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Thermal and mechanical stability of micelle-templated silica supports for catalysis

Anne Galarneau*, Delphine Desplantier-Giscard, Francesco Di Renzo, François Fajula

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS-ENSCM,
8, rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

Abstract

Thermal and mechanical properties of hexagonal micelle-templated silica (MTS) (like MCM-41, SBA-3, SBA-15) are critical features for their application as catalysts and catalyst supports. Care should be taken in the interpretation of catalytic results which strongly depend on MTS stability. A decrease in conversion of more than 60% in a reaction of *n*-hexadecane isomerization has been observed by compressing MTS beyond a critical crushing pressure. Stability data have already been reported in literature, but they are extremely scattered, and can only be understood if the synthesis conditions which control the properties of MTS are taken into account. We show in this study that thermal stability is strongly dependent on wall thickness, a property which can be controlled by adjusting the alkalinity and the surfactant/silica ratio in the synthesis. The crushing of MTS under uniaxial compression follows the same mechanism as macroscopic hexagonal honeycomb structure. Their crushing strength varies as the square of the ratio between wall thickness and cell parameter. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mesoporous silica; MCM-41; Thermal stability; Mechanical strength

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1. Introduction

The disclosure in 1992 by Mobil researchers [1] of micelle-templated silica (MTS) materials with uniform distributions of pore diameters (20–100 Å), like MCM-41 and MCM-48 [1], SBA-3 [2] or more recently SBA-15 [3], has aroused a great interest in the scientific community. These materials are especially promising catalysts because of their high pore volume (>0.7 ml/g), surface area (>700 m^2/g) and large pore opening (>20 Å) with narrow size distribution. MTS are synthesized from micelles of surfactants which, under the addition of an inorganic reactant, reorganize themselves into a mesophase-like structure with hexagonal, cubic or lamellar symmetry. Calcination removes the surfactants and make the porosity accessible. MTS offer the opportunity to extend shape-selective catalysis beyond the micropore domain typical of the zeolite, allowing larger molecules to be transformed, with large potential applications in fine chemistry, like pharmaceuticals preparation or perfume industry [4]. Thanks to their mild acidity and the peculiar properties of fluid in small mesopores, they have also proven to be stable catalysts in butene oligomerization in comparison with zeolites or amorphous silica–alumina which severely deactivated by coking [5]. MTS are also good supports for noble metals in the hydroconversion of long chain aliphatic where they showed a high selectivity in hydroisomerization [4]. The size of their pores allow them to

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* Corresponding author. Tel.: +33-4-6714-4329;
fax: +33-4-6714-4349.
E-mail address: galarne@cit.enscm.fr (A. Galarneau).

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be grafted with functionalized organic molecules. In this way, effective catalysts can be prepared for basic catalysis, for instance by grafting tertiary amine for monoglyceride synthesis [6], for acidic catalysis by grafting sulphonic acids [7], for epoxidation catalysis by grafting salen complexes [8] and for enantioselective catalysis (alkylation or epoxidation) by grafting chiral complexes [9].

The performance of MTS in catalysis is strongly dependent on their pore volume and pore size which allow a fast diffusion of the reactants and products. Pore volume, pore size and surface area are controlled by the synthesis, but a step of calcination is needed to make the porosity accessible and a step of pelletizing is often also needed to shape the catalyst. It is very important to check the stability of MTS after these kinds of treatments. The first published data about MTS stability have shown these kinds of materials as very fragile under crushing pressure [10]. Nevertheless, we previously showed that the stability of MTS is a function of the properties of the material. Each MTS, which corresponds to one set of synthesis conditions, presents its own stability properties [11]. This report aims to be a useful tool to evaluate the stability of any hexagonal MTS.

2. Experimental

Hexagonal MTS have been prepared at 115°C for 24 h from a synthesis system of composition 1 SiO_2/0.1 or 0.2 CTAB/0.1–0.9 NaOH/0.025 $NaAlO_2$/25 H_2O, where CTAB stands for cetyltrimethylammonium bromide. Hexagonal MTS of 80 Å pore size has been prepared at the same temperature from a synthesis system of composition 1 SiO_2/0.1 CTAB/1.3 TMB/0.25 NaOH/0.025 $NaAlO_2$/25 H_2O, where TMB stands for 1,3,5-trimethylbenzene. The solids were then filtered, washed with distilled water and dried at 80°C overnight. The surfactants were removed by calcination for 8 h in air at different temperature levels. Thermal stability has been investigated by calcining the MTS at 550, 750 or 850°C. For the mechanical stability study, the samples have been calcined at 550°C.

