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MESOSTRUCTURED MATERIALS

Water intrusion-extrusion in silicalite-1 with tunable mesoporosity prepared in fluoride medium

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Abstract Experimental water intrusion–extrusion isotherms were performed at room temperature on mesoporous silicalite-1 samples, prepared in fluoride medium and using carbon black or surfactant, [3-(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride, as porogen and templating agents, respectively. The increase of the porous volume observed for the silicalite-1 sample prepared in the presence of carbon black leads to an increase of the water intruded volume at high pressure (100 MPa). Therefore, the amount of stored energy in this water–zeolite system is greater than for a conventional "water–silicalite-1" system. However, the fluoride route appears to be a less effective method than the alkaline route.

Introduction

Recently, a new field of application concerning the energetics was highlighted for hydrophobic zeolites in particular for silicalite-1 [1]. In these materials, the adsorption of water is extremely weak when the pressure is below the water saturation vapor pressure. By submitting these systems to an increasing hydrostatic pressure, the intrusion of the liquid into the pores of the solid is observed. During the intrusion of water, a large interface carrying the surface energy is created. Depending on the external pressure, the molecules of the liquid can penetrate or are expelled from the cavities. The water condensation (intrusion) is obtained by applying high hydraulic pressure, approximately of 100 MPa for silicalite-1. The "water–silicalite-1" system constitutes a real molecular spring, which can store and restore mechanical energy (≈ 10 J g^{-1}). For increasing the stored energy, it is important to increase the water intruded volume and therefore the pore volume of the zeolite. During the past decade, significant efforts have been devoted for developing methods that introduce mesoporosity in zeolite materials by different approaches as reported in two recent reviews [2, 3]. In practice, the mesopores can be of two types, i.e., inter- or intracrystalline pores. The first one can be obtained by aggregation of nanosized zeolite crystals and the second one by creating an additional porosity in each individual crystal.

In a very recent work [4], we have reported the synthesis of mesoporous silicalite-1 in hydroxide medium using carbon black [5] or surfactant, [3-(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride [6], as porogen and templating agents, respectively. The porous volume of silicalite-1 was successfully increased by the creation of an additional porosity (mesoporosity) but also by a slight increase of the microporous volume which led to an increase of the intruded volume at high pressure (~ 100 MPa) and thus to an increase of the stored energy compared to a classical silicalite-1 sample. However, silicalite-1 prepared in hydroxide medium can display defect sites (silanol groups) [7, 8] and such defects lead to a decrease of the features observed during the water intrusion–extrusion process [9] which is not the case for the corresponding material prepared in fluoride medium where the stored energy is higher. The fluoride route was extensively used to prepare large crystals of zeolite [10] and more recently for synthesizing nanostructured oxide materials such as TiO_2 hallow microspheres [11, 12].

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Therefore, this paper focuses on the synthesis of mesoporous silicalite-1 samples prepared in fluoride medium. The obtained materials were fully characterized and the pressure–volume diagrams of the "water–zeolite" systems were established. The results were compared with the meso-silicalite-1 prepared in alkaline medium (sample Si-CB-2) [4].

Experimental section

The carbon black (CB) from Cabot corresponds to particles of about 20 nm in diameter, forming aggregates of approximately few micrometers. Its BET surface area and total pore volume are about 500 $m^2\ g^{-1}$ and 0.7 $cm^3\ g^{-1}$, respectively.

The surfactant agent, [3-(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride (Su), was synthesized according to the protocol of Shaojie et al. [13] by mixing 0.1 mol of dimethyloctadecylamine (Accros, 89%) with 0.12 mol of chloropropyltrimethoxysilane (ABCR, 97%) in absolute methanol. The potassium iodide (0.006 mol, Fluka, 99.5%), acting as a catalyst, is then added. The mixture was then refluxed for 4 days. A solution of [3-(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride (62% by weight in methanol) is obtained.

