# Synthesis of Mesoporous MSU-*X* Materials Using Inexpensive Silica Sources

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MSU-*X* materials are a family of ordered mesoporous silica obtained through an assembly mechanism between nonionic poly(ethylene oxide)-based surfactants and silica precursors. Until now, among many advantages, the main drawback of this synthesis was the cost of the silica source, a silicon alkoxide that prevented any application where large amounts of material are required. We report that a new two-step synthesis pathway implying first the stabilization of a microemulsion made of both nonionic surfactants and a silica source and then the silica condensation through a fluoride-helped catalysis can be extended to cheaper silica sources than the silicon alkoxide usually used. Both sodium silicate or colloidal silica lead to sodium- and fluoride-free materials that exhibit exactly the same structures and properties as those previously reported [Boissiere et al. *J. Chem. Soc. Chem. Commun.* **1999**, *20*, 2047]. In addition, with the process occurring in slightly acidic aqueous medium, at moderate temperatures, and in open-air containers, the use of both surfactant and low-cost silica reagents opens up the field of large-scale preparation for the mesoporous MSU-*X* silica.

## Introduction

Since their first report,[1,2] ordered mesoporous materials such as MCM-41 have been demonstrated to be promising materials for several applied properties, especially catalysis. Syntheses implied organic assembly agents such as long chain quaternary ammonium cationic surfactants,[1,2] anionic surfactants,[3] or long chain amines,[4] and a route implying polyoxyethylene nonionic surfactants was also explored. The latter involved different kinds of molecules that led to the family of MSU-*X* ($X = 1-4$), where *X* refers to the surfactant molecules that can be either alkyl-PEO, alkylaryl PEO, polypropylene oxide PEO block-copolymers, or ethoxylated derivatives of the fatty esters of sorbitan (Tween), respectively.[5−7] These molecules provided new features in the field of MTS: first of all, they offered new pore topologies, with a 3D worm-hole pore structure. However it was rapidly shown that hexagonal structures could be obtained when the synthesis is performed with block-copolymer under highly acidic conditions,[8,9] in the liquid crystal domain,[10−12] after a postsynthesis treatment,[13] or by choosing a specific nonionic template agent.[14,15] The second advantage of nonionic surfactants is that they are relatively inexpensive, environmentally compatible, and biodegradable. For years, our approach in the field of MSU-*X* materials has been based on the use of small amounts of fluoride as a polycondensation catalyst.[6,16] This catalyst is removed by washing and does not remain in the final material. Besides, we recently showed that an improved way to prepare these materials could go through a two-step pathway, where, first, a homogeneous mixture made of a dilute solution of surfactant ($2 \times 10^{-2}$ M) mixed with the silica precursor was stabilized in a pH 2−4 range and, second, the silica condensation was induced by the addition of sodium fluoride.[14,15] This new synthesis pathway, which was performed in open-air containers at room temperature and in slightly acidic pH, led to micrometric particles with a well-defined porous framework and a yield close to 100%, and it allowed us to obtain reproducible preparation conditions, even when large batches of silica were prepared.

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(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; et al. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(4) Tanev, P., T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

(5) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.

(6) Prouzet, E.; Pinnavaia, T. J. *Angew. Chem. Int. Ed. Eng.* **1997**, *36*, 516.

(7) Prouzet, E.; Cot, F.; Nabias, G.; Larbot, A.; Kooyman, P. J.; Pinnavaia, T. J. *Chem. Mater.* **1999**, *11*, 1498.

(8) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(9) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(10) Attard, G. S.; Glyde, J. C.; Göltner, C. G. *Nature* **1995**, *378*, 366.

(11) Attard, G. S.; Coleman, N. R. B.; Elliott, J. M. In "*Mesoporous Molecular Sieves 1998*"; Bonneviot, L., Beland, F., Danumah, C., Giasson, S., Kaliaguine, S., Eds.; Elsiever Science: Amsterdam, 1998; Vol. 117, p 89.

