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Highly Active 2D Hexagonal Mesoporous Titanium Silicate Synthesized Using a Cationic–Anionic Mixed-Surfactant Assembly

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New highly ordered 2D hexagonal mesoporous titanium silicate materials have been synthesized using a mixture of anionic (sodium lauryl sulfate, SDS) and cationic (cetyltrimethylammonium bromide, CTAB) surfactants as the structure-directing agent (SDA) in the presence of tartaric acid (TA) as a mineralizer of Ti. XRD, N_2 adsorption, and TEM data indicate that these mesoporous materials have very high surface areas (1136–1418 $m^2 g^{-1}$) and highly ordered pore arrangements. N_2 adsorption studies further suggest that, in addition to uniform mesopores, small micropores with average diameters of ca. 0.58 nm also exist in the pore wall. UV–visible and FTIR spectroscopic studies indicate the incorporation of highly dispersed tetrahedral titanium(IV) species in the silica mesophase. These mesoporous titanium silicate samples showed excellent catalytic activity and selectivity in the epoxidation of styrene using dilute aqueous H_2O_2 as the oxidant.

Introduction

Titanium silicates with nanoporous framework structures have attracted widespread attention because of their versatile catalytic role in a range of eco-friendly, selective, and industrially important oxidative organic transformations in the presence of dilute aqueous H_2O_2 as an oxidant.¹ The medium-pore titanium silicates TS-1 and TS-2 have shown outstanding catalytic activity in a wide range of oxidation reactions, e.g., oxidations of C–H, N–H, and S–H; epoxidations, hydroxylations, ammoxidations, etc.^{1–4} However, their catalytic activities were limited to smaller organic molecules only (C_2 – C_7) because of their pore size constraints. With the discovery of highly ordered mesoporous silica^{5,6} and its titanium silicate analogue,⁷ it was expected that these mesoporous materials would overcome this difficulty in catalyzing bulky organic molecules. However, mesoporous titanium silicates synthesized by the self-assembly of cationic surfactants alone are found to be catalytically less active in partial oxidation reactions using dilute aqueous H_2O_2 as the oxidant because of the surface hydrophilicity in these materials resulting from the presence of excess surface Si–OH groups. In the supramolecular assembly of cationic surfactant, the polar headgroups are oriented toward the edge of the micelle and are thus responsible for the excess surface silanol density. Moreover, Ti-containing mesoporous silicas have usually shown relatively better activity when organic peroxides were used as oxidants, which reduced the environmental and economic advantages of the titanium silicate/ H_2O_2 system, where H_2O is the only byproduct. The management of the organic byproducts is a major drawback in this case. Another important aspect is that the loadings of titanium in highly ordered titanium silicate mesoporous materials synthesized using cationic surfactants were relatively low.^{7,8} Hence, mesoporous titanium silicates (preferably Ti-rich),⁹ which can be active in liquid-phase partial oxidation reactions in the presence of a dilute aqueous H_2O_2 as

an oxidant, are very important for their practical applications in syntheses of organic fine chemicals.^{10–15} Very recently, ordered mesoporous silicas have been synthesized using a combination of cationic/nonionic,¹⁶ cationic/anionic surfactant mixtures,¹⁷ or microemulsion,^{18,19} some of them having well-defined particle sizes and morphologies. Because of partial charge neutralization or decreasing charge density of the micelle in mixed-surfactant systems,^{16–23} the surfaces of these materials are usually more hydrophobic than that of mesoporous silica synthesized using ionic surfactants alone.²⁰ Because the frameworks of these mesoporous materials synthesized using mixed-surfactant routes are composed of inactive silica only, an active transition metal has to be incorporated in the mesoporous frameworks to achieve the desired catalytic activity in a liquid-phase partial oxidation reaction. Herein, we first report the synthesis of highly ordered mesoporous titanium silicates using a mixture of cetyltrimethylammonium bromide (CTAB) and sodium lauryl sulfate (SDS) as a supramolecular structure-directing agent (SDA) in the presence of tartaric acid (TA) and tetramethylammonium hydroxide (TMAOH) under alkaline pH conditions. These mesoporous titanium silicate samples showed excellent catalytic activity in the liquid-phase partial oxidation of styrene to styrene oxide using dilute aqueous H_2O_2 as oxidant.

