Accepted Manuscript

Title: Rapid Room Temperature Synthesis of Tin-based Mesoporous Solids: Influence of the Particle Size on the Production of Ethyl Lactate

Authors: Nicolas Godard, Xavier Collard, Alvise Vivian, Lucia Anna Bivona, Sonia Fiorilli, Luca Fusaro, Carmela Aprile



S0926-860X(18)30072-3
https://doi.org/10.1016/j.apcata.2018.02.014
APCATA 16554
Applied Catalysis A: General
8-12-2017
4-2-2018
13-2-2018

Please cite this article as: Godard N, Collard X, Vivian A, Bivona LA, Fiorilli S, Fusaro L, Aprile C, Rapid Room Temperature Synthesis of Tin-based Mesoporous Solids: Influence of the Particle Size on the Production of Ethyl Lactate, *Applied Catalysis A, General* (2010), https://doi.org/10.1016/j.apcata.2018.02.014

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Rapid Room Temperature Synthesis of Tin-based Mesoporous Solids: Influence of the Particle Size on the Production of Ethyl Lactate

Nicolas Godard,^a Xavier Collard,^a Alvise Vivian,^a Lucia Anna Bivona,^a Sonia Fiorilli,^b Luca Fusaro,^a Carmela Aprile^{*,a}

^a Laboratory of Applied Material Chemistry (CMA), University of Namur, 61 rue de Bruxelles, 5000 Namur (Belgium)

^b Department of Applied Science and Technology, Polytechnic of Turin, Institute of Chemistry, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy

[©]Corresponding author at Laboratory of Applied Material Chemistry (CMA), University of Namur, 61 rue de Bruxelles, 5000 Namur (Belgium)

E-mail address: carmela.aprile@unamur.be Graphical abstract



Highlights

- A rapid room temperature synthesis protocol was successfully conceived
- A series of porous solids bearing Sn inserted as single site was prepared
- The solids were obtained with a precise control of the particle size
- An excellent correlation between particles size and catalytic activity was observed
- The best catalyst allows obtaining a full conversion of DHA with total selectivity

Abstract

A series of tin-based mesoporous catalysts was prepared via a novel straightforward sol-gel procedure leading to an extremely short synthesis time decreased up to 5 min at room temperature. This synthesis, together with the precise control of the selected particle size, represents an advancement compared to the state of the art and be can easily applied to large scale production. Characterization of the materials revealed the presence of MCM-41 like architecture with a high specific surface area, narrow pore size distribution, insertion of tin in tetrahedral coordination and a good balance of Lewis/Brønsted acidity. Moreover, all these characteristics were almost identical for the entire series thus making these solids an ideal case study to investigate the influence of the particle size on the catalytic behavior. The Sn containing materials were tested as catalysts in the conversion of dihydroxyacetone into ethyl lactate. The excellent correlation between particles size and catalytic performances proves the importance of the size control. In addition, the absence of leaching was proved via hot filtration experiments and the materials preserved their activity in multiple catalytic cycles.

Keywords: mesoporous materials; fast synthesis; size control; heterogeneous catalysis

1. Introduction

Mesoporous materials containing different metal elements as single sites within the silica structure may act as highly efficient catalysts for various applications including epoxidations [1], Baeyer-Villiger oxidations [2], Meerwein-Ponndorf-Verley-Oppenauer redox reactions [3],

alkyl lactate production [4,5], among others. Due to the importance of these materials for both academic and industrial purposes [6,7], a great effort has been devoted to the optimization of the reaction conditions leading to their preparation [8,9]. One of the most widely studied porous systems is represented by MCM-41 based architectures bearing a metal center inserted in the silica framework (M-MCM-41 with M=Ti, Sn, V, Ga ...) [1,10–12].

Rapid synthesis together with the development of alternative procedures to the standard hydrothermal treatment under static conditions, are some of the most explored approaches in order to reduce the economic impact and favor a more sustainable large scale production [13,14]. Moreover, it is known that one key parameter in catalysis is represented by the accessibility to/from the active sites which can be hindered by diffusion limitations [15]. A precise control of the diffusivity within the porous materials can be achieved by tuning the diameter of the mesopores as well as the particle size [16,17].