(12) Attard, G. S.; Bartlett, P. N.; Coleman, N. R. B.; Elliott, J. M.; Owen, J. R.; Wang, J. H. *Science* **1997**, *278*, 838.

(13) Bagshaw, S. A. *J. Chem. Soc., Chem. Commun.* **1999**, 271.

(14) Boissière, C.; van der Lee, A.; El Mansouri, A.; Larbot, A.; Prouzet, E. *J. Chem. Soc., Chem. Commun.* **1999**, *20*, 2047.

(15) Boissière, C.; Larbot, A.; van der Lee, A.; Kooyman, P. J.; Prouzet, E. *Chem. Mater.*, in press.

(16) Voegtlin, A. C.; Ruch, F.; Guth, J. L.; Patarin, J.; Huve, L. *Microporous Mater.* **1997**, *9*, 97.

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Until now, the main drawback of this synthesis was the need for an expensive source of silica, tetraethoxisilane alkoxide (TEOS, $Si(OCH_2CH_3)_4$), that prevented any large-scale preparations. Sierra and Guth reported the first synthesis of a mesoporous silica based on both poly(ethylene oxide) surfactant and sodium silicate as silica source.[17] This synthesis was based on a basification of the reacting solution, to induce the polycondensation of the sodium silicate solution. Depending on the preparation conditions and the calcination temperature, they managed to obtain materials with a well-defined porous framework. Kwon et al. used also inorganic sources of silica by working in a 12 M solution of HF in order to prepare in situ the $H_2SiF_6$ molecule, prior to the reaction.[18] However, until now we did not try to check if sources of silica other than the silicon alkoxide could be used in our process. In our trial to increase the domain of application of mesoporous MSU-*X* materials, we report hereinafter the development of this synthesis to other sources of silica, such as sodium silicate or colloidal silica. The characteristic features or this reaction, like the possibility to modify the pore size, along with the stability of these materials to both pressure and hydrothermal conditions, are also examined.

## Experimental Section

Tergitol 15S12 ($CH_3(CH_2)_{14}(EO)_{12}OH$), a linear nonionic polyoxyethylene-based surfactant kindly provided from Union Carbide Chemicals, was used as the assembling agent. The silica sources were a sodium silicate solution (27 wt % $SiO_2$, 14 wt % NaOH from Aldrich), a colloidal silica (LUDOX HS30 from Aldrich), and a silicon alkoxide (TEOS: $Si(OEt)_4$ from Avocado). Sodium fluoride (Fluka), sodium chloride (SDS), sodium hydroxide (SDS), and hydrochloric acid (SDS) were analytical grade compounds. All reagents were used as received.

The general synthesis process was operated according to the two-step synthesis pathway recently developed.[14,15] Typically, a 0.02 M solution of surfactant was prepared by the dissolution of 1.47 g of Tergitol 15S12 in 100 mL of acidified deionized water. The pH had been first adjusted at pH 2 by mixing 13.9 mL of hydrochloric acid (1 M) with 80 mL of water. This solution was left at 2 °C in order to prevent any precipitation of silica.[17] The silicate (3.7 g) solution was then slowly dispersed under strong mechanical stirring. The final $SiO_2$: Tergitol 15S12 molar ratio was equal to 8. As previously reported, when TEOS was used as the silica precursor, one obtained a colorless solution that contains both surfactant and silica associated in micellar aggregates.[14] This system is much less stable than that obtained with TEOS, but it can be kept for 2 h at room temperature and at least for 24 h at 2 °C without any reaction. The solution was left to stand at 2 °C for 1 h. Afterward it was placed into a thermostated shaking bath until its temperature was raised to the wished value (between 20 and 70 °C). The final condensation step was induced by the addition of sodium fluoride ($NaF:SiO_2 = 0.01-0.1$ M). Though the reaction started within 30 min, the solution was allowed to stand for 3 days. We obtained a white powder, at a yield close to 100%, which was filtered off, dried, and calcined in air at 620 °C for 6 h with a 6 h preliminary step at 200 °C (heating rate of 3 °C $min^{-1}$). Preparation of larger batches was also successful without any degradation of the material. One may notice also that, as for TEOS, syntheses performed with sodium silicate alone (without surfactant) led to a low density wet gel, unlike the synthesis performed with surfactant, which gave a powder and confirms the assembly mechanism between surfactants and sodium silicate.

