	a_0/nm	S_{BET}/m^2 g^{-1}	V/cm^{3}g^{-1}	D/nm	t/nm
V20	10.3	414–518	0.67–0.78	5.2–5.6	4.7–5.1
V20-MgCl$_2$	10.4	480–560	0.75–0.91	5.7–6.2	4.2–4.7
V40	10.2	502–583	0.63–0.74	4.0–4.4	5.8–6.2
V40-MgCl$_2$	10.2	536–643	0.71–0.75	4.2–4.6	5.4–6.0

a_0: cell parameter; V: pore volume; D: pore diameter; t: wall thickness.

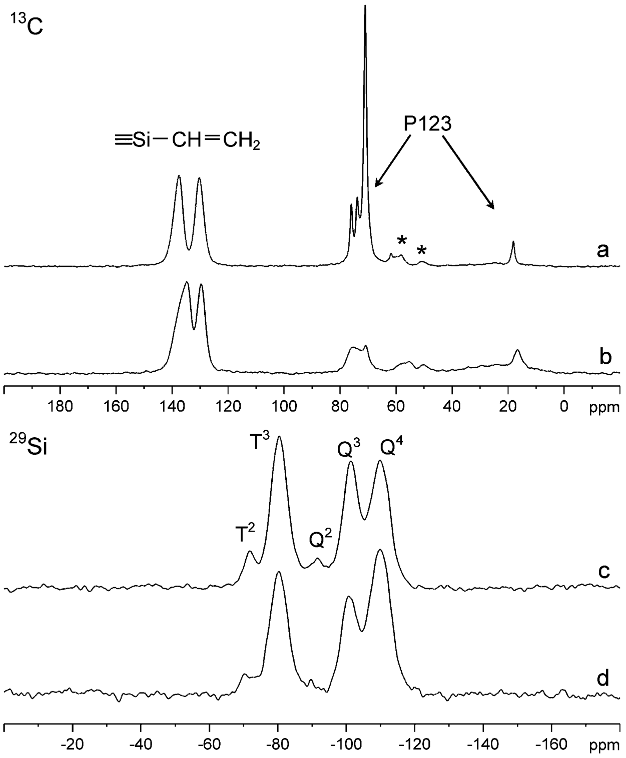

Fig. 3 ^{13}C CP/MAS NMR (a,b) and ^{29}Si MAS NMR (c,d) of as-synthesized (a,c) and H_2SO_4-treated (b,d) V40/SBA-15 materials with $MgCl_2$. Asterisks denote spinning sidebands.

Notes and references

‡ All syntheses and analyses were repeated at least three times. While the *d*-spacings were reproducible within 1 Å, sorption data have the scatter indicated in the table. This is probably due to the strong sensitivity of the template removal to slight changes of the conditions.

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