Mesoporous silicalite-1 samples, prepared in fluoride using carbon black, were synthesized from the starting molar compositions reported in Table 1. Tetraethoxysilan (TEOS, Aldrich, 98%) was used as the silica source. The other reactants were tetrapropylammonium bromide (TPABr, Fluka, purum), ammonium fluoride (NH_4F, Fluka, 99 wt%), and different amounts of carbon black (CB). After homogenization, the mixtures were introduced in a Teflon-lined stainless-steel autoclave and heated at 200 °C during 7 days. After synthesis, the products were filtered, washed with distilled water, and dried at 60 °C overnight. The solid was then calcined at 600 °C under air to completely liberate the porosity.

Syntheses of meso-silicalite-1 performed with the surfactant using the fluoride route (Table 1) are similar to those using carbon black. The only differences are the replacement of carbon black by the surfactant and the presence of methanol as described by Choi et al. [6]. Several synthesis parameters were modified like the time of synthesis (Si-Su B) and the amount of water (Si-Su C) or surfactant (Si-Su D and Si-Su E).

The samples were characterized by powder X-ray diffraction (XRD), collected on a PANalytical MPD X'Pert Pro diffractometer. The nitrogen adsorption–desorption isotherms were performed using a Micromeritics ASAP 2010 after the calcined samples were outgassed at 350 °C under vacuum. The size and the morphology of the crystals were determined by scanning electron microscopy (SEM) using a Philips XL 30 FEG microscope. The intrusion–extrusion of water was performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV) described in reference [4]. The experimental intrusion–extrusion curve is obtained after subtraction of the curve corresponding to the compressibility of pure water. Pressure is expressed in MPa and volume variation in mL per gram of anhydrous calcined samples. The experimental error is estimated to 1% on the pressure and on the volume.

Results and discussion

The X-ray diffraction patterns of calcined samples, prepared with carbon black (Fig. 1), are very similar to that of

Table 1 Composition of the reaction mixtures of the different silicalite-1 samples

Samples	Molar composition							Time (day)	Temperature (°C)	XRD results
	TEOS	TPABr	NH_4F	CB	Su	H_2O	CH_3OH			
Silicalite-1[a]	1	0.1	0.2	0	0	30	0	7	200	MFI
Si-CB A	1	0.1	0.2	0.625	0	30	0	7	200	MFI
Si-CB B	1	0.1	0.2	1.25	0	30	0	7	200	MFI
Si-CB C	1	0.1	0.2	2.5	0	30	0	7	200	MFI
Si-CB D	1	0.1	0.2	5	0	30	0	7	200	MFI + cristobalite
Si-Su A	1	0.1	0.2	0	0.04	30	0.38	7	200	Amorphous
Si-Su B	1	0.1	0.2	0	0.04	30	0.38	21	200	Amorphous
Si-Su C	1	0.1	0.2	0	0.04	10	0.38	7	200	Amorphous
Si-Su D	1	0.1	0.2	0	0.08	30	0.76	7	200	Amorphous
Si-Su E	1	0.1	0.2	0	0.02	30	0.19	7	200	Amorphous

CB carbon black, *Su* [3-(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride

[a] Reference sample prepared without carbon black or surfactant

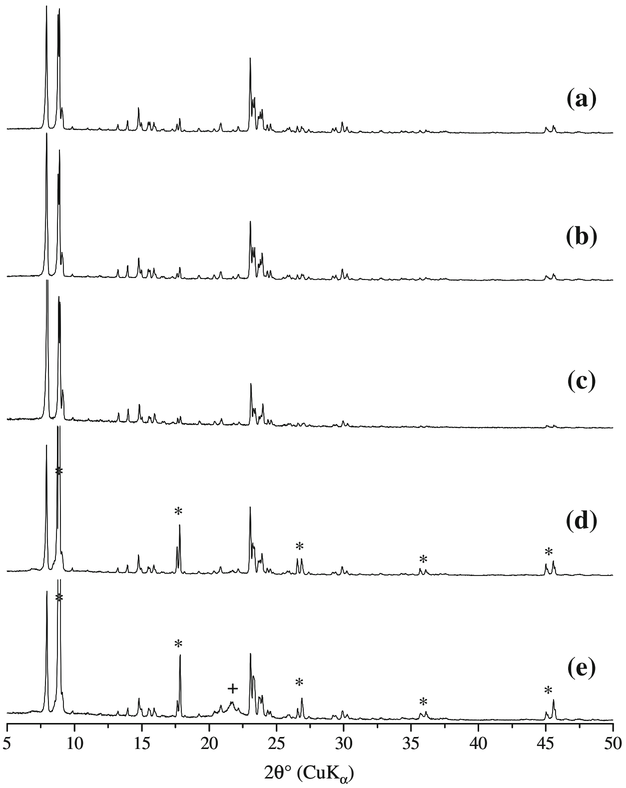


Fig. 1 X-ray diffraction patterns of calcined materials (*a*) silicalite-1, (*b*) Si–CB A, (*c*) Si–CB B, (*d*) Si–CB C, and (*e*) Si–CB D. $^+$ Impurity at $d = 4.10$ Å ($\approx 22°(2\theta)$) corresponding to cristobalite. * Preferential orientation

the silicalite-1 reference sample. They are well defined and correspond to a pure crystallized silicalite-1 zeolite except for the Si-CB D sample which presents a small amount of cristobalite. When the C/Si molar ratio is high (samples Si-CB C and Si-CB D) the intensity of the X-ray peaks corresponding to the (0k0) and (h00) planes is enhanced revealing thus some preferential orientations for these samples. All the XRD patterns can be indexed in the monoclinic symmetry (space group $P2_1/n$). Addition of carbon black in the synthesis mixture does not prevent the growth of the MFI structure. On the contrary, the syntheses performed in fluoride medium using the surfactant were unsuccessful. In all cases whatever the synthesis parameters an amorphous material is obtained. However, to our knowledge, meso-silicalite-1 prepared in the presence of surfactant in fluoride medium was never reported in the literature. Indeed, Choi et al. [6] have prepared their materials in hydroxide medium. They have shown that during the synthesis of meso-silicalite-1, a XRD peak at 2.3° corresponding to the mesophase decreased in intensity while a XRD peak at 0.7° appeared. These changes might support that the initial mesophase is dissolved into the solution, and then the mesoporous/microporous zeolite crystals grow by using the dissolved species as the crystal nutrients. Such a solution-mediated crystallization mechanism is very common for zeolite synthesis under alkaline conditions [14]. The absence of crystallization in fluoride medium might be explained by the absence of dissolution of the initial mesophase. Indeed, the XRD line at 2.3° (2θ) is continuously observed (see Fig. 2).

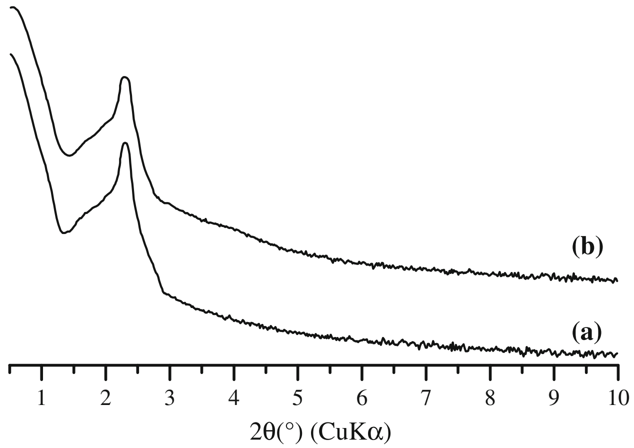
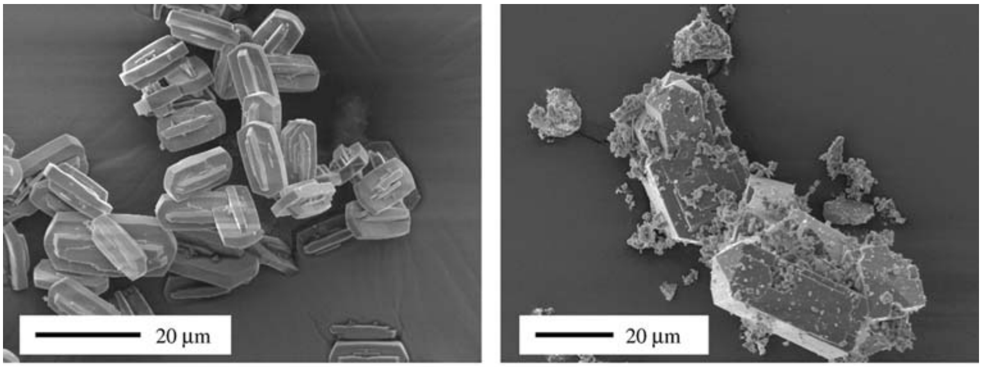