However, despite the recognized relevance of this last point there are only few reports addressing the full control of the particle size of the M-MCM-41 materials. On the other side, there is a large variety of synthesis procedures illustrating the preparation of mesoporous solids obtained via a very short reaction time. In the recent literature, various sol-gel syntheses of mesoporous materials entailing an aging time of few hours were described [18]. However, in some of these approaches, additional steps such as evaporation to dryness were involved [19]. Alternative protocols that allow obtaining high quality MCM-41 solids were also reported. In one of them, mesoporous materials were obtained only after 1 min reaction under ultrasound irradiation, but additional post-treatments (for a least 3 h) were also required [20]. If the isomorphic substitution of silicon with a metal element is entangled, the synthesis procedure may become even more challenging. Kong and co-workers reported the fast synthesis of MCM-41 and they also achieved a high control of the particle size distribution. However, the transformation of the synthesized materials into vanadium supported catalysts was achieved via a 12 h post treatment at room temperature [21]. Pescarmona et al. published the fast preparation of Ti-MCM-41 in a one-pot sol-gel procedure. Inspired to this approach we recently reported the synthesis of Sn [5], Ga [22] and Zn [23] based MCM-41 solids with extra-small size. Despite the fact that no hydrothermal treatment under static conditions was required, the shortest protocol implied a 2 h approach. Moreover, the particle size was reduced below 200 nm but with no control of the particle size in the extra-small region (between 50 and 250 nm). The preparation of metal containing porous silicates via syntheses strategies different from the solgel procedure were also published. A microwave-assisted hydrothermal method implying 3 h irradiation at 373 K, represents one of the most recent examples [24]. In recent years, the aerosol-assisted sol-gel process also emerged as an innovative and effective way for the continuous production of porous solids [25–28]. However, due to the fast evaporation-induced self-assembly of the surfactant and condensation of the inorganic precursors, a careful control of the particle size can be hardly obtained.

Herein, we report a straightforward one-pot preparation of Sn containing mesoporous solids (Sn-mp) requiring extremely short reaction time at room temperature and displaying a full control of the particle size distribution in the extra-small region (below 250 nm). The synthesis of a series of five materials with an average particle size ranging from 60 (for Sn-mp-F) to 210 nm (for Sn-mp-J) was successfully achieved. Since all the main parameters such as specific surface area, pore size distribution, insertion of Sn as single site and Brønsted /Lewis acidity are almost identical in the whole series, the solids can be considered an ideal case study to investigate the direct influence of the particle size on the catalytic performances.

For this purpose, the industrial relevant synthesis of ethyl lactate was selected as target reaction. It was recently reported that porous structured silica embedding Sn in tetrahedral coordination

within the framework, can be active and selective catalysts for the conversion of dihydroxyacetone to alkyl lactates [5,29,30].

All the solids obtained via our rapid synthesis protocol displayed outstanding activity in the synthesis of ethyl lactate. An excellent correlation between particle size and catalytic performances was observed. In addition, the materials preserved their activity in multiple catalytic cycles. Additional tests, proved that the synthesis time of the Sn based solids can be further reduced to 5 min without affecting the catalytic performances of the material. Moreover, under optimized conditions a quantitative conversion with a selectivity superior to 95% was achieved thus supporting both the possible large scale production and industrial application of the selected solid.

2. Experimental section

2.1 Material and Methods

Transmission electron microscopy (TEM) images were performed using a Philips Tecnai 10 microscope operating at 80 kV. Samples were prepared by dispersion of a small quantity of material in absolute ethanol and deposited onto a copper grid. Nitrogen adsorption-desorption analyses were carried out at 77 K with a volumetric adsorption analyser (Micromeritics Tristar 3000). Prior to the analysis, the samples were pre-treated at 150 °C for 16 h under reduced pressure (0.1 mbar). The Brunauer-Emmet-Teller (BET) method was applied in the 0.05-0.30 P/P_0 range to calculate the specific surface area, while the pore size distributions were calculated from the adsorption isotherm using the Barrett–Joyner–Halenda (BJH) method. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert diffractometer with Cu Ka radiation ($\lambda = 1.54178$ Å). Energy-dispersive X-ray (EDX) spectroscopy was performed using a JEOL 7500F scanning electron microscope operating at 15 kV coupled with an EDX probe. The Si environment and the coordination of the Sn atoms were studied by ²⁹Si Magic Angle Spinning (MAS-NMR) and static ¹¹⁹Sn Nuclear Magnetic Resonance. ²⁹Si NMR spectra were recorded at room temperature on a Bruker Avance-500 spectrometer operating at 11.7 T (99.3 MHz for ²⁹Si) using a 4 mm CP-MAS Bruker probe. The sample was packed in a 4 mm zirconia rotor and measured with a spinning frequency of 8000 Hz. Quantitative ²⁹Si spectra were recorded using the following acquisition parameters: 300 s relaxation delay, 3 μ s (90°) excitation pulse, 52 ms acquisition time. CP-MAS spectra were recorded using a 5 s relaxation delay and 5 ms contact time. The processing comprised exponential multiplication of the FID with a line broadening factor of 30 Hz, zero-filling, Fourier transform, phase and baseline corrections. The chemical shift scale was calibrated at room temperature with respect to a sample of solid 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) (0.0 ppm). ¹¹⁹Sn NMR spectra were recorded at room temperature on a Varian VNMRS-400 spectrometer operating at 9.4 T (149 MHz for ¹¹⁹Sn) using a 5 mm wideline probe. The sample was packed in a 5 mm glass tube and studied in static condition. ¹¹⁹Sn spectra were recorded using the Hahn echo pulse sequence and following acquisition parameters: 60 s relaxation delay, 1.5µs (90°) excitation pulse, 5 ms acquisition time. The processing comprised exponential multiplication of the FID with a line broadening factor of 1000 Hz, zero-filling, Fourier transform, phase and baseline corrections. The chemical shift scale was calibrated at room temperature with respect to the isotropic shift of SnO_2 to -603 ppm [38].