Mechanical stability of hexagonal MTS was investigated as follows: 0.2 g of the samples were compressed in a steel die of 2.5 cm^2 using a hand-operated press, for 1 min under air. Compressing the powder longer, for instance during 1 h, had no further effect on pore volume, surface area and pore size.

Nitrogen adsorption–desorption isotherms at 77 K were recorded with a ASAP 2010 apparatus (Micromeritics), samples were outgassed at 250°C until a stable vacuum of 3×10^{-3} Torr.

Platinum (of 0.4 wt.%) has been incorporated in NH_4^+-MTS (Si/Al = 10) by ionic exchange with $Pt(NH_3)_4Cl_2$ in ethanol. The catalysts were then washed, dried and calcined at 450°C under air. The catalysts were then shaped by pelletizing under two pressures, 80 and 160 MPa, and sieved to obtain grains between 180 and 450 mm. The reduction of the catalyst was realized in situ under hydrogen at 500°C. The catalytic test performed was the hydroconversion of *n*-hexadecane which was carried out in a fixed bed down flow reactor, at 350°C under a total pressure of 40 bar. The feed of hydrocarbon was adjusted to get H_2/n-hexadecane = 11.

3. Results and discussion

3.1. Thermal stability of hexagonal MTS

The geometry of the nanometer-scale hexagonal honeycomb structure of MTS is defined by a cell parameter (a) and a wall thickness (t) as shown in Fig. 1. The thermal stability of hexagonal MTS depends mainly on their wall thickness. The wall thickness of calcined MTS can be calculated in a geometrical way by using the cell parameter evaluated from X-ray Diffraction (XRD) and the void fraction (ε) of the material determined from the pore volume (V) resulting from nitrogen adsorption measurement and by Galarneau et al. [12]:

$$t = a - a\sqrt{\varepsilon} \quad \text{with} \quad \varepsilon = \frac{V}{V + 1/\rho_{Si}}$$

ρ_{Si} being the density of the silica walls and equal to 2.2 [13]. For as-synthesized MTS, the “void” fraction is determined from the micelle volume which can be calculated from thermogravimetric analysis (TGA) corrected for 1 g of silica and where 0.77 is the density of the organic chain, m_{CTMA} the weight loss of organic and m_{H_2O} the weight loss of water

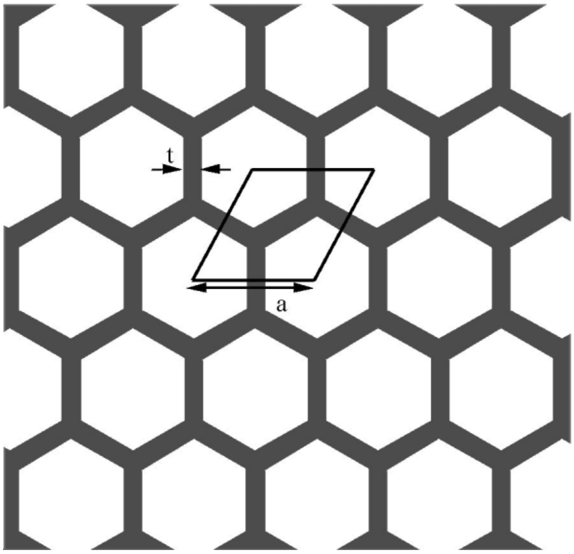

Fig. 1. Schematic representation of the section of MTS with cell parameter (*a*) and wall thickness (*t*).

$$\varepsilon = \frac{m_{\mathrm{CTMA}}/0.77 + m_{\mathrm{H_2O}}}{m_{\mathrm{CTMA}}/0.77 + m_{\mathrm{H_2O}} + 1/\rho_{\mathrm{Si}}}$$