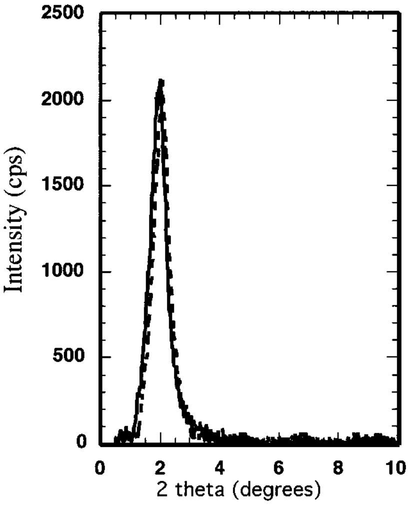

**Figure 1.** X-ray patterns of two calcined MSU silica obtained with TEOS (dashed line) or sodium silicate (continuous line), performed with Tergitol 15S12 and a Na/Si molar ratio of 2% at 30 °C.

"Home-made" sodium silicate could also be used by starting with a colloidal silica solution as silica source: 0.5 g of dried NaOH was added under stirring into a polypropylene vessel with 3.2 g of LUDOX solution, which was then left at 70 °C for 24 h in order to obtain a sodium silicate solution. Within a few minutes, a white gel was formed that became a clear and viscous solution after several hours. The synthesis was then performed as before, using this silica source in place of the silicate source. The synthesis performed with TEOS was done according to a previously reported process.[14]

All compounds were characterized by scanning electron microscopy (SEM), X-ray diffraction, and nitrogen adsorption. SEM micrographs were obtained on a Hitachi S-5400 FEG microscope. Nitrogen adsorption isotherms were measured at 77 K on a Micromeretics 2010 sorptometer using standard continuous procedures, and samples were first degassed at 150 °C for 15 h. Surface areas were determined by the BET method in the 0.05−0.2 relative pressure range and pore diameter distribution by a polynomial relationship based on that of Broekhoff and de Boer (BdB).[7,19] The X-ray diffraction patterns were recorded with a Bruker D5000 diffractometer in Bragg−Brentano reflection geometry. Cu L3,2 radiation was employed that was monochromatized by a graphite single crystal in the diffracted beam. These X-ray patterns exhibit a single peak that was fitted by a Gaussian curve, after background subtraction, to determine both the *d* spacing and the peak broadening (fwhm).

## Results

First we compared these materials with those prepared with TEOS as the silica source.[14,15] Two calcined materials using the same synthesis parameters ($SiO_2$: Tergitol 15S12 = 8 and $NaF:SiO_2 = 0.02$ molar ratio, synthesis temperature of 30 °C) were first compared. Their X-ray patterns are displayed in Figure 1. Both patterns exhibit the same single narrow peak assigned to the pore center to pore center correlation length, which has been described as characteristic of the wormhole structure of the porous framework of MSU com-

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(17) Sierra, L.; Guth, J. L. *Microporous Mesoporous Mater.* **1999**, *27*, 243.

(18) Kwon, O.-Y.; Kim, S.; Choi, S.-W. *Microporous Mesoporous Mater.* **1999**, *27*, 255.

(19) Broekhoff, J. C. P.; de Boer, J. H. *J. Catal.* **1968**, *10*, 377.