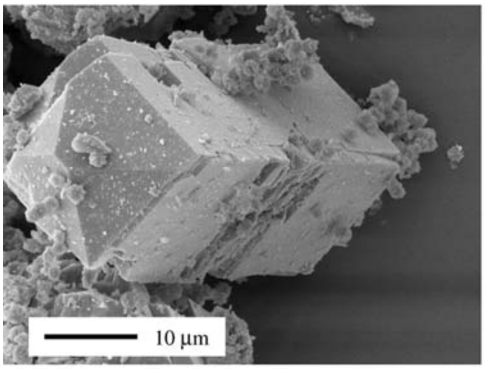
Fig. 2 X-ray diffraction patterns of Si-Su B in the 2θ range 0.5–10° (*a*) after 1 day reaction time and (*b*) after 21 days reaction time

The crystal morphology of MFI-type samples was examined by scanning electron microscopy (Fig. 3). For the silicalite-1 reference sample, twinned crystals with sizes close to $15 \times 7 \times 2\ \mu m^3$ are obtained. For samples prepared with a small amount of carbon black (Si-CB A and Si-CB B samples), the crystals display a prismatic morphology but they are larger with sizes close to $50 \times 25 \times 5\ \mu m^3$. A quite similar morphology is observed for samples prepared with a higher amount of carbon black (Si-CB C and Si-CB D samples), but the average crystal size ($25 \times 15 \times 15\ \mu m^3$) is different. Indeed, the height (*b* axe) and the width (*a* axe) of the crystals are equal. Therefore, the faces corresponding of (h00) and (0k0) planes of the Si-CB C and D samples are of similar size, which could explain the preferential orientation observed on the X-ray diffraction patterns in Fig. 1. As it can be seen on the micrographs of the Si-CB B and Si-CB C samples, small particles corresponding probably to amorphous material (not detected by XRD) are also visible. Moreover, the scanning electron microscopy study shows that unlike the samples prepared in hydroxide medium using carbon black, where aggregates of few micrometers, composed of small crystallites of silicalite-1 with dimensions ranging from 100 nm to 3 μm, are observed [4], the crystals of samples prepared in fluoride medium are larger.

N_2 adsorption–desorption isotherms and textural characteristics of the calcined Si-CB samples are reported in Fig. 4 and Table 2, respectively. The isotherm of the reference silicalite-1 sample is of type I with the presence of a clear step for relative pressures slightly above 0.15. This



Silicalite-1 Si-CB B



Si-CB C

Fig. 3 Micrographs of calcined materials: silicalite-1, Si-CB B, and Si-CB C

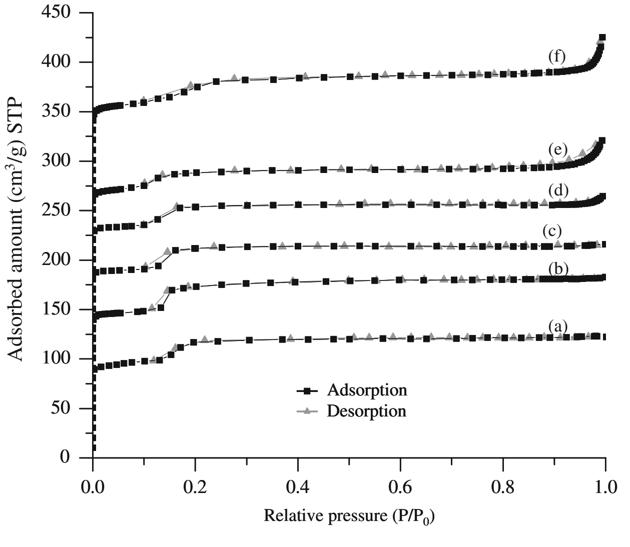


Fig. 4 N_2 adsorption–desorption isotherms of calcined materials (*a*) silicalite-1 starting to 0 $cm^3\ g^{-1}$, (*b*) Si-CB A starting to 50 $cm^3\ g^{-1}$, (*c*) Si-CB B starting to 100 $cm^3\ g^{-1}$, (*d*) Si-CB C starting to 150 $cm^3\ g^{-1}$, (*e*) Si-CB D starting to 200 $cm^3\ g^{-1}$ and Si-CB2 [4] starting to 250 $cm^3\ g^{-1}$