Experimental Section

Tetraethyl orthosilicate (TEOS, Aldrich) and titanium(IV) tetrabutoxide (TBOT, Aldrich) were used as silica and titanium sources, respectively. TA (Loba Chemie) was used because of the stability of its complex with Ti(IV) in aqueous medium, which could assist the incorporation of more active Ti centers in the internal surface of the mesopores. In a typical synthesis procedure, CTAB (Loba Chemie, 2.96 g) was mixed with an aqueous solution containing SDS (Loba Chemie, 0.4694 g) and TA (1.31 g) in 60 g of H_2O under vigorous stirring at room temperature for 30 min. Gel formation occurred immediately, leading to a viscous suspension. TEOS (3.5 g) was added to this suspension under continuous stirring for 30 min. After 2 h

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of constant stirring, 0.2287 g of $\text{Ti}(\text{OBu})_4$, taken in 3 g of isopropyl alcohol, was added slowly to the mixture. After the resulting mixture had been stirred for another 4 h, TMAOH was added dropwise, and the solution became white. The pH of the final mixture was ca. 11.0. The resultant mixture was aged overnight under stirring at room temperature and then transferred into a polypropylene bottle and heated at 353 K for 72 h without stirring. The solid product was recovered by filtration, washed several times with water, and dried at room temperature. The resulting powder was calcined at 703 K to remove the organic surfactants. The molar ratios of various constituents for samples 1 and 2 were 50 TEOS:(1.0–2.0) $\text{Ti}(\text{OBu})_4$:25 CTAB:5 SDS:50 TA:4960 H_2O .

After the hydrothermal treatment, the solid products were filtered, washed repeatedly with water, and dried in air. Sample 3¹⁵ was prepared hydrothermally at 413 K under tumbling conditions using CTAB alone as the SDA (TEOS/CTAB = 2.0) with a Si/Ti mole ratio of 60 (57.4 in the final product). Sample 4 was synthesized following a synthesis procedure identical to that for samples 1 and 2 but without the addition of TA and the Ti source. All samples were synthesized more than once, and in all of the batches, the results showed excellent reproducibility in yield, XRD patterns, etc. All samples were identified by powder XRD using a Seifert 3000P X-ray diffractometer on which small- and wide-angle goniometers were mounted. The X-ray source was Cu $\text{K}\alpha$ radiation ($\alpha = 0.15406$ nm) with an applied voltage and current of 40 kV and 20 mA, respectively. Mesophases of different samples were analyzed using a JEOL JEM 2010 TEM at an accelerating voltage of 200 kV. N_2 adsorption measurements were carried out using a Quantachrome Autosorb 1-C instrument at 77 K. Pretreatment of the sample was done at 473 K for 2 h under high vacuum. A JEOL JEM 6700F field-emission scanning electron microscope with an EDS attachment was used for the determination of surface morphology and chemical composition. UV–visible diffuse reflectance spectra were recorded on a Shimadzu 2401PC UV–visible spectrophotometer with an integrating sphere attachment using BaSO_4 as the background standard. For the Fourier transform infrared (FTIR) measurements, a Nicolet Magna IR 750 Series II instrument was used. A Perkin-Elmer 2380 AAS was used for wet chemical analysis. Liquid-phase oxidation reactions were carried out under stirring in a two-neck round-bottom flask fitted with a water condenser and placed in an oil bath at 333–353 K. Dilute aqueous H_2O_2 (25% aqueous) was added immediately before the start of the reaction. At different time intervals, the products were collected from the reaction mixture and analyzed by capillary gas chromatography (Agilent 4890D, FID). The products were identified by known standards.

