

# Characterization and catalytic properties of tin-containing mesoporous silicas prepared by different methods

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Available online 27 June 2005

## Abstract

Tin containing mesoporous silicas with various tin contents were prepared by reaction of tetrabutyl tin with the surface silanol groups of calcined MCM-41 followed by thermal treatment under oxygen. Various physicochemical methods (XRF, FTIR, XRD, HRTEM, N<sub>2</sub> adsorption, UV–vis spectroscopy, . . .) and the catalytic hydroxylation of phenol by H<sub>2</sub>O<sub>2</sub> were used to characterize the resulting materials. It is shown that the materials prepared by this way have a better hydrothermal stability and a higher catalytic activity than tin containing MCM-41 prepared by conventional methods (mechanical mixture of nano-sized SnO<sub>2</sub> and MCM-41, impregnation of MCM-41 by SnCl<sub>4</sub> or hydrothermal synthesis).

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**Keywords:** Mesoporous silica; Tetrabutyltin; Hydroxylation of phenol; Surface organometallic chemistry

## 1. Introduction

Since its discovery in 1992, MCM-41 mesoporous silica has attracted a great interest, due to its large pore size and its high specific surface area [1,2]. However, its poor hydrothermal stability and the absence of catalytically active centers on its surface have limited its applications in catalysis [2,3]. In order to solve these problems, a lot of solutions has been proposed, using various methods [4,5].

Acidic properties were given to MCM-41 by introduction, in the channels, of strongly acidic compounds. For example, Kozhevnikov et al. impregnated MCM-41 with a solution of heteropolyacid, leading to materials showing good performances in the alkylation of *p*-diisobutyl phenol by isobutene [6]. Unfortunately, the preparation method led to steric hindrances in the pores rendering these materials less interesting in catalysis [3,7].

Another way to increase the catalytic activity of mesoporous silica is to introduce, during the synthesis, metal atoms in the framework, in replacement of silicon. Tin containing MCM-41 was prepared by using this approach and used for the catalytic hydroxylation of phenol and 1-naphthol [8] and the polymerization of lactide [9].

The metal can also be introduced after the synthesis and removal of the template by calcination, by deposition of a volatile organometallic species. For example, Burch et al. prepared a tin containing MCM-41 by chemical vapor deposition of tetraethyl tin followed by a thermal treatment in air [10]. The resulting catalyst showed a very good activity for the reduction of crotonaldehyde to crotyl alcohol, propan-2-ol being used as the hydrogen transfer reagent. However, multiple layers of tin oxide species had been deposited on the surface by repeating the process and the solids were highly heterogeneous.

In an alternative approach surface organometallic chemistry was used for the post-synthesis modification of MCM-41. For example, Maschmeyer et al. modified MCM-41 by grafting reaction of a titanocene complex and used it for the epoxidation of cyclohexene [11]. This

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material had better catalytic performances than that prepared by framework substitution [12]. The grafting reaction of organotin compounds on various surfaces including Aerosil silica, MCM-41 and zeolites has also been reported [13–20]. However these studies focussed on the grafting process and the characterization of the grafted species and no application in catalysis was reported.

We report in this paper the synthesis, characterization and catalytic properties of tin modified mesoporous silicas obtained by reaction of tetrabutyltin with MCM-41 and further heating. The properties of these solids were compared to those of tin containing mesoporous silicas obtained by classical ways.

## 2. Experimental

### 2.1. Preparation of samples

All chemicals were purchased by Aldrich or Schuchardt and used as received.

Siliceous MCM-41 was prepared by a classical way with  $C_{16}H_{33}N(CH_3)_3Br$  (CTMABr) and  $Na_2Si_3O_7$  [21]. The sample was calcined in air at 200 °C during 4 h and then at 540 °C during 10 h. The crystallinity of the sample before and after calcination was in agreement with literature data [1].