The analysis of Brønsted and Lewis acidity of the catalysts was performed by adsorption/desorption of ammonia monitored by Fourier Transform Infrared Spectroscopy (FT-IR). The measurements were performed on a Bruker Tensor 27 spectrometer equipped with a liquid nitrogen-cooled mercury–cadmium–telluride (MCT) detector, operating at 2 cm⁻¹

resolution. Pre-treatments were carried out using a standard vacuum frame, in an IR cell equipped with KBr windows. Wafers were outgassed 1 hour at 673 K before adsorption of ammonia at room temperature. Adsorption of ammonia was studied in the pressure range 0.01-20.0 mbar: the reversible fraction of the adsorbates was then removed by prolonged outgassing at room temperature.

All the components for the conversion of DHA into EL were analysed by Gas chromatography on a Trace GC Ultra from Interscience, with a narrow-bore UltraFast UFC-1 column (specifications: 0.1 mm, 0.1 μ m, 5 m, Rtx-1 stationary phase – 100% polydimethylsiloxane) using nitrogen as carrier gas at constant flow rate of 2.0 mL/min. The FID detector operated at 250 °C with a split ratio of 140. The oven temperature was maintained at 40 °C for 1.29 min, then increased to 200 °C at 150 °C/min and finally maintained at 200 °C.

All reagents were purchased from Sigma-Aldrich: tetraethylorthosilicate (TEOS, 99.9% purity), cetyltrimethylammonium bromide (CTAB, 95% purity), concentrated ammonium hydroxide aqueous solution (28 wt% NH₃), tin(IV) chloride pentahydrate (SnCl₄·5H₂O, 98% purity).

2.2 Synthesis procedure of mp

The synthesis procedure was inspired from the method reported by Cai *et al.* [39] CTAB (691 mg, 1.80 mmol) was introduced into a 1000mL PP bottle and dissolved in milli-Q water (314 g, 17.40 mol) under 800 rpm stirring at room temperature (25 °C). A concentrated aqueous solution of ammonium hydroxide (10.8 g, 0.57 M) was slowly added to the mixture. After 30 min, TEOS was added dropwise and the molar ratios in the synthesis mixture were therefore: 1 TEOS : 0.125 CTAB : 11.4 NH₃ : 1238 H₂O. Then, the reaction mixture was stirred and the synthesis time was varied from 5 to 120 min. In particular, the various solids were synthetized at 5, 15, 30, 60, 90 and 120 min. After this time, the white precipitate was filtered and washed three times with milli-Q water and EtOH, alternatively.

The same procedure was used to study the effect of the base concentration. Increasing amounts of aqueous ammonium hydroxide solution 28% (material A: 1.0 g; material B: 2.0 g; material C: 3.0 g; material D: 4.0 g; material E: 5.0 g) were slowly added to the CTAB/H₂O mixture. After 30 min, TEOS (3.00 g, 14.4 mmol) was added dropwise to the basic solution. After 30 min, the white solid was filtered and washed three times with milli-Q water and EtOH, alternatively.

Molar ratios: 1 TEOS : 0.125 CTAB : 1.1 (A), 2.3 (B), 3.4 (C), 4.6 (D), 5.7 (E) NH₃ : 1213 (A), 1216 (B), 1218 (C), 1221 (D), 1224 (E) H₂O.

All products were dried overnight at 60 °C and the structure directing agent was removed via calcination in air at 550 °C for 6 h (heating and cooling rate: 3 °C min⁻¹).

2.3 Synthesis procedure of Sn-mp

The synthesis of Sn-mp was performed in a similar way. The Si/Sn ratio in the synthesis mixture was 74 for all Sn-mp materials. Tin(IV) chloride pentahydrate (69.6 mg, 0.195 mmol) was dissolved in absolute EtOH (1.00 mL, 17.1 mmol). The resulting solution was mixed with TEOS before addition to the synthesis medium. The synthesis time was 30 min and increasing amounts of concentrated aqueous solution of ammonium hydroxide (28%) were initially added to the CTAB solution (material F: 1.0 g; material G: 2.0 g; material H: 3.0 g; material I: 4.0 g; material J: 5.0 g). All the other reaction parameters remained unchanged.

Molar ratios: 1 TEOS : 0.0135 SnCl₄· 5H₂O : 0.125 CTAB : 1.1 (F), 2.3 (G), 3.4 (H), 4.6 (I), 5.7 (J) NH3 : 1213 (F), 1216 (G), 1218 (H), 1221 (I), 1224 (J) H2O : 1.19 EtOH.