Results and Discussion

We have prepared two mesoporous titanium silicate samples using a mixed-surfactant assembly with Si/Ti mole ratios of 50.0 and 25.0 in the synthesis gel. Chemical analysis data for samples 1 and 2 revealed Si/Ti mole ratios of 47.8 and 29.7, respectively. Small-angle X-ray diffraction patterns of a representative sample 2 are shown in Figure 1. All four peaks for the 100, 110, 200, and 210 planes of the 2D hexagonal mesophase^{6,7} were observed for the as-synthesized sample, whereas for the calcined sample, the intensity of the 210 plane was very weak. The XRD patterns suggest that these materials are highly ordered. Samples synthesized in the absence of TA are mostly disordered mesophases. This result suggests that the presence of TA helps in the incorporation of a large amount of Ti into the ordered hexagonal mesophase. In Figure 2, N_2

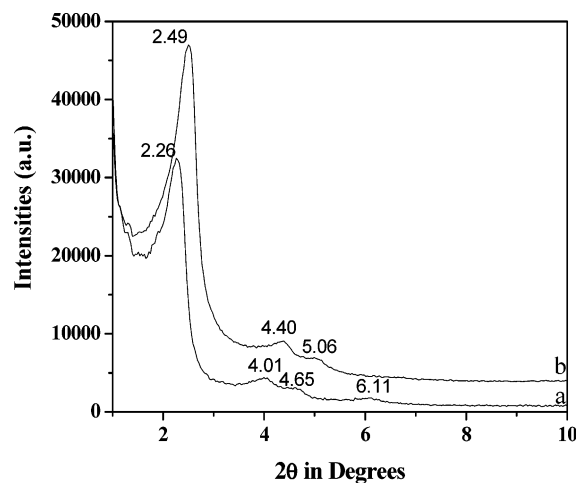


Figure 1. XRD pattern of (a) as-synthesized sample 1 and (b) calcined sample 1.

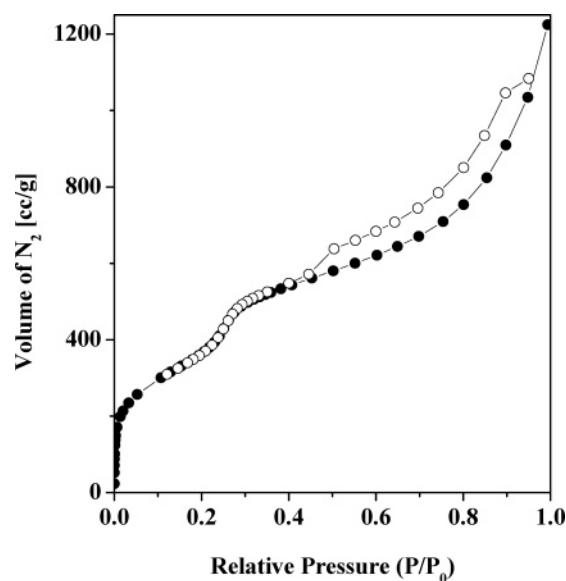


Figure 2. N_2 adsorption/desorption isotherms for sample 2. Adsorption points are marked by solid circles, and desorption points are marked by open circles.

sorption isotherms for sample 2 at 77 K are shown. A typical type IV isotherm with a steep rise due to capillary condensation, characteristic of other mesoporous materials,^{5–7} can be seen. The BET surface area and average pore diameter for samples 1 and 2 were 1136 and 1418 $\text{m}^2 \text{g}^{-1}$ and 2.40 and 2.36 nm, respectively. The low-pressure steep section of the isotherms in Figure 2 and the upward orientation of the left end of the BJH pore size distributions (Figure 3A) are indicative of the presence of microporosity in our mesoporous titanium silicate samples. This was confirmed by the micropore size distribution plot obtained from the N_2 adsorption isotherm using the Horvath–Kawazoe method.²⁴ The corresponding distribution is shown in Figure 3B. For sample 2, the observed peak in the micropore diameter was 0.58 nm. Titanium silicates with mixed micro- and mesopore systems²⁵ are of particular interest for carrying out selective oxidation reactions. The pore wall thicknesses, calculated from the unit cell parameters and pore diameters (Table 1), are quite low. This result suggests that the active titanium sites are mostly located at the surface of the catalyst. A TEM image for as-synthesized sample 2 is shown in Figure 4. The hexagonal arrangement of the pores with a different contrast than that of the pore walls is very clear. The

Table 1. Physicochemical Properties of Different Mesoporous Samples^a

sample	Si/Ti mole ratio		BET surface area (m ² g ⁻¹)	mesopore volume (cm g ⁻¹)	pore diameter (Å)	wall thickness ^b (Å)
	gel	product				
1	50.0	47.8	1136	0.67	24.0	16.9
2	25.0	29.7	1418	0.84	23.6	18.3
3	60.0	57.4	1020	0.64	24.8	19.8
4	∞	—	976	0.50	25.2	15.6

^a Sample 4 was synthesized in the absence of any Ti source. ^b Wall thickness = $(2d_{100}/\sqrt{3})$ - pore diameter.