The tin modified MCM-41 was prepared following a procedure previously reported [20]. The calcined MCM-41 was first treated under dynamic vacuum ( $10^{-4}$  Torr) at 500 °C during 5 h. After cooling to room temperature the desired amount of tetrabutyl tin was introduced with a syringe via a septum. The system was then kept at 150 °C during 10 h. A liquid nitrogen trap was used intermittently to ensure a good contact between the tin complex and MCM-41. Unreacted tetrabutyl tin and evolved gases were then removed by evacuation at the reaction temperature during 3 h. Finally, the sample was calcined in flowing oxygen at 500 °C during 12 h. Depending on the amount of tetrabutyl tin used for the grafting reaction, solids with various tin contents were obtained. In the following these materials will be denoted G- $x$  (for Grafting) where  $x$  is the Si/Sn molar ratio in the sample as determined by chemical analysis.

For comparison, three other tin containing MCM-41 were prepared by more classical ways.

- The sample M-98 (M for Mechanical) was prepared by a mechanical mixture of nanometer  $SnO_2$  and MCM-41. For this purpose, nanometer  $SnO_2$  was prepared according to the literature [22]. Filtration through siliceous MCM-41 led to the desired solid which was then washed with deionized water, dried at 60 °C and finally calcined in air at 540 °C during 10 h. Its Si/Sn molar ratio was 98.
- The sample I-103 (I for Impregnation), was prepared by impregnation of MCM-41 with an aqueous solution of  $SnCl_4$  (at pH 3). The resulting solid was dried at room

temperature during 24 h and then calcined in air at 500 °C during 10 h. Its Si/Sn molar ratio was 103.

- The sample S-100 (S for Synthesis), was prepared by hydrothermal synthesis. The composition of the gel, which crystallized, was 1.00 Si/0.2 CTMABr/0.01 Sn/102  $H_2O$ . It was prepared by addition of  $SnCl_4$ ,  $5H_2O$  to a solution of CTMABr and  $Na_2Si_3O_7$  under vigorous stirring. The pH was then adjusted at 8.5 by addition of 1 M HCl. The resulting mixture was transferred into a stainless-steel autoclave equipped with a Teflon liner and heated at 100 °C during 3 days. The powder was recovered, washed with deionized water, dried at 60 °C and calcined in air at 540 °C during 10 h.

### 2.2. Physicochemical characterization

Powder X-ray diffraction (XRD) spectra were recorded on a Phillips X'Pert MPD spectrometer using the  $Cu K\alpha$  radiation ( $\lambda = 0.1541$  nm). Elemental analyses were performed on a Phillips Magix PW2424 X fluorescence spectrometer. Nitrogen adsorption–desorption isotherms were measured at 77 K on a OMINIC 100 CX gas adsorption instrument. Before measurement, the samples were treated under vacuum ( $10^{-5}$  Torr) at 300 °C. The pore size distribution was calculated by the BJH method [23]. The UV–vis diffuse reflectance spectra (DRS) were recorded on a Varian 500 spectrometer using  $BaSO_4$  as reference. Infrared spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer using a home-made in situ cell equipped with  $CaF_2$  windows. Thermogravimetry (TG) analysis was carried out on a Perkin Elmer thermogravimetric analyzer (heating rate 10 °C/min). High resolution transmission electron microscopy (HRTEM) photographs were obtained on a 200 CX Jeol microscope operating at 200 kV.

### 2.3. Hydroxylation of phenol by $H_2O_2$

The reaction was studied in a batch reactor. One gram of phenol and 0.1 g of catalyst were introduced in 8.4 ml of deionized water. The pH of the solution was then adjusted to 3–4 by addition of 1 M HCl. Finally 1.1 ml of 30%  $H_2O_2$  (corresponding to a molar ratio  $H_2O_2$ /phenol of 1) was added and the reactor was then heated at 60 °C during 12 h under stirring. The reaction mixture was then analyzed with a Agilent 6890 N gas chromatograph equipped with a FID detector and a 30 m HP-5 capillary column.