**Table 1. Physicochemical Properties of Calcined MSU Silica**

| silica source | NaF/ $SiO_2$ | synthesis temp | *d* spacing (Å) | fwmh (Å) | surface area ($m^2\ g^{-1}$) | pore vol ($cm^3\ g^{-1}$) | pore diameter (Å)[e] | wall thick. (Å) | silica/organic molar ratio | % yield |
|---|---|---|---|---|---|---|---|---|---|---|
| TEOS | 1% | 30 | 41 | 6.0 | 910 | 0.44 | <24 | >17 | 0.52 | 94 |
| TEOS | 2% | 30 | 43 | 6.5 | 1078 | 0.60 | 31 | 12 | 0.51 | 91 |
| SiNa | 1% | 30 | 40 | 6.0 | 737 | 0.34 | <24 | >16 | 0.68 | 92 |
| SiNa | 1% | 40 | 42 | 6.5 | 986 | 0.38 | <24 | >18 | 0.61 | 91 |
| SiNa[a] | 1% | 40 | 43 | 5.5 | 796 | 0.51 | <24 | >19 | 0.61 | 92 |
| SiNa | 2% | 30 | 45 | 7.5 | 1144 | 0.70 | 33 | 12 | 0.69 | 94 |
| SiNa | 2% | 50 | 47 | 7.0 | 1147 | 0.75 | 34 | 13 | 0.55 | 95 |
| SiNa | 4% | 30 | 46 | 6.5 | 1190 | 0.75 | 34 | 12 | 0.59 | 99 |
| SiNa | 4% | 50 | 50 | 7.5 | 1026 | 0.73 | 37 | 13 | 0.61 | 93 |
| SiNa | 10% | 70 | 57 | 9.5 | 858 | 1.16 | 52 | 5 | 0.58 | 92 |
| SiNa | 2% | 30 | 45 | 7.5 | 1144 | 0.70 | 33 | 12 | 0.69 | 94 |
| SiNa[b] | 2% | 30 | 45 | 7.5 | 1028 | 0.57 | 31 | 14 | 0.69 | 94 |
| SiNa[c] | 2% | 30 | 45 | 9.0 | 839 | 0.63 | 34 | 11 | 0.69 | 94 |
| SiNa[d] | 2% | 30 | 45 | 7.5 | 1073 | 0.65 | 33 | 12 | 0.69 | 94 |
| LUDOX | 2% | 20 | 41 | 6.0 | 871 | 0.44 | <24 | >17 | 0.68 | 91 |

[a] Synthesis done in salted water: the final $NaCl/SiO_2$ molar ratio was equal to 230% instead of 72%. [b] After 24 h in water at room temperature. [c] After 24 h in boiling water. [d] After 3 h stay under 600 bar. [e] From BdB pore distribution.

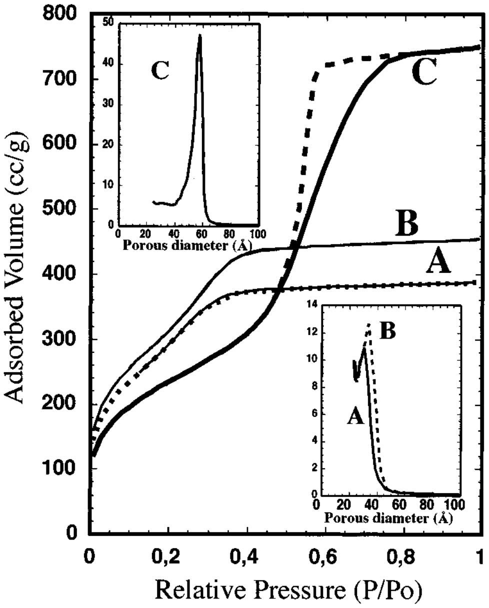

**Figure 2.** Nitrogen adsorption (line) and desorption (dash) isotherm of MSU silica obtained with (A) TEOS or (B) sodium silicate, performed at 30 °C with Tergitol 15S12 and a NaF/Si molar ratio of 2%. (C) The isotherm of a silica obtained with sodium silicate at 70 °C and a NaF/Si molar ratio of 10%. Insets: Broekhoff and de Boer pore diameter distribution deduced from the adsorption isotherm.