2.4 Catalytic tests

The catalytic tests were performed in batch using a simple reflux apparatus. DHA, nonane (GC internal standard) and absolute EtOH were introduced in a 25 mL round bottom flask. The mixture was stirred during 30 min at 50 °C (or 40 °C) at 800 rpm. After this time, the catalyst was added, (if needed) the reaction mixture was heated at 90 °C and stirred at 1200 rpm for 6 h. After reaction, the mixture was cooled at room temperature, the catalyst was removed by centrifugation (10 min at 4500 rpm) and the remaining solution analyzed via gas chromatography on a Trace GC Ultra from Interscience.

2.5 Leaching tests

For the leaching tests, DHA (90.1 mg, 1.00 mmol) was dissolved in absolute EtOH (3.92 g, 5.00 mL) containing nonane (12.5 mg, 0.097 mmol) at 50 °C and stirred for 30 min at 800 rpm. Then, Sn-mp catalyst (20 mg) was added and the reaction mixture was heated at 90 °C and stirred at 1200 rpm. After 30 min, the catalyst was separated from the reaction mixture via hot filtration (~90 °C). A small amount of the filtrate (200 μ L) was analyzed via GC (diluted 5 times in EtOH prior to GC analysis). The remaining amount of filtrate was stirred at 90 °C for additional 5 h 30 min. A second GC analysis of the reaction mixture was then performed.

2.6 Recycling tests

The recycling tests were performed using 0.4 M DHA. DHA (541 mg, 6.00 mmol) was dissolved in absolute EtOH (11.8 g, 15.0 mL) containing nonane (75.0 mg, 0.585 mmol) and stirred for 30 min under 800 rpm at 50 °C. The Sn-mp catalyst (150 mg) was then added and the mixture was kept at 90 °C for 3 h under 1200 rpm stirring. The catalyst was then separated by centrifugation (10 min at 4500 rpm). A sample of the supernatant was taken out for GC analysis. The supernatant was carefully removed from the centrifuge tube and the catalyst was rinsed with EtOH and centrifuged (twice). After this, the catalyst was calcined in air at 500 °C for 2 h (heating rate: 2 °C min⁻¹). The subsequent catalytic tests were carried out by repeating this procedure from the beginning (the quantities were adapted in function of the mass of recovered catalyst).

2.7 Preparative test

DHA (450 mg, 5.00 mmol) was dissolved in absolute EtOH (25 mL) at 50 °C for 30 min under 800 rpm stirring. Then, Sn-mp catalyst (250 mg) was added and the mixture was kept at 90 °C under 1200 rpm stirring. After 6 h, the catalyst was separated by centrifugation (10 min at 4500 rpm). The supernatant was then removed and EtOH was used to wash the catalyst by centrifugation. Then, the supernatants were reunited and the mixture was evaporated under reduced pressure. EL was isolated in 84% yield and characterized by ¹H and ¹³C NMR.

3. Results and discussion

Prior to the synthesis of Sn-mp materials, a study of the standard mp solids was performed in order to investigate the parameters allowing a careful control of the particle size distribution as well as a possible decrease of the synthesis time (ST). The target range in terms of size was fixed in the extra-small region [23] between 30 and 300 nm.



Fig. 1 Mean particle size of mp and Sn-mp materials as function of the ammonia solution (NH4OH) concentration

Standard MCM-41 solids are, hence, considered as large particle size materials and are not included in the present investigation.

It is known that the dimensions of mesoporous silica particles are mainly influenced by three parameters: concentration of the silica precursor, pH and synthesis time [31]. In this work, the synthesis conditions in terms of concentration of TEOS and structure directing agent were maintained constant while the attention was focused on the effect of the base concentration. In order to explore the possibility of a further decrease of the synthesis time (in the previous investigations was already shortened to 2 h [5]) particular attention was also devoted to the study of this parameter. Five different solids obtained at ST ranging from 5 min to 2 h were prepared (see experimental for more details). Transmission electron microscopy (TEM) investigation revealed a similar particle size distribution (Figure S1) even at 5 min.

Surprisingly, the full characterization of the materials via TEM, nitrogen physisorption, X-ray diffraction and ²⁹Si NMR (Figure S2 and S3) did not evidence important structural and textural differences among the porous solids, indicating that an extremely short synthesis time could be selected. Only a slight decrease of the yield was observed after 5 and 15 min reaction suggesting that 30 min can be selected as best compromise between structure and yield. It is worth noting that no additional hydrothermal treatment under static conditions was needed in order to obtain the final solids. As anticipated, the effect of the base concentration was investigated as well. Five different base concentrations (see experimental) were selected for the synthesis of a series of mp materials, labelled with letters from A to E.