## 3. Results and discussion

### 3.1. Structure and hydrothermal stability of the samples

Fig. 1 shows the XRD patterns of all samples. In all cases, the spectra are quite comparable to literature data (see for example Ref. [1]) and correspond to mesoporous materials of the MCM-41 family. For the grafted samples, slight

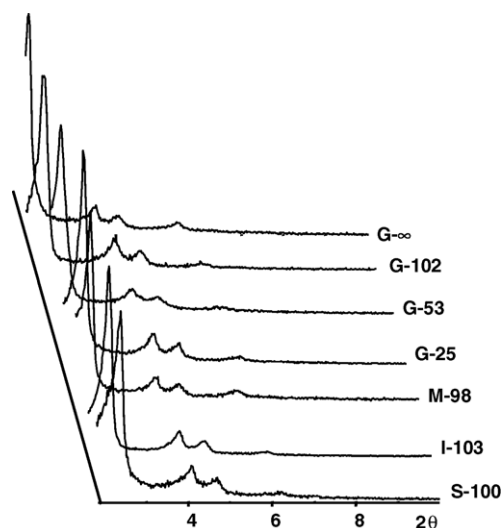


Fig. 1. X-ray powder diffraction spectra of the various tin-containing mesoporous silicas.

variations of the  $d$ -spacings can be observed as a function of the tin content. Similar trends had also been reported for Al-MCM-41 [24], Ti-MCM-41 [25] and V-MCM-41 [26] materials. Whatever the preparation method and the tin loading, no other peaks, which could be attributed to tin oxide for example, were observed. The unit cell parameters deduced from the data of Fig. 1 were used, together with those of nitrogen adsorption–desorption (see below), to calculate the walls thickness of the different materials. The results are summarized in Table 1.

Fig. 2 shows a HRTEM photograph of the G-102 sample. The hexagonal structure of MCM-41 type materials is clearly seen, in agreement with the XRD data. One can also see that, at this scale, the solid seems homogeneous as if the tin atoms had been deposited uniformly.

Nitrogen adsorption–desorption isotherms are very useful for the characterization of mesoporous silicas. Figs. 3 and 4 show the nitrogen adsorption–desorption isotherms and the corresponding pore sizes distributions for the catalysts. In

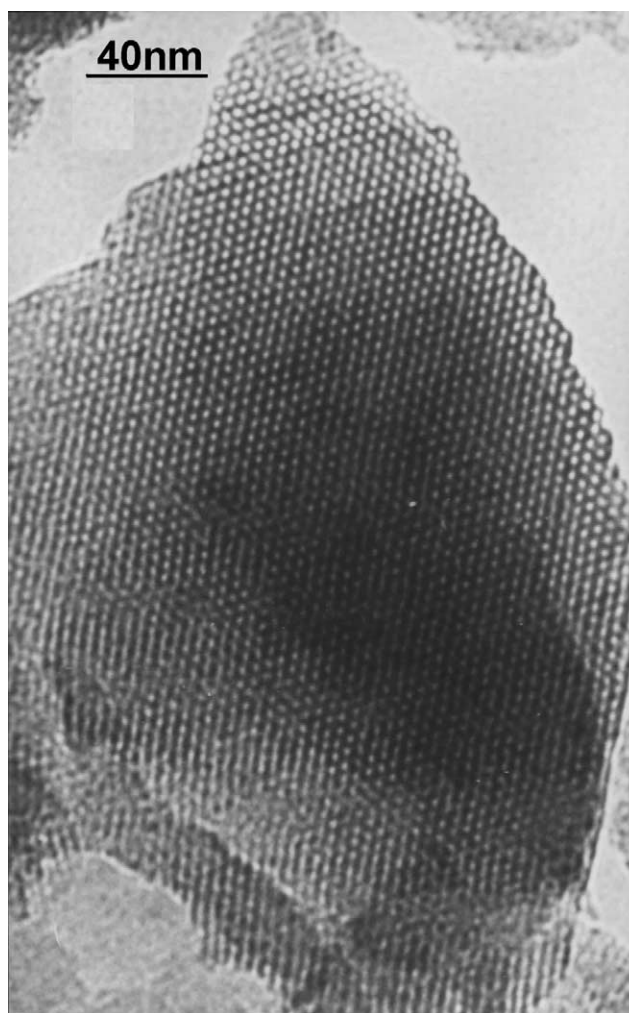


Fig. 2. HR-TEM micrograph of sample G-102.

all cases a typical type IV isotherm, characteristic of mesoporous materials, is obtained, with a relatively narrow pore size distribution, as expected for MCM-41.