pounds. The *d* spacing values are very close ($d \approx 43$ and 45 Å for the TEOS and silicate, respectively), which reveals that the structure remains the same whatever the silica source. The peak broadening and the intensity are identical too (see Table 1). The nitrogen adsorption–desorption isotherms displayed in Figure 2 (curve A and B) are typical of a well-defined structural porous framework. The lack of any additional nitrogen adsorption for the higher relative pressure values means that there is no textural porosity. The pore size distribution reveals a quite narrow pore diameter distribution, centered around 31 and 33 Å for the TEOS and silicate, respectively. The SEM study (Figure 3) confirmed that synthesis with the sodium silicate source and the TEOS source led to MSU-1 powders that present the same morphology, that is, spherical micrometric particles with a mean diameter of 5 $\mu$m.

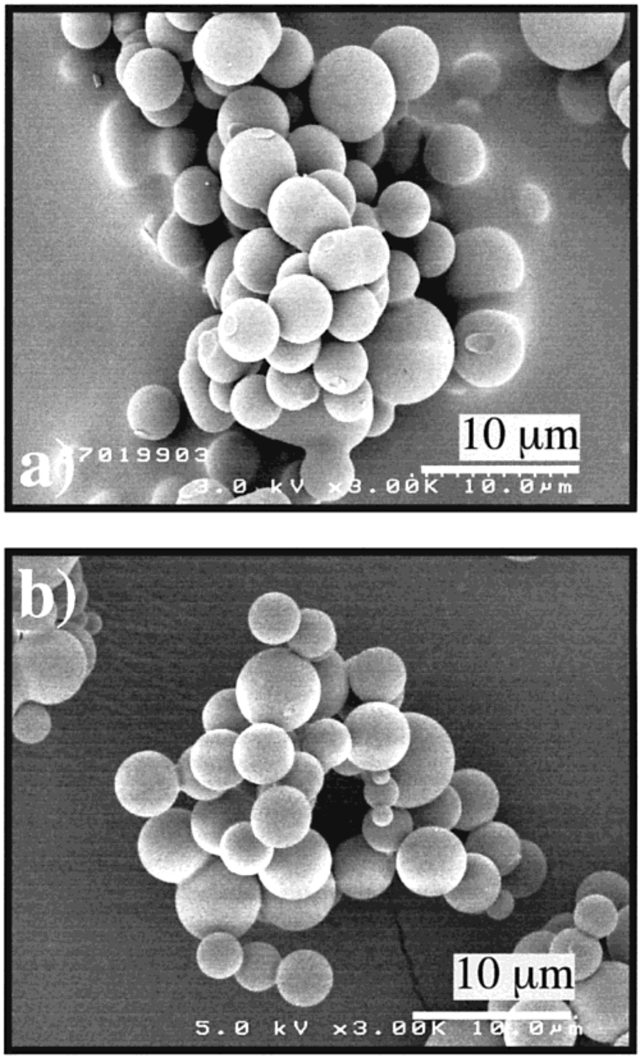

**Figure 3.** SEM photograph of calcined MSU silica obtained with (a) TEOS and (b) sodium silicate, performed at 30 °C with Tergitol 15S12 and a NaF/Si molar ratio of 2%. Both samples exhibit the same spherical micrometric particle morphology.

Both the hydrothermal and pressure resistance of this new material were also demonstrated. After a constant 600 bar pressure had been applied for 3 h, the porous structure was not modified. The diameter of the pores remained unchanged and equal to 33 Å. A slight

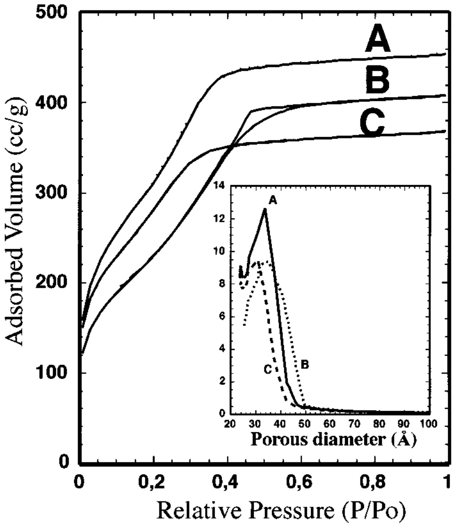

**Figure 4.** Nitrogen adsorption desorption isotherm of MSU silica obtained with sodium silicate, performed at 30 °C with Tergitol 15S12 and a NaF/Si molar ratio of 2%. (A) initial material, (B) after 24 h in boiling water, (C) after 24 h in water at room temperature. Insets: Broekhoff and de Boer pore diameters distribution deduced from the adsorption isotherm.