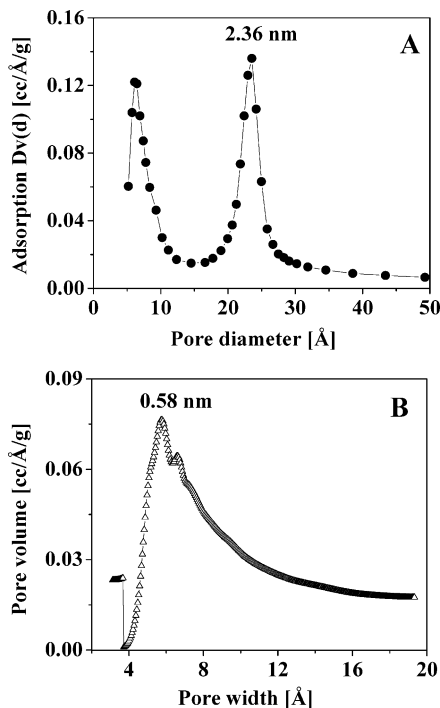


Figure 3. (A) BJH and (B) HK method pore size distributions obtained from the Figure 2 adsorption isotherm for sample 2.

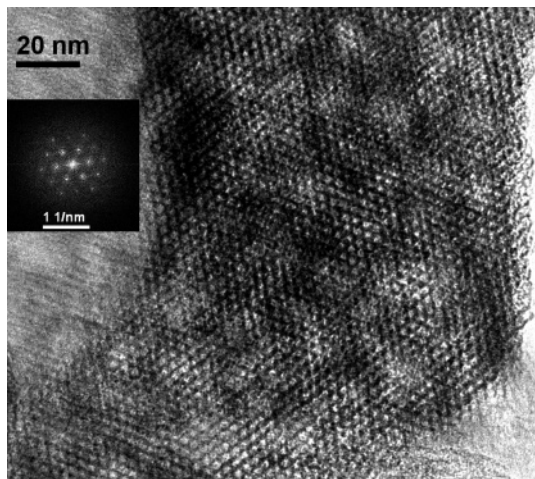


Figure 4. TEM image of sample 2 (electron diffraction pattern shown in the inset).

selected-area electron diffraction pattern shown in the inset of this image suggests hexagonal ordering of the channels.

In Figure 5 are shown UV–visible diffuse reflectance spectra of the different mesoporous titanium silicate samples after the removal of the surfactants. A strong UV–visible absorption band at 200–290 nm was observed for all samples. This band is due to the electronic transition from O²⁻ to Ti⁴⁺. Similar high-energy absorption edges due to tetrahedral coordination of Ti have been observed for other titanium-containing mesoporous molecular sieves.^{4,11,12,26} The high-energy absorption

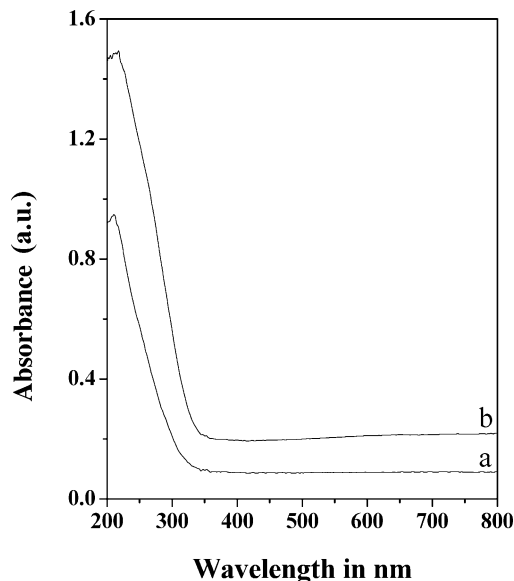


Figure 5. UV–visible spectra of calcined samples (a) 1 and (b) 2.