When looking on the data of Table 1, some remarks can be made. First of all, the BET surface area of the grafted

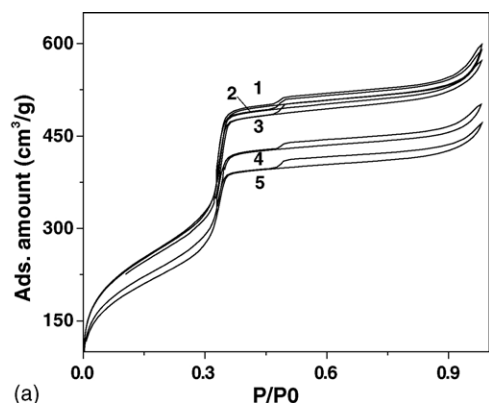
Table 1  
Physico-chemical characteristics of the various tin-modified MCM-41

Sample	Si/Sn th <sup>a</sup>	Si/Sn exp. <sup>b</sup>	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Mean pore radius (nm)	Wall thickness (nm) <sup>c</sup>
G-14	12	14	843	1.41	0.85
G-25	25	25	886	1.44	0.82
G-53	50	53	981	1.46	0.81
G-102	100	102	992	1.47	0.80
G-217	200	217	1000	1.48	0.80
G-357	300	357	1005	1.48	0.79
G-801	600	801	1008	1.49	0.79
G-∞	∞	∞	1008	1.49	0.80
M	100	98	753	1.46	0.81
I	100	103	866	1.40	0.75
S	100	100	912	1.52	0.61

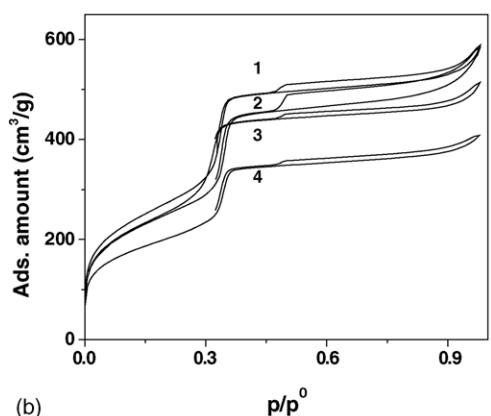
<sup>a</sup> Theoretical Si/Sn ratio based on the quantities introduced during the preparation.

<sup>b</sup> Experimental Si/Sn ratio from chemical analyses.

<sup>c</sup> Deduced from XRD patterns and adsorption experiments.



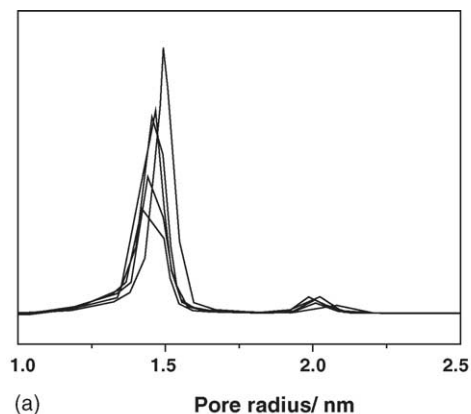
(1) G = ∞; (2) G-102; (3) G-53; (4) G-25; (5) G-14.



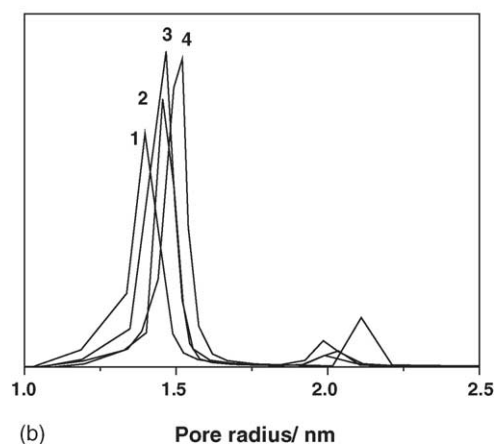
(1) I-103; (2) M-98; (3) G-102, (4) S-100.