decrease of the surface area (1144−1073 $m^2\ g^{-1}$) and of the porous volume (0.70−0.65 $cm^3\ g^{-1}$) was only observed. SEM observation showed that particles were not fragmented and that they kept a spherical morphology, with only grain boundary prints visible from former aggregates. Powders left for 24 h in water, either at room temperature or in boiling water, undergo a slow hydrolysis (quicker in boiling water) that leads to a broader pore size distribution (Figure 4). This loss of structure appears also through the broadening of the diffraction peak (see fwhm in Table 1).

As for MSU-*X* made from TEOS, the nanostructure of these materials can be monitored by the accurate control of the synthesis parameters (see Table 1). For example, pore diameters are very dependent on the amount of fluoride.[14] Keeping other parameters constant, a jump from 1 to 2% NaF leads to a pore diameter evolution from less than 20 to 33 Å. The synthesis temperature, which has been shown to be a determinant parameter when TEOS is used for silica precursor,[6] was also explored. From these preliminary results it appears that syntheses performed with sodium silicate are not as sensitive to these parameters as those performed with TEOS. The faster polymerization kinetics of the silicate, compared with TEOS, which could “freeze” the structural modification, could explain this difference. Nevertheless, a reaction combining the two parameters (a $NaF:SiO_2$ molar ratio of 10% and a synthesis temperature of 70 °C) allowed us to obtain a well-defined material with pores of 52 Å and a porous volume of 1.16 $cm^3\ g^{-1}$ (see Figure 2C).

## Discussion

Sierra and Guth were the first ones to demonstrate that sodium silicate can be used as an inorganic silica source to synthesize MSU-type mesoporous silica. When they performed the silica condensation through a basification of the reacting medium, it appeared that raising the solution pH value above 2 (the silica neutral charge point) requires the compensation of the negatively charged silica with the sodium counterions. They observed indeed that the stability of the material was increased when they adjusted the sodium concentration in syntheses performed at pH 5−7, which could be explained by the ionization of silanol groups into $SiO^-$, compensated by $Na^+$ counterions.[17] By the way, they experimented that increasing the Na:Si ratio modified the porous diameter of the material.

Our reaction proceeds from a fluoride-helped catalysis of the silica polycondensation. Thus the reaction can be performed at slightly acidic pH (pH ≈2−4), where the silica oligomers remain neutral. Unlike the synthesis reported by Sierra and Guth, there are no interactions between the silica precursors and counterions. By example, adding sodium chloride up to three times the sodium amount of the ordinary synthesis (solubilization of sodium chloride prior to the addition of sodium fluor helped in order to get a final Na:Si molar ratio of 230%) induced no change on the final structure (see Table 1). The two-step synthesis that we developed allows us to obtain a MSU silica with near 100% yield, good reproducibility, and accurate control of the final material structure through slight changes in the synthesis parameters. Unlike results reported by Sierra and Guth, calcination of our materials at 600 °C for 6 h does not destroy the material and we verified that it could even stand a 2 h heating at 900 °C without any drastic change in its nanostructure.

Until now this synthesis was performed with organic silica sources, but this work shows that all the properties are maintained even with inexpensive inorganic silica sources. Compared with other syntheses, the fluoride-catalyzed two-step pathway, which gives both sodium- and fluoride-free materials, allowed us to obtain a material that exhibits a well-defined 3D worm-hole pore structure characteristic of MSU-*X* silica and resists temperature, pressure, and, in a certain range, hydrothermal conditions.

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