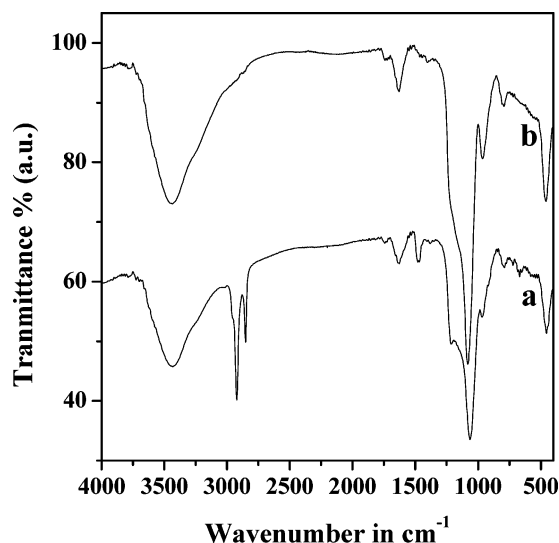


Figure 6. FTIR spectra of (a) as-synthesized and (b) calcined sample 2.

band for the titanium silicate material suggests that highly dispersed tetrahedral Ti(IV) in an isolated silica environment dominates in this material. FTIR spectra of different template-free samples are shown in Figure 6. Strong bands at 960–965 cm⁻¹ can be observed for both of the calcined samples, which can be attributed to the Si–O–Ti stretching vibration.^{8,15} Peaks at ca. 790, 1084, and 3344 cm⁻¹ can be attributed to the different characteristic Si–O–Si vibrations and defect Si–O–H stretching vibrations. Peaks at ca. 1630 cm⁻¹ can be attributed to the adsorbed residual water. These spectra suggest the presence of Si–O–Si and Si–O–Ti bonding in the mesoporous titanium silicate samples. In Figure 7 is shown the SEM image of the as-synthesized mesoporous titanium silicate sample 2. Quite uniform spherical particles of ca. 100 nm were observed for

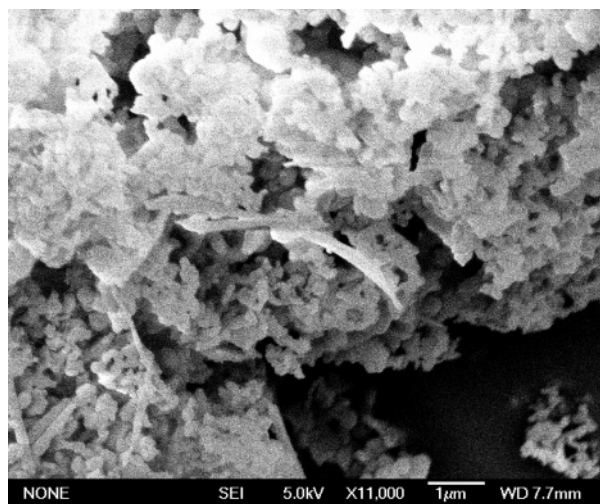


Figure 7. FE-SEM image of as-synthesized sample 2.

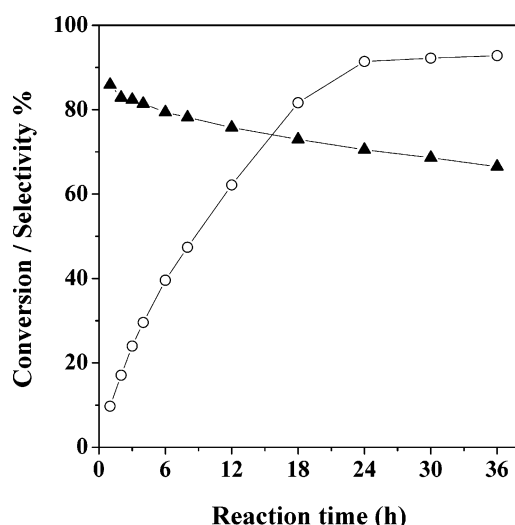


Figure 8. Plots of (a) styrene conversion and (b) styrene oxide selectivity over sample 2 as functions of reaction time.