Fig. 3. Nitrogen adsorption–desorption isotherms of some selected samples.

samples decreases when the amount of tin increases. In fact, it can be easily checked that this decrease corresponds simply to a lower amount of MCM-41 in presence of tin than in the pure sample (the surface areas calculated per gram of MCM-41 in the sample vary between 975 and 1027 m<sup>2</sup>). Moreover for the grafted samples, the mean pore radius decreases slightly when the amount of tin increases while the wall thickness increases. The sum of these two values remains constant, as it can be expected. Indeed, the samples were prepared by reaction of MCM-41 with tetrabutyltin and at a calcination temperature at which the mesoporous support is stable. So, the silicate framework should remain unchanged. The decrease of the pore size can be explained by the presence of tin (as tin oxide) which will cover the silica framework, resulting in both an increase of the walls thickness and a decrease of the pore sizes. Regarding the homogeneity of the tin coverage on the support, Fig. 4 shows that the distribution of pore radii is relatively sharp, even when high amounts of tin are present. As a consequence, we can reasonably suppose that the walls are covered, relatively uniformly, by a thin thickness of tin oxide. It can be pointed out that even for the highest amount of tin (Si/Sn = 14) this value corresponds to one tin atom for 0.14 nm<sup>2</sup>, that is less than what is necessary for a monolayer.



Curves from left to right correspond to samples G-14 (1), 25 (2), 53 (3), 102 (4), and ∞ (5), respectively.



(1) I-103; (2) M-98; (3) G-102, (4) S-100.

Fig. 4. Pore size distributions as deduced from nitrogen desorption isotherms.

When comparing samples with the same amount of tin but obtained by different procedures, the grafting method gives the highest surface area material. The sample obtained by mechanical mixture shows the lowest surface area, probably due to a pore blocking effect by the tin oxide nanoparticles. The sample obtained by impregnation is probably less homogeneous than that prepared by grafting (see Fig. 4) while that prepared by hydrothermal synthesis seems relatively homogeneous. However in that sample, and in contrast to other samples, tin is probably localized not only at the surface but also in the walls where it is inaccessible to reagents.

In conclusion of the data reported in Table 1 and of the preparation methods one can propose that the dispersion of tin at the surface of the samples varies in the order:

$$M < I < G$$

The sample prepared by hydrothermal synthesis having probably tin in its framework.

Another interesting feature of the samples prepared by grafting reaction of tetrabutyltin is their hydrothermal

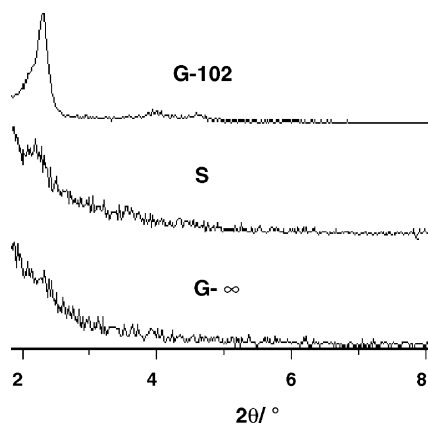
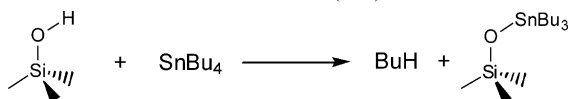


Fig. 5. X-ray powder diffraction spectra of G-102, G-∞ and S samples after treatment in water at 100 °C during 24 h.

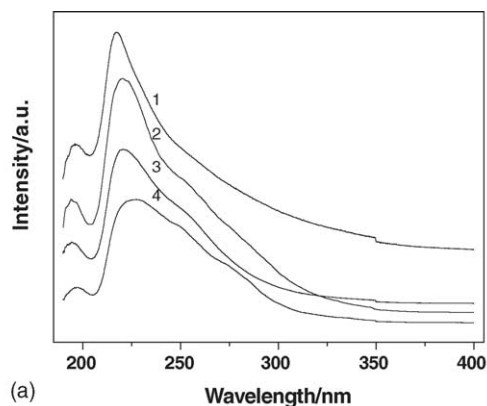
stability. Fig. 5 shows the X-ray diffraction powder spectra of G-102, G-∞ and S samples after treatment in water at 100 °C during 24 h. It can easily be seen that only the G-102 sample has retained its mesoporous structure. This stability is probably related to the structure of tin in these materials, as shown below and should be compared to previous observations on Y zeolites where samples obtained by reaction of H-faujasite with SnMe<sub>4</sub> and further calcination were totally inactive towards water [19]. One reason could be that in the grafted samples the amount of surface silanols is lower than in the other samples, due to their consumption during both the grafting and calcination steps (see below). These samples should then be more hydrophobic and therefore less sensitive to water.