Entry	Material	[NH4OH]	MPS ^a	$\mathbf{S}_{\text{BET}}^{b}$	PSD ^c	ao	Pore Vol. (cm ³ g ⁻¹)		Si	/Sn
		(mol L ⁻¹)	(nm)		(nm)	(nm)	Tot. ^d	Int.e	Syn.	Exp. ^f
1	mp-A	0.05	32 ± 5	1086	2.3	4.2	1.89	0.76	_	-
2	mp-E	0.26	103 ± 15	1101	1.9	3.7	1.19	0.71	_	_
3	Sn-mp-F	0.05	62 ± 12	1066	2.4	3.6	1.30	0.72	74	50
4	Sn-mp-J	0.26	210 ± 20	1089	1.9	3.7	0.75	0.65	74	39

Table 1 Synthesis conditions and properties of mp and Sn-mp materials.

^a MPS (mean particle size) data estimated from 100 measurements with TEM microscopy. ^b S_{BET} - specific surface area calculated from adsorption data in relative pressure range of 0.20-0.30 p/p₀ for all materials. ^c PSD (pore size distributions)

determined from the adsorption isotherm using the Barrett–Joyner–Halenda (BJH) method. ^d Total pore volume calculated at the relative pressure of 0.98. ^e Internal pore volume determined for p/p_0 from 0.0 to 0.8. ^f Determined by EDX.

Based on the previous investigation, a synthesis time of 30 minutes was privileged. Interestingly, TEM observations (Figure S4) evidenced a linear increase of the mean particle size (average estimated over 100 measurements) with the ammonium hydroxide concentration. The mean particle size of mp materials as function of the ammonium hydroxide concentration is reported in Figure 1 (light grey). This linear increase can be explained considering the mechanism involved in the synthesis of silica-based materials. It is known that the formation of silica particles in basic aqueous conditions is governed by two phenomena: the base-catalyzed hydrolysis of TEOS and the condensation of the Si(OH)₄ monomers. If the hydrolysis proceeds faster than the condensation, the nucleation process and the formation of small particles will be favored. Conversely, if the condensation is faster, the lower monomer concentration will favor the condensation between existing particles, i.e. particle growth. Matsoukas et al. [32] suggested that the increase in ammonium hydroxide concentration promotes both reactions, with a preference for condensation. As consequence, hydrolysis becomes the rate-determining step leading to the formation of larger particles. The structural and textural characteristics of samples A and E are reported in Table 1 (entries 1 and 2) as well as in supporting information (Figures S5 and S6).

Once the main parameter controlling the particle size distribution was identified, a similar synthesis procedure was used for the preparation of a series of five materials displaying a MCM-41 like structure and limited percentage of tin inserted as single site within the silica organization (Sn-mp). The tin-based solids obtained at different ammonium hydroxide concentrations were labelled with letters from F to J. It is important to highlight that the synthesis time was of 30 min for the entire series.



Fig. 2 TEM micrographs of Sn-mp particles synthesized in different ammonia concentrations (F: 0.05 M; G: 0.11 M; H: 0.16 M; I: 0.21 M; J: 0.26 M). The scale is identical for all micrographs

All the synthesized tin silicates were extensively characterized (see Table 1 entries 3-4). The data concerning the whole series of mp (from B to D) and Sn-mp (from G to I) solids can be found in Supplementary Information (Table S7).



Fig. 3 Small-angle XRD patterns (a), nitrogen adsorption-desorption isotherms (b), and pore size distributions (c) of materials Sn-mp-F and J

Due to the similarities between the samples, only the full characterization of the two materials corresponding to the two extreme ammonium hydroxide concentrations is discussed herein. The characterization of the remaining samples is included in the Supporting Information material (Figures S8 to S11). In order to verify the reproducibility of the synthesis protocol, a second batch of Sn-mp materials was prepared and full characterized, leading to analogous results. TEM investigation performed on the Sn-mp series revealed a trend similar to the pure silica mp solids (Figure 2) with a linear dependence of the particle size distribution from the ammonium hydroxide concentration. However, the tin containing solids exhibited a larger average diameter (Figure 1, dark grey).

The presence of tin(IV) chloride is therefore assumed to play an important role in particle growth. Plugotarenko *et al.* mentioned that the presence of $SnCl_4$ in the reaction mixture decreases the rate of hydrolysis of the silica precursor thus leading to particles with increased size [33]. A modification of the morphology was also observed with a gradual variation from spherical to elongated particles increasing the amount of base [30,34].

Small-angle XRD patterns of Sn-mp materials display the typical features of MCM-41 solids suggesting that the incorporation of tin did not affect the hexagonal arrangement nor the long-range ordering (Figure 3a and S8). The absence of defined signals corresponding to the d₁₁₀ and d₂₀₀ reflections in the case of sample F (as well as G and H, see Figure S8) can be ascribed to the extremely small size of the particles [5]. Nitrogen adsorption-desorption isotherms and pore size distributions of Sn-mp-F and J are reported in Figure 3b and 3c. All solids display a type IV isotherm and similar specific surface areas (see Table 1 and Figure 3b as well as S9 to S11). The hysteresis loop observed on the isotherm of the material Sn-mp-F arises from the presence of a second mesoporosity between 10 and 70 nm, as better evidenced by the pore size distribution (Figure 3b), attributed to the presence of cavities between small-sized particles due to inter-particle interactions.