step was described by Llewellyn et al. [15] and corresponds to a density change of the adsorbed phase. After this step, a plateau is observed. The BET surface area is about 400 $m^2\ g^{-1}$ and the microporous volume of 0.186 $cm^3\ g^{-1}$. The shapes of N_2 adsorption–desorption isotherms of Si-CB samples are similar to that of the reference sample. However, the microporous volume of sample Si-CB A is larger ($\sim$0.194 $cm^3\ g^{-1}$) while for the other samples it decreases when the amount of carbon increases, which might be explained by the presence of an amorphous phase (confirmed by SEM) in the corresponding samples. Moreover a condensation step which appears at P/P_0 close to 1 reveals the presence of macropores for samples Si-CB C and Si-CB D. The microporous volume was only increased for sample Si-CB A which will then be tested in water intrusion. For comparison, the N_2 adsorption–desorption isotherm of a mesoporous silicalite-1 sample prepared in alkaline medium in the presence of carbon black (sample Si-CB2, ref 4), is also reported. This isotherm is similar to that of the reference sample. However, the microporous volume is larger ($\sim$0.206 $cm^3\ g^{-1}$) and the condensation step which appears at P/P_0 close to 1 shows the presence of macropores (macroporous volume = 0.065 $cm^3\ g^{-1}$). It can be concluded that the increase of microporous volume using carbon black is more important for the synthesis prepared in alkaline medium than those performed in fluoride medium.

Experimental water intrusion diagrams of the reference and Si-CB A samples performed at room temperature are reported in Fig. 5. Characteristics data are given in Table 3. These results are compared with those obtained

Table 2 N_2 adsorption data of the different silicalite-1 samples

Samples	S_{BET} (m^2 g^{-1})	Microporous volume (cm^3 g^{-1})	Mesoporous volume (cm^3 g^{-1})	Total porous volume (cm^3 g^{-1})[b]	Macropore diameter (nm)[c]
Silicalite-1[a]	389	0.186[d]	0	0.196	–
Si-CB A	380	0.194[d]	0	0.206	–
Si-CB B	361	0.176[d]	0	0.179	–
Si-CB C	333	0.164[d]	0	0.178	>50
Si-CB D	295	0.140[d]	0	0.187	>50
Si-CB2[e]	438	0.206[d]	0	0.271	>50

[a] Reference sample prepared without carbon black or surfactant

[b] Determined at $P/P_0 = 0.99$

[c] Determined by the BJH method on the adsorption curve

[d] Determined at $P/P_0 = 0.20$

[e] Result obtained for meso-silicalite-1 prepared in alkaline medium (sample Si-CB2) [4]

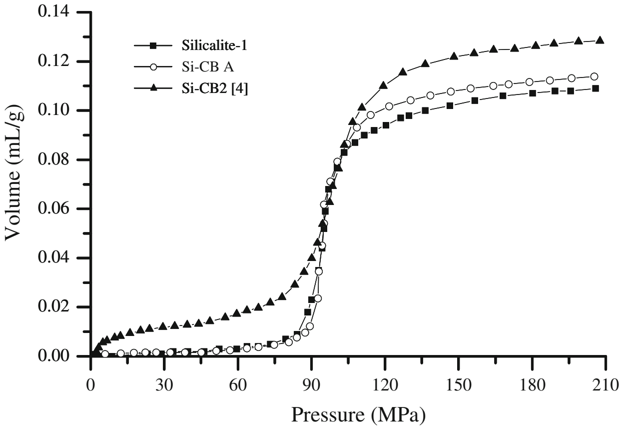


Fig. 5 Pressure–volume diagrams of "water–zeolite" systems at room temperature

for the meso-silicalite-1 prepared in alkaline medium (sample Si-CB2) [4]. For readability and because the extrusion curves are almost similar to the intrusion curves (very slight hysteresis), only the water intrusion curves are reported in Fig. 5.