Pore diameter (D) is then equal for as-synthesized and calcined MTS

$$D = 1.05\,a\sqrt{\varepsilon}$$

For this study, MTS have been synthesized by using CTAB as surfactant. For MTS with 5–7 Å wall thicknesses, XRD patterns are well resolved, much better than for MTS with 10–15 Å wall thicknesses, but these thin wall materials are much less resistant to the calcination. Three MTS with as-synthesized wall thickness 6, 11 and 13 Å have been calcined at 550, 750 and 850°C for 8 h. The nitrogen adsorption isotherms (Fig. 2) show a decrease in pore volume when the temperature of calcination increases. This decrease is much larger for MTS with thinner walls, as can be seen for MTS with 6 Å wall thickness compared to the materials with wall thickness 11 or 13 Å. In the case of the material with the thinnest walls, a significant decrease of pore size is observed, through a low-pressure shift of the pore filling step of the isotherm. A quantitative evaluation of MTS thermal stability can be attempted by assessing at which extent the volume of the micelle in as-synthesized material is recovered as porous volume in the calcined material. The volume of the micelle is calculated from TGA by the relation (for 1 g of silica):

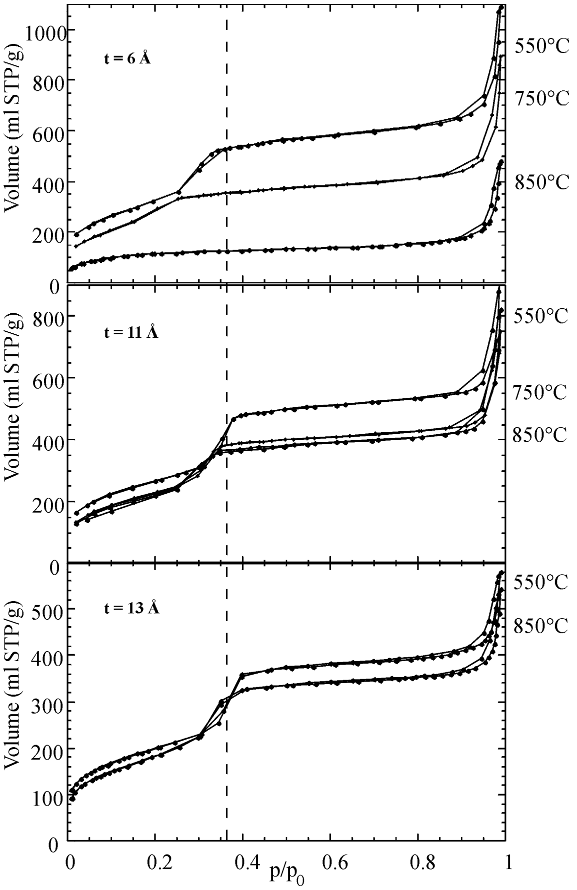

Fig. 2. Nitrogen adsorption–desorption isotherms of MTS with wall thicknesses in as-synthesized form of 6, 11 and 13 Å calcined at 550, 750 and 850°C for 8 h in air.

$$\text{Micelle volume} = \frac{m_{\mathrm{CTMA}}}{0.77} + m_{\mathrm{H_2O}}$$

In Fig. 3, the evolution of pore volume and pore diameter are reported as function of the calcination temperature for the materials with initial wall thickness 6 and 11 Å. The MTS with 6 Å wall thickness looses more than 40% of its initial volume for calcination at 550°C, and nearly 90% when calcined at 850°C. On the other hand, MTS of 11 Å wall thickness will not loose pore volume after a calcination at 550°C and no more than 20% for calcination at 850°C. Furthermore,