This observation is also reflected on the pore volume. As expected, the extra-pore contribution to the total pore volume (calculated in the region $0.8 < p/p_0 < 1$) is more important for small particles.

The presence of tin was confirmed via energy dispersive X-ray (EDX) analysis performed via scanning electron microscopy. Elemental mapping images recorded using SEM indicate a homogenous distribution of Sn and Si within the samples and allow excluding the presence of large separated domains of SnO_2 (S14). Interestingly, the Si/Sn ratios determined by EDX (averaged over at least 5 analyses for each sample) decreases almost linearly with the increasing ammonium hydroxide concentration (Table 1 and Figure 4).



Fig. 4 EDX Si/Sn ratio evaluated for the series of Sn-mp materials as function of the ammonium hydroxide concentration in the synthesis medium

In order to better understand the role of the base on the formation of the tin silicates and exclude the formation of extra-framework tin oxides, solid state NMR experiments were performed as well. It is known that the isomorphic substitution of silicon with tin in the MCM-41 structure can be addressed by means of solid state NMR spectroscopy. ¹¹⁹Sn NMR spectra were recorded at room temperature in static conditions for samples F and J (Figure 5). Only one, broad signal centered at about -690 ppm was observed in both cases, which is assigned to intra-framework Sn(IV) connected to four oxygen bridges [1,2]. No signal related to a relevant presence of extra-framework SnO₂ was observed. This result suggests that high concentrations of base did not favor self-condensation of the two inorganic precursors with consequent formation of separate domains of SnO₂. ²⁹Si MAS-NMR (S12) revealed a good degree of condensation.

The acidity of Sn-mp materials was investigated via FTIR of adsorbed ammonia, which can interact with both silanol groups (Brønsted acidity) and coordinatively unsaturated Sn atoms (Lewis acidity). In order to evidence both contributions, two selected regions of the FTIR difference spectra are reported in Figure 6. The spectra of the samples outgassed at 400 °C before ammonia dosages were subtracted from the spectra recorded after each NH₃ equilibrium pressures, as well as after the prolonged outgassing following the adsorption experiment.



Fig. 5 Solid state ¹¹⁹Sn static NMR of materials Sn-mp-F (a) and Sn-mp-J (b)



Fig. 6 FTIR difference spectra relative to the adsorption of NH_3 on materials Sn-mp-F (a) and Sn-mp-J (b) outgassed at 400 °C. Curves 1 and 2 were obtained under 5 and 1 mbar NH_3 equilibrium pressures and curve 3 corresponds to prolonged outgassing at room temperature after NH_3 dosages. The spectra show a break in the 2500-1950 cm⁻¹ range

The negative absorption bands therefore represent the species that were consumed upon NH₃ adsorption. The dosages and outgassing were similarly performed on all Sn-mp materials and analogous results were obtained in terms of concentration and strength of detected acidic sites. Representative spectra of ammonia adsorption on Sn-mp-F and J are shown in Figure 6. The

analogous spectra performed on samples Sn-mp-G, H and I can be found in supporting information (S15). The negative bands at 3740, 3710 and 3550 cm⁻¹ can be respectively attributed to free, terminal and H-bonded silanol groups [35,36].

On the other side, vibrational changes in the region between 1700 and 1400 cm⁻¹ can be directly correlated with the Lewis and Brønsted acid properties of the Sn-mp solid. The absorption band at 1635 cm⁻¹ corresponds to the bending mode of NH₃ molecules H-bonded to silanol groups, whereas the broad signal at 1465 cm⁻¹ is attributed to the bending mode of NH_4^+ ions formed by proton transfer from Brønsted acidic silanol groups. This suggests that the insertion of Sn within the silica framework of MCM-41 enhances the Brønsted acidity of the neighbouring silanol groups, which become acidic enough to protonate NH₃. In contrast, the surface silanols of nondoped MCM-41 interact with NH₃ via hydrogen-bonding rather than via proton transfer. After a prolonged outgassing of the samples at room temperature, residual signals due to adsorbed ammonia were still observed. In particular, the characteristic signal of NH₄⁺ ions became less intense upon outgassing (reversible proton transfer), the absorption band attributed to NH₃ physisorbed on silanols (1635 cm⁻¹) decreased in intensity and was red-shifted up to 1610 cm⁻¹ for the fully outgassed samples (residual pressure $< 1 \cdot 10^{-3}$). This last signal is ascribed to the formation of adducts between ammonia and coordinatively unsatured Sn atoms, acting as Lewis acidic centres, present as single sites on the surface of the Sn-mp material [23]. Analogous observations were obtained for all the analyzed Sn-mp materials, indicating that they display similar Brønsted/Lewis acidic properties (compare spectra shown in Fig. 6 and S15).