### 3.2. State of tin in the various samples

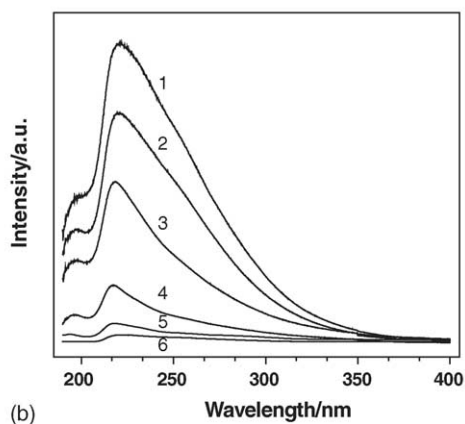
It had been reported previously [13,20] that tetrabutyltin reacts with the silanol groups of silica or MCM-41 leading to the formation of (≡Si-O)<sub>x</sub>SnBu<sub>(4-x)</sub> species.



Upon treatment at 500 °C these grafted species further react with residual hydroxyl groups leading to (≡Si-O)<sub>4</sub>Sn species. In order to have a further proof of this and to determine the state of tin in the samples prepared by the other ways we have undertaken a study by UV–vis spectroscopy of the various Sn/MCM-41 solids. Indeed, this spectroscopy can be very useful for the study of the coordination state of tin (tetrahedral or octahedral). Typically tetrahedrally coordinated tin gives an absorption band near 220 nm while hexacoordinated tin will lead to an absorption band near 280 nm [27,28]. Fig. 6 shows the UV–vis diffuse reflectance spectra of the different tin-containing MCM-41. For all G samples, the spectrum is mainly composed of a very intense absorption at 220 nm, in agreement with a tetrahedrally coordinated tin. For high tin loadings, a small shoulder, characteristic of



(1) G-102; (2) I-103; (3) S-100; (4) M-98.



(1) G-14; (2) G-25; (3) G-53; (4) G-102; (5) G-217; (6) G-∞

Fig. 6. UV–vis diffuse reflectance spectra of tin-containing MCM-41.

hexacoordinated tin, can be observed near 260 nm. In contrast, the samples prepared by the other ways display always non-negligible absorptions near 260–280 nm which can be ascribed to the presence of hexacoordinated mono- and/or polymeric tin.

In conclusion, the samples prepared by grafting reaction of tetrabutyltin contain mainly tetrahedral tin, hexacoordinated being only observed for high tin loadings, while the samples prepared by the other ways (mechanical mixture, impregnation or direct synthesis) contain more hexacoordinated tin.

### 3.3. Catalytic activity

It had been reported that tin-containing mesoporous molecular sieves were active catalysts for the selective oxidation of aromatics and the hydroxylation of phenol and 1-naphthol with peroxides [8]. So we choose the hydroxylation of phenol by H<sub>2</sub>O<sub>2</sub> as a comparison test for the different Sn/MCM-41 described above. The results are shown in Table 2 which gives, for each catalyst, the conversion of phenol, the selectivity to the desired products (catechol and hydroquinone) and the efficiency of H<sub>2</sub>O<sub>2</sub> for the reaction (calculated as the amount of consumed

Table 2  
Catalytic performances of the tin-modified MCM-41 for the hydroxylation of phenol

Sample	Phenol conversion (mol%) <sup>a</sup>	Diphenol distribution (mol%) <sup>b</sup>		Efficiency of H <sub>2</sub> O <sub>2</sub> (%) <sup>c</sup>
		Catechol	Hydroquinone	
G-25	24.8	nd	8.9	7.6
G-53	30.3	0.5	9.0	9.0
G-102	38.8	39.1	17.3	66.0
G-217	39.9	40.8	17.5	72.2
G-357	38.9	39.4	18.3	71.1
G-801	35.2	29.4	17.2	49.8
G-∞	5.5	1.37	0.9	0.4
M	28.8	16.0	13.3	26.5
I	29.3	32.3	14.7	42.4
S	36.4	37.6	18.4	66.7
SnO <sub>2</sub>	2.1	1.64	–	0.1

Reaction conditions: amount of the catalyst = 100 mg; volume of the solvent (water) = 10 ml; H<sub>2</sub>O<sub>2</sub>/phenol (mol/mol) = 1; temperature = 60 °C; pH = 3–4; reaction time = 12 h; nd refers to not detected.