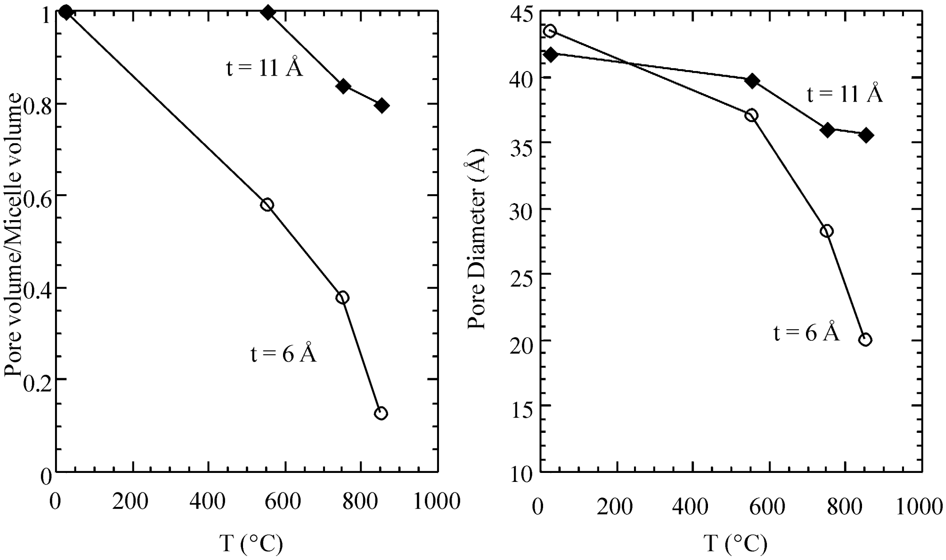

Fig. 3. Evolution in function of the calcination temperature for: (left) the pore volume compared to the micelle volume (their ratio is 1 if no degradation occurs during calcination); (right) the pore diameter. Data for MTS of initial wall thickness of 6 and 11 Å.

the calcination leads to a decrease in pore size which is more important for MTS with thinner walls. At 850°C, the average pore size is about half the initial value for MTS of 6 Å walls. For an MTS of 11 Å walls, the decrease in pore size is only 6 Å, the pore size decreases from 42 to 36 Å, with the shrinking normally observed in the calcination of MTS [14]. No intergranular porosity evolution is observed during the thermal activation as can be seen on the isotherms in Fig. 2.

MTS with wall thicker than 10 Å show the highest thermal stability. They are indeed more stable than silica particles of the same surface area [15], so small silica particles rapidly evolve by spontaneous mass transfer from regions at positive curvature towards contact regions at negative curvature. This sintering mechanism does not occur inside the pore of MTS, notwithstanding the high negative curvature of the corners of the hexagonal pores. This difference comes from the specific nature of the MTS surface. Opposite to silica particles which offer a silanol-rich surface, hexagonal MTS present a surface with some very hydrophilic parts (adjacent silanols) and some hydrophobic parts (isolated silanols and siloxane bridges) [16]. This difference of silica surface has been examined by calorimetry of water adsorption and by FTIR analysis. A study by EPR [17] using TEMPO probes on the surfactant head groups has allowed to identify these two different zones: the hydrophilic parts are the flat sides of the pores and the hydrophobic parts are the corners of the hexagonal section. The hydrophobic zone covers nearly 5 Å at each side of the corner whatever the size of the pore (Fig. 4). The weak reactivity of the siloxane-rich corners eliminates the thermodynamical driving force of the mass transfer.

The surface area and pore volume of MTS with thicker walls are lower. At increasing wall thicknesses (in the as-synthesized form) of 6, 11 and 13 Å surface areas are 1172, 967 and 713 m^2/g, respectively, when calcined at 550°C. These data are in good agreement with the calculated surface area of a hexagonal honeycomb

$$S = 4 \times 10^4 \frac{1 - (t/a)}{t\rho_{\mathrm{Si}}(2 - (t/a))}$$

with thickness (t) and cell parameter (a) in Å and surface area (S) in m^2/g [18]. For cell parameter larger than 40 Å, the t/a ratio is small and surface area is inversely proportional to wall thickness for any pore size. This is the case of most MTS syntheses and this explains the difference of surface area and pore volume between MTS samples calcined at 550°C. A high

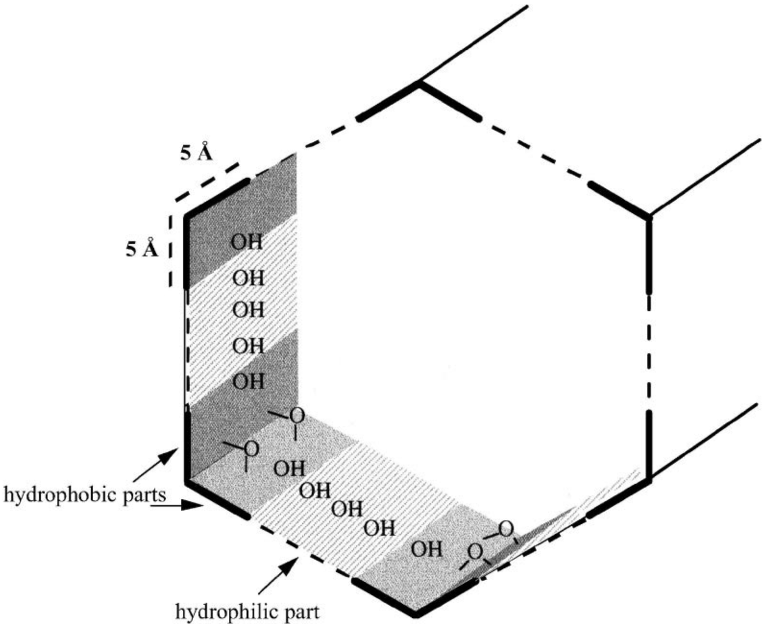

Fig. 4. Schematic view of the hydrophobic and hydrophilic parts in a hexagonal pore of MTS. The width of the hydrophobic fraction is around 5 Å whatever is the pore size.