This last result, together with all the previously described characterizations, evidences that the series of Sn-mp samples represent an achievement, from a synthesis point of view, in terms of high control of the particle size distribution. In addition, they are also a perfect case study to investigate the influence of the size of the catalyst on the activity. All the other key parameters such as specific surface area, pore size distribution, insertion of Sn as single site and Brønsted/Lewis acidity are almost identical in the whole series and can be considered as constant in the evaluation of the catalytic behavior of the solids.

All the synthesized Sn-mp materials were tested as catalysts in the conversion of dihydroxyacetone (DHA) to ethyl lactate (EL) selecting 90 °C as target reaction temperature. A simplified reaction scheme is shown in Table 2. A more detailed study on the proposed reaction mechanism was already reported in literature [36].

		HOOH Dihydroxyacetone	-H ₂ O Pyruvic	O EtOF	H→ OH O Ethyl Lact	ate	
Entry	Material	Si/Sn	Conv (%)	Sel (%)	TON _c	TON _p	Ref.
1	Sn-mp-F	50	86	89	100	90	This work
2	Sn-mp-G	47	93	98	102	100	This work
3	Sn-mp-H	43	93	89	93	83	This work
4	Sn-mp-I	41	95	93	92	86	This work

Table 2 Conversion of DHA to ethyl lactate catalyzed by Sn-mp materials.^a

5	Sn-mp-J	39	>99	99	94	94	This work
6	Sn-MCM-41-LP	49	49	94	41	25	Li et al [30]

^a Reaction conditions: 50 mg of catalyst, 5 mL of 0.4 M DHA solution in EtOH, nonane as internal standard (0.194 mmol), 6 h at 90 °C under 1200 rpm stirring.

In order to allow a meaningful comparison among the series of catalysts, as well as with reference solids reported in literature, two different turnover numbers (TON) were calculated. The TON based on the conversion (TON_c defined as moles of DHA converted/moles of Sn) and the TON based on the product formation (TON_p defined as moles of EL obtained/ moles of Sn) were determined for all materials (Table 2).

This preliminary investigation revealed no significant difference in the catalytic performances of the Sn-mp solids. Very similar turnover numbers in terms of TON_c were obtained within the whole series. Slightly lower TON_p were observed for catalyst H as consequence of the different selectivity. However, relevant differences in the catalytic performances were evidenced when the Sn-mp solids were compared to conventional Sn-MCM-41 material consisting of large particles (compare entries 1-5 with entry 6 in Table 2) as well as with MCM-41 like mesoporous solids displaying Zn instead of Sn in the silica framework[23]. This result evidences the excellent performances of the Sn-mp materials and suggests that the selected reaction conditions were not the most appropriate to highlight the diversity in terms of catalytic performances within the series of solids (e.g. compare samples F to J).

In order to better understand the catalytic behavior and clarify if a strong link between activity and particle size exists, the conversion of DHA into EL was tested at lower temperature (Figure 7). The reaction conditions were selected in order to achieve a conversion lower than 100% in all the tests.



Fig. 7 Comparison of Sn-mp materials in terms of turnover number. Reaction conditions: 50 mg of catalyst, 5 mL of 0.4 M DHA solution in EtOH, nonane as internal standard (0.194 mmol), 12 h at 50 °C or 24 h at 40 °C under 1200 rpm stirring

Interestingly, an evident decrease of the catalytic activity with increasing particle size was observed when the reaction temperature was decreased to 50 °C. This result can be attributed to an improved accessibility of the active sites in smaller particles (compare sample F and sample J) thus to a reduced diffusion limitation of reactants and products. This effect was even more evident when the synthesis of ethyl lactate was performed at 40 °C further supporting the previous statements. Figure 7 unambiguously displays the dependence of the catalytic

performances on the particle size. It is important to underline that the catalytic experiments were repeated twice with high reproducibility.

A kinetic investigation was also performed by monitoring the evolution of the concentration of the various species (reactant, product and reaction intermediates) over time. Only one sample of the series was selected for a deeper evaluation of the activity and the experiment was performed using 20 mg of catalyst (Figure 8). The kinetic study (see experimental for more details) revealed the presence of an intermediate product, whose concentration rapidly increased during the initial 30 min. After reaching a maximum of concentration, the intermediate product was slowly converted into EL. Based on literature, the intermediate can be identified as the diethyl acetal of pyruvic aldehyde. The proposed mechanism for this reaction is described elsewhere [37].

In the evaluation of the catalytic activity of the materials, this intermediate should not be considered as a byproduct. The selectivity to EL increases over time and, as will be discussed later on, > 95% selectivity can be achieved just selecting the appropriate conditions (time and amount of catalyst).