<sup>a</sup> As the formation of all products.

<sup>b</sup> CAT is catechol, HQ is hydroquinone; the other products are tar.

<sup>c</sup> H<sub>2</sub>O<sub>2</sub> selectivity = mol% of H<sub>2</sub>O<sub>2</sub> consumed in the formation of catechol and hydroquinone excluding tar.

hydrogen peroxide used for the production of catechol and hydroquinone). These data are quite comparable to those of literature. For example a conversion of 20–25% of phenol is obtained with tin or titanium silicates with the MFI structure [29] with a H<sub>2</sub>O<sub>2</sub> efficiency of 55–68%. Quite the same results were also obtained on titanium mesoporous silicas [30].

When looking at the results obtained with the grafted samples, it can be seen that the catalytic activity increases with the amount of tin and reaches a maximum for sample G-217. For higher tin contents, the catalytic activity decreases and becomes about zero for pure SnO<sub>2</sub>. Similarly the yield of desired products and the efficiency of H<sub>2</sub>O<sub>2</sub> are the highest for the G-217 sample. When comparing these results to those obtained with the other preparation methods, it is evident that M and I solids are less effective for the same tin content while the sample prepared by hydrothermal synthesis has an activity comparable to that of G-102.

It has been reported that the catalytic hydroxylation of phenol depends on numerous parameters such as the pore size [31] and the specific area of the catalysts [3], their dispersion [10] and the chemical forms of the active species [29,32]. In our case, pore size effects can be excluded due to the great difference between the sizes of phenol (ca. 0.7 nm) and the channels of MCM-41 (ca. 3 nm). Similarly, a specific area effect is not predominant as for the G samples the surface area decreases continuously when the tin content increases while the catalytic activity shows a maximum. The results are more probably related to the state of tin in the solids which is different in the various samples. Indeed, we have shown that the main characteristics of G samples with low tin content is the presence of isolated tetrahedrally coordinated tin atoms. This is in agreement with the results of Ramasamy et al. who proposed that Sn<sup>4+</sup> ions well-dispersed in the silicalite framework are able to form peroxo intermediates in presence of H<sub>2</sub>O<sub>2</sub> and are active in oxidation reactions [33]. The best

results are obtained for the G-217 sample. In this sample there are ca. 80 μmol of tin per gram, corresponding to ca. 0.05 tin atom per nm<sup>2</sup>, a value which can seem relatively low for the obtention of well-dispersed tin atoms. If one assumes that the fact that higher tin loadings do not lead to better catalytic results is related to the presence of non-isolated tin species, we can conclude from these data that tin is not distributed homogeneously on the surface. Such a conclusion is in agreement with literature data on silica dehydroxylated at high temperature and double quantum 2D <sup>1</sup>H MAS NMR on mesoporous silicas dehydroxylated at various temperatures [34,35].

#### 4. Conclusion

Several tin-containing mesoporous silicas were synthesized and characterized by various physicochemical methods including X-ray diffraction and nitrogen adsorption. It has been shown that the samples prepared by reaction of tetrabutyltin with the hydroxyl groups of MCM-41 give more homogeneous materials where all tin is located at the surface and (except for very high tin loadings) is tetrahedrally coordinated. These solids were used as catalysts for the hydroxylation of phenol by H<sub>2</sub>O<sub>2</sub>. The catalytic activity can be correlated to the amount of tetrahedral tin and so the samples obtained by reaction of SnBu<sub>4</sub> are the most active.

#### Acknowledgements

The authors acknowledge the support of National Nature Science Foundation of China (No. 20173009, 20133010, 20373011) and the Nature Science Foundation of Fujian Province of China (No. E0210008).

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