surface area for MTS samples means thin walls and, as a consequence, a poor thermal stability of the material.

MTS wall thickness can be controlled in the synthesis by adjusting the alkalinity (OH^-/SiO_2) of the synthesis media and the surfactant/silica ratio (Fig. 5). Higher the alkalinity and thinner the walls, wall thicknesses can be adjusted between 17 and 6 Å for OH^-/SiO_2 between 0.1 and 0.9, respectively. At high pH, silica is more soluble, then less silica takes part in the formation of the hybrid material. The amount of surfactant in the synthesis also influences the wall thickness. At a given alkalinity, a higher concentration of surfactants leads to a decrease in wall thickness. This indicates that the micelle surface and the alkaline solution compete for the silicate species, and that MTS are equilibrium materials, whose competition can be continuously adjusted by modifying the composition of the surrounding solution.

If the thermal stability can be evaluated from the ratio between pore volume and micelle volume, the more stable materials are MTS with wall thicknesses higher than 10 Å, as can be seen in Fig. 6, where data on MTS synthesized in several conditions are collected. For thinner walls, mechanisms of local reorganization or mass transfer occur and minimize the exposed surface. As a consequence, the materials loose during calcination a significant fraction of their potential pore volume (Fig. 6).

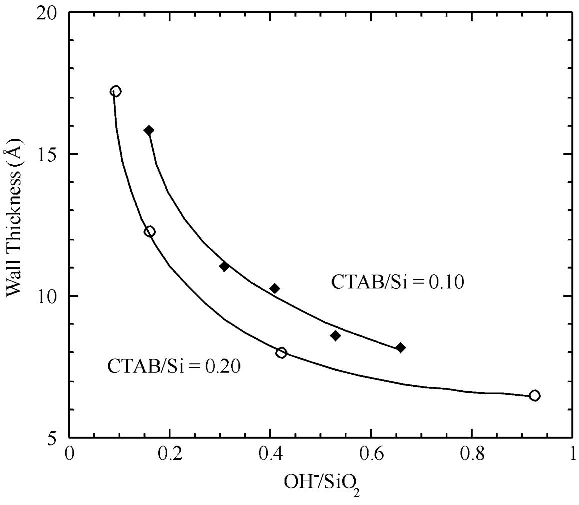

Fig. 5. Wall thickness of as-synthesized MTS as a function of the alkalinity (OH^-/SiO_2) of the synthesis media and in function of CTAB/Si ratio.

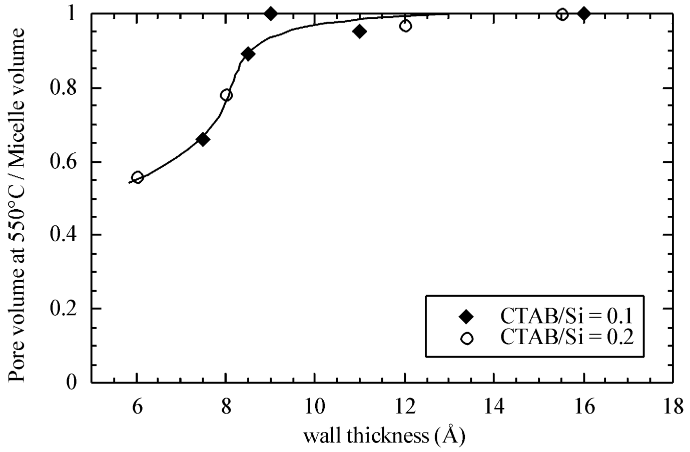

Fig. 6. Evolution of the pore volume of MTS calcined at 550°C compared to the micelle volume, as a function of the wall thickness of as-synthesized MTS.