In the case of the reference silicalite-1 sample when the pressure increases and the capillary pressure is reached ($P_{int} = 96$ MPa), an important variation of volume is observed (V_{int}). Water molecules penetrate into the microporous volume of the zeolitic framework. A complete filling of the pores takes place at higher pressure. When the pressure is released, the phenomenon is reversible (not reported). The intruded volume calculated with a water density of 1 is close to 0.109 cm^3 g^{-1} which is far away from the one determined from N_2 adsorption measurements (0.186 cm^3 g^{-1}, Table 2). However, this result is in agreement with a water density in the MFI structure of ~0.6 as it was shown by Desbiens et al. [16].

The water intrusion curve of Si-CB A samples is similar to that of the reference silicalite-1. When the pressure is released, the phenomenon is still reversible (not reported). Only an increase of the intruded volume is observed (0.114 cm^3 g^{-1}). Therefore, the "water–Si-CB A" system stores more energy than the "water–silicalite-1" system (+5%).

For Si-CB2 sample [4] (Fig. 5), by comparing the pressure–volume diagram with that of the reference sample, a significant difference was observed. The intrusion curve is clearly composed of two zones. The first, about 5 MPa (zone 1), can be attributed to the existence of an additional porosity. The absence of intrusion in zone 1 for the mesoporous silicalite-1 synthesized in fluoride medium

Table 3 Characteristics of the "water–zeolite" systems

Samples	Intrusion pressure (MPa)		Intruded volume (cm^3 g^{-1})		Microporous volume[b] (cm^3 g^{-1})
	Zone 1	Zone 2	Zone 1	Zone 2	
Silicalite-1[a]	–	96	–	0.109	0.186
Si-CB A	–	95	–	0.114	0.194
Si-CB2[c]	5	99	0.012	0.117	0.206

[a] Reference sample prepared without carbon black or surfactant

[b] Determined by N_2 adsorption

[c] Result obtained for meso-silicalite-1 prepared in alkaline medium (sample Si-CB2) [4]

in the presence of carbon black can be explained by the lower macroporous volume (total porous volume—microporous volume), determined by nitrogen adsorption. It is equal to 0.065 $cm^3\ g^{-1}$ for Si-CB2 sample and to 0.012 for Si-CB A. However, the amount of stored energy in zone 1 is negligible and does not increase significantly the storage capacity of the "water–zeolite" systems. The second intrusion step which occurs at high pressure ($\sim$100 MPa) is identical to that of the reference sample and corresponds to the filling of micropores. However, an increase of the intrusion pressure and intruded volume are observed in zone 2 ($P_{\mathrm{int}} = 99$ MPa and $V_{\mathrm{int}} = 0.117\ \mathrm{cm}^3\ \mathrm{g}^{-1}$). Therefore, the "water–Si-CB2" system stores more energy than the "water–silicalite-1" and "water–Si-CB A" systems (+11% compared to the silicalite-1 reference). Contrary to what was expected at the beginning of this study, it appears that the energy storage, in the system composed of water and mesoporous silicalite-1 prepared in the presence of carbon black, is more efficient when the synthesis is performed in hydroxide medium. However, the increase of porous volume by using carbon black as porogen agent seems to be a good method to improve the energetic performance of the "water–silicalite-1" system.

Conclusions

The porous volume of silicalite-1 zeolite was successfully increased by the creation of an additional porosity using carbon black in fluoride medium. But the syntheses performed in fluoride medium using the surfactant were unsuccessful. The absence of crystallization in fluoride medium might be explained by the absence of dissolution of the initial mesophase. The formation of additional micropores leads to an increase of the intruded volume at high pressure ($\sim$100 MPa) and thus an increase of the amount of stored energy compared to a classical silicalite-1 (+5%). However, contrary to what was expected from previous studies, the mesoporous zeolites, prepared by the fluoride route in the presence of carbon black, allows storing less energy than those prepared in hydroxide medium. Nevertheless, this work highlights that the creation of additional micropores is an excellent solution to increase the energetic performance of "water–silicalite-1" system.

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