Table 2. Oxidation of Styrene over Mesoporous Titanium Silicates Using H_2O_2 as the Oxidant^a

sample	reaction time (h)	conversion (%)	epoxide selectivity (%)	TOF ^b
1	36	82.7	75.4	3.45
2	24	91.4	70.5	3.55
3 ^c	30	16.2	54.0	0.91
4	36	0.35	32.4	—
2 ^d	24	83.4	74.1	3.24

^a Styrene/ H_2O_2 = 1: 1 (mol/mol); solvent, acetone, reaction temperature, 333 K; catalyst, 20 wt % with respect to the substrate. ^b Turn over frequency = moles of substrate converted per mole of Ti per hour. ^c Ti-MCM-41 (Si/Ti = 57.4, surface area = $1020 \text{ m}^2 \text{ g}^{-1}$) synthesized using CTAB only.¹⁵ ^d Sample 2 was reused as the catalyst in the third cycle.

this mesoporous titanium silicate sample. In a few places, the spherical particles agglomerate to form rod-like particles.

Mesoporous titanium silicate samples 1 and 2 were used for the liquid-phase epoxidation of styrene using dilute aqueous H_2O_2 as the oxidant under mild conditions (333 K). Styrene oxide was observed as the main product, together with some hydrolyzed diols and a minor amount of over-oxidized products. Conversion, epoxide selectivity, and turn over frequency (TOF) results for the samples are reported in Table 2. Catalytic data for reference Ti-MCM-41 and pure silica MCM-41 samples synthesized using CTAB only¹⁵ are included here for comparison. Interestingly, samples 1 and 2, synthesized with cationic—

anionic mixed-surfactant systems, showed much better conversion, epoxide selectivity, and TOF than the reference Ti-MCM-41 (sample 3), suggesting the presence of more active Ti sites at the surface of the former. The pure silica sample showed almost no catalytic activity, which indicates the catalytic role of Ti in these mesoporous titanium silicate samples. In Figure 8, the conversion and epoxide selectivity over sample 2 at different times of reaction are shown. Although the selectivity for styrene oxide was higher at the initial stages of the reaction, after 24 h, both the conversion and epoxide selectivity reached their optima. The titanium hydroperoxo species²⁷ generated in situ in the presence of H_2O_2 helped to form styrene oxide as the major product. No leaching of Ti was observed in either of the reaction mixtures after the reactions. This result suggests that the liquid-phase oxidation of styrene over the mesoporous titanium silicate synthesized using mixed-surfactant systems is purely catalytic in nature and that active Ti sites are present in this mesoporous titanium silicate material. After the reaction, the catalyst was filtered, washed with water, dried, and calcined at 773 K. Regenerated catalyst obtained by this method was used for two additional cycles, and in both cases, high conversion and selectivity were obtained. In the third cycle on sample 2, as high as 83.4 % conversion of styrene and 74.1% selectivity for styrene oxide were obtained (Table 2). These data clearly suggest that our mesoporous titanium silicate samples are efficient catalysts for repeated use.

Interestingly, this highly ordered 2D hexagonal mesoporous titanium silicate was synthesized using a much higher concentration of Ti in the synthesis gel. Under conventional synthesis conditions using a cationic surfactant alone as the supramolecular assembly, such a high loading of Ti usually leads to a wormhole-like disordered mesostructure.⁹ Here, the decrease in charge density of the self-assembled mixed-surfactant micelle²⁰ might help to incorporate the high loading of Ti, which, in turn, might be responsible for the high catalytic efficiency of these mesoporous titanium silicate samples in liquid-phase partial oxidation reactions using dilute H_2O_2 as an oxidant.

Conclusions

Highly ordered 2D hexagonal mesoporous titanium silicate has been synthesized using the self-assembly of a mixture of anionic and cationic surfactants under alkaline pH conditions. Characterization results suggest a 2D hexagonal arrangement of the channels with uniform mesopores of 2.36–2.40-nm size in these samples. In addition to the mesopores, micropores of average dimension ca. 0.58 nm were also observed in the pore wall for these samples. Spectroscopic results suggest that most of the titanium sites present in these samples are tetrahedrally coordinated Ti(IV). A high loading of Ti(IV) in the ordered mesoporous titanium silicate network could be achieved by using a mixed-surfactant system as the SDA in the presence of TA as a mineralizer. This material showed much higher catalytic activity and selectivity in the epoxidation of styrene using dilute aqueous H_2O_2 as the oxidant than mesoporous titanium silicate synthesized using cationic surfactant alone.

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