3.2. Mechanical stability of hexagonal MTS

Mechanical tests have been performed on MTS with pore walls about 11 Å thick to get the best compromise between high surface area materials and thermal stability. MTS of two pore sizes, 35 and 80 Å, were calcined at 550°C and pelletized under pressure levels from 80 to 470 MPa. Compressed MTS were analyzed by nitrogen adsorption at 77 K and XRD. The evolution of the isotherms with crushing pressure (Fig. 7) suggests that mechanical and thermal degradation follow two different mechanisms. Indeed, the surface and the volume are decreasing as for the thermal treatment, but the intergranular porosity is changing and, especially, the pore size remains the same. The MTS is destroyed by zones, some zones remain intact and some others are totally crushed. The cell parameter remains the same, only a decrease in intensity of the XRD peaks is

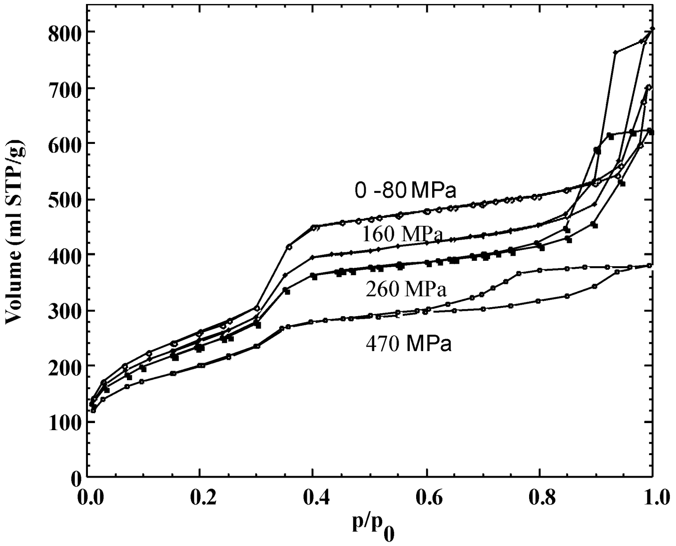

Fig. 7. Evolution of nitrogen adsorption–desorption isotherm of MTS (35 Å pore size and 9 Å wall thickness) calcined at 550°C and compressed at different pressure levels from 80 to 470 MPa.

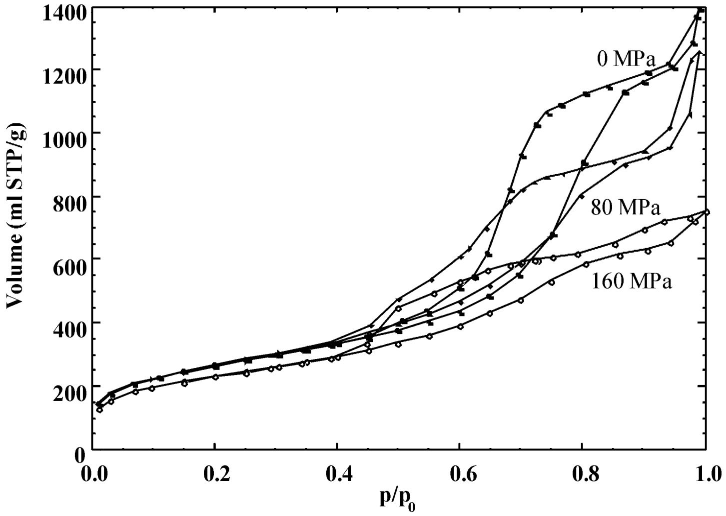

Fig. 8. Evolution of nitrogen adsorption–desorption isotherms of MTS (80 Å pore size and 11 Å wall thickness) calcined at 550°C and compressed at different pressure levels from 80 to 160 MPa.

observed, the long distance ordering is decreasing. A hysteresis loop appears in the high-pressure part of the nitrogen isotherm (Fig. 7), and reveals pore between particles. The study of the intergranular porosity shows that under pressure the particles are getting closer. A model of rigid spherical particles of similar size allows to relate the intergranular volume with the number of contacts between particles. The coordination number of the particles will be six under a pressure of 80 MPa and 12 the highest possible for indeformable sphere, for a pressure of 260 MPa. At still higher pressure, the particles are loosing their spherical shape, the hysteresis loop is broadened, corresponding to the formation of ink-bottle porosity trapped between particles. The isotherms of a MTS of 80 Å pore size (Fig. 8) compressed in a similar way shows a loss of pore volume under lower pressure than for the MTS of 35 Å pore size. By plotting the pore volume evolution

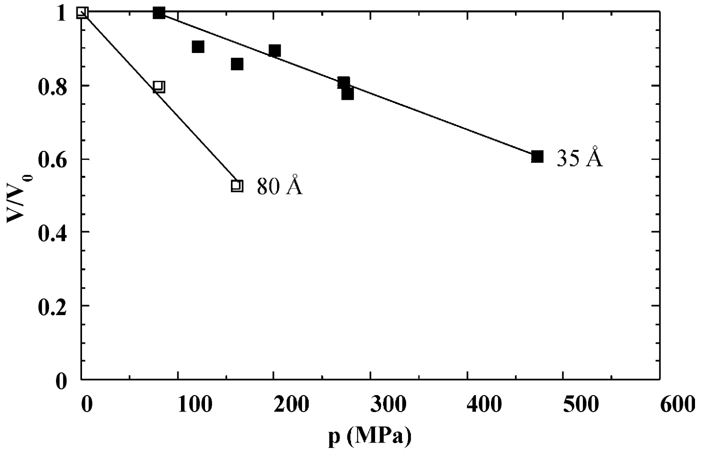

Fig. 9. Pore volume of MTS of pore size 35 and 80 Å as a function of pressure.

(V) compared to the uncompressed pore volume (V_0), it appears that MTS of 80 Å pore size are much less stable than MTS of 35 Å pore size (Fig. 9).

To understand the evolution of porosity of MTS under pressure, calculation methods used for macroscopic cellular solids have been applied. Indeed, for hexagonal honeycomb macroscopic solids (pore size at the millimeter scale), a mechanism of degradation by zones has been observed when a pressure perpendicular to the pore axis is applied [19]. MTS materials would so behave in the same way as their macroscopic homologues. The mechanical strength of macroscopic cellular materials is analyzed in literature [19,20] in terms of the evolution of the strain ($\lambda = (l - l_0)/l_0$) under a stress σ (l_0 being the initial thickness of the sample and l the thickness of the strained material). The strain evolution of cellular materials show three domains:

- The first domain presents a linear relationship between strain and stress, and corresponds to an elastic deformation, where, when the pressure is released, the material recovers its initial shape. From this linear part, the Young's modulus can be calculated, it represents the slope of the stress–strain relationship. The end of the linear relationship corresponds to the elasticity limit of the material, σ_c^*. The elasticity limit for a hexagonal honeycomb σ_c^* can be calculated from the elasticity limit of the corresponding bulk material σ_c by the relation:

  $$\sigma_c^* = \frac{4}{3}\left(\frac{t}{a}\right)^2 \sigma_c$$

  indicating that the elasticity limit of a hexagonal honeycomb material is controlled by the square of the wall thickness/cell parameter ratio.
- The second domain shows an important degradation of the material, where, for a same stress, the material is irreversibily crushed by entire planes, starting from the center of the material. For a ceramic material like silica, the failure occurs by brittle crushing. The material is getting denser and denser as more and more cells collapse.
- The third domain appears when the density of the compressed material approaches half of the density of the bulk material.

To apply these macroscopic mechanisms to the mechanical stability of MTS, relationships have to be found to:

- Transform the porosity data (V/V_0) given by nitrogen adsorption measurement given for the whole powder into the strain of a single particle of MTS.
- Convert the nominal force applied to the entire powder bed (the pellet) in the effective stress applied to the resistant part of the particle.

To transform the nominal pressure (p) into the effective stress, an analogy has been done with what is known of the compression of powder during the filling of catalytic beds [21,22]. The calculation is based on a model of spherical particles compressed between two flat surfaces. In this model, to calculate the effective pressure and so the effective stress (σ) from the nominal pressure (p), it is important to take into account that the stress on a spherical particle is transmitted along an axial cylinder whose area vary with the strain λ of the sphere. Furthermore, only the solid fraction of the sample transmits the stress and the intergranular porosity ε_{ig} has to be removed from calculations. This gives the following relationship:

$$\sigma = \frac{p}{-\lambda(\lambda+2)(1-\varepsilon_{ig})} \quad \text{with}$$

$$\varepsilon_{ig} = \frac{V_{ig}}{V_{ig} + V + 1/\rho_{Si}}$$

where V_{ig} is the intergranular volume.

To link the loss of pore volume (V/V_0) observed on the powder to the strain of a sphere ($\lambda = l - L/L$, where L is the diameter of the sphere), it has to be taken into account that the loss of volume is equal to the loss of porosity of the two crushed caps of the sphere plus the loss of porosity corresponding to the silica volume of the cap pushed into the resistant cylinder. This will end up in the following relationship:

$$\frac{V}{V_0} = 1 - \frac{\lambda^2(3+\lambda)}{2\varepsilon_0} \quad \text{with} \quad \varepsilon_0 = \frac{V_0}{V_0 + 1/\rho_{Si}}$$

The lost pore volume data in function of the compression pressure have been transformed using these equations in terms of strain (λ) in function of stress (σ). The values of elasticity limit for the two MTS were determined experimentally from the curves (Fig. 10). They are 670 and 270 MPa for MTS with

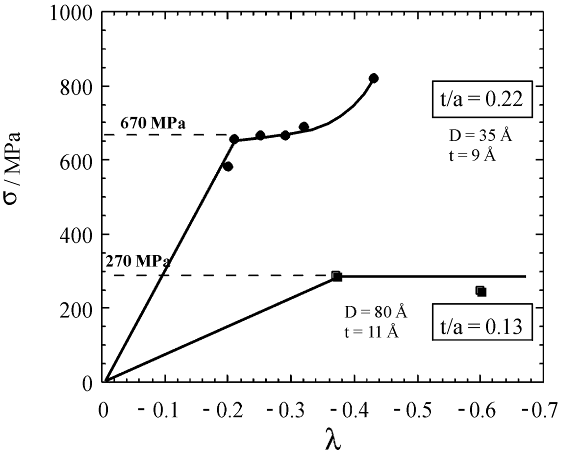

Fig. 10. Stress–strain (σ–λ) diagram for two MTS of pore size 35 and 80 Å.

35 and 80 Å pore size, respectively. The wall thickness was around 10 Å for both samples which gives $t/a = 0.22$ and 0.13, respectively. These values of elasticity limit are in good agreement with the strength of macroscopic silica honeycomb with the same wall thickness/cell size ratio. For bulk silica $\sigma_c = 7200$ MPa, which gives using previous equation $\sigma_c^* = 441$ MPa for $t/a = 0.22$ and $\sigma_c^* = 153$ MPa for $t/a = 0.13$. The experimental values obtained for MTS are slightly higher, the calculation stayed on the safety side, by assuming the worst-case hypothesis with all the particles compressed perpendicularly to the pore axis. A compression parallel to the pore axis would give a higher strength. For a hexagonal MTS with 80 Å pore size, the same mechanical stability as a MTS with 35 Å pore size could be afforded only by a wall thickness of 23 Å corresponding to the same value of the *t*/*a* ratio. This value has not been reached yet by using the synthetic way of MCM-41 (alkyltrimethylammonium surfactant in basic media) by adding TMB. SBA-3 materials synthesized from alkyltrimethylammonium surfactant in acidic media give thin walls around 6 Å and are not suitable for applications under pressure.

4. Conclusion

The MTS seems to be stable enough for most operations involved in the shaping of catalysts and in the filling of reactors or chromatographic columns. Nevertheless, care should be taken of verifying by nitrogen adsorption the state of the porosity after each treatment. It is necessary to measure its pore volume before any application. As an example, the conversion of *n*-hexadecane on an MTS catalyst support of 35 Å pore size and 10 Å wall thickness was 40% for a support still intact after pelletization at 80 MPa. The conversion decreased to 15% after pelletization at 160 MPa. The selectivity in isomerization of the reaction was not touched, some zones of the materials being undamaged and the other totally destroyed.

Stability of MTS is strongly dependent on their properties of pore size and wall thickness. These parameters can be controlled during the synthesis of the material. The most stable MTS present the thicker walls but in the meantime the lowest surface area. To get a good compromise between high surface area and stability, it is important to really control the chemistry of MTS synthesis. If hexagonal MTS are well ordered (with no defects) with walls thick enough, MTS represent very stable materials, well fit for a majority of the applications. Their elasticity limit favourably compare with several engineering alloys, notwithstanding a wood-like density [20]. Quite often, the hydrothermal stability can be more critical that thermal or mechanical stability. It is always of paramount importance to check systematically the state of the porosity of MTS after each elementary operation.

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