Hot filtration experiments, to verify the absence of leaching of the catalytically active species, were performed as well. Figure 9 evidences that after removal of the catalyst, the yield of ethyl lactate remains constant over time (blue line for material J and red line for material F), thus proving that the reaction was performed in presence of a true heterogeneous catalyst.

The absence of leaching is a key factor, but in the evaluation of the catalytic performances, other parameters should be considered. An ideal heterogeneous catalyst should be also stable under the selected reaction conditions, hence reusable in multiple catalytic cycles.



Fig. 8 Kinetic study of the conversion of DHA to EL by Sn-mp-J (EL: ethyl lactate; Int: intermediate product). Reaction conditions: 20 mg of catalyst, 5 mL of 0.2 M DHA solution in EtOH, nonane as internal standard (0.097 mmol), 90 °C under 1200 rpm stirring



Fig. 9 Hot filtration tests for materials F and J (red and black, respectively): yield of EL after 0.5 h and 6 h (catalyst removed). Reaction conditions: 20 mg of catalyst, 5 mL of 0.2 M DHA solution in EtOH, nonane as internal standard (0.097 mmol), 0.5 h at 90 °C under 1200 rpm stirring with catalyst, then 5.5 h at 90 °C after removal of catalyst

Recycling experiments are shown in Figure 10 and evidence the stability of catalyst F and J under the reaction conditions. Due to the excellent performances of the solids, we decided to challenge even more our materials and the synthesis of sample J was repeated using only 5 min synthesis time. Interestingly the novel sample preserved the structural and textural properties (see Figure S13) typical of the whole series. Moreover, a test performed under the conditions reported in Table 2 confirms that the catalytic activity is in line with the previously observed results with a conversion equal to 90 % and a corresponding TONc of 102.

Finally, a preparative test was performed in order to verify that a quantitative and highly selective conversion of dihydroxyacetone into ethyl lactate can be realized.

This test represents a proof of concept and demonstrates that this process could potentially be implemented on industrial scale. A quantitative conversion of dihydroxyacetone into ethyl lactate avoids any additional separation step which would otherwise be mandatory. Under optimized conditions (see experimental), a quantitative conversion of dihydroxyacetone with complete selectivity was obtained. After reaction, separation of the catalyst was easily achieved by centrifugation and the product was isolated just via solvent removal through evaporation under reduced pressure. The ¹H and ¹³C NMR spectra of the isolated product can be found in Supporting Information (S16 and S17).



Fig. 10 Recycling tests for materials F and J (grey and light grey, respectively). Reaction conditions: 150 mg of catalyst, 15 mL of 0.4 M DHA solution in EtOH, nonane as internal standard (0.585 mmol), 3 h at 90°C under 1200 rpm stirring

4. Conclusion

A precise control of particle size distribution was achieved in the synthesis of extra small Snmp nanoparticles. A series of solids displaying a mean particle diameter ranging from 50 (sample F) to 250 nm (sample J) was successfully prepared. All the materials exhibited high specific surface areas, narrow pore size distributions and large pore volumes. The amount of Sn was estimated through EDX, while its insertion as single sites within the silica framework was established via solid-state ¹¹⁹Sn NMR. The presence of Brønsted and Lewis acidity was confirmed via FTIR dosages of ammonia. All the main parameters influencing the catalytic performances such as specific surface area, pore size distribution, insertion of Sn as single site and Brønsted /Lewis acidity were almost identical in the whole series making of these solids an ideal case of study to investigate the influence of the size of the catalyst on the activity. The series of Sn-mp solids (samples F to J) were hence tested as catalysts selecting the conversion of DHA into EL as target reaction. Under the appropriate reaction conditions, a clear influence of the mean particle size on the DHA conversion was observed. The decrease in particle size was associated to an evident increase in catalytic activity. This behavior was attributed to the reduced diffusion limitations of reactants and products to/from the active sites in the particles of smaller diameter. The absence of leaching as well as the ability to be recycled in multiple catalytic runs were successfully demonstrated. Finally, a preparative catalytic test performed in presence of the best catalyst allows obtaining a quantitative conversion of DHA with total selectivity thus confirming the possible industrial applications of the selected solid.

Acknowledgements

The authors acknowledge the 'Communauté française de Belgique' for the financial support, including the PhD fellowship of A. Vivian and the postdoctoral contract of. L. A. Bivona, through the ARC programme (15/20-069). This research used resources of the nuclear magnetic resonance service located at the University of Namur. This Service is member of the "Plateforme Technologique Physico-Chemical Characterisation" - PC^2 ."

References

- [1] K. Chaudhari, T. K. Das, P. R. Rajmohanan, K. Lazar, S. Sivasanker, A. J. Chandwadkar, J. Catal. 183 (1999) 281– 291.
- [2] M. Renz, T. Blasco, A. Corma, V. Fornés, R. Jensen, L. Nemeth, Chem. A Eur. J. 8 (2002) 4708–4717.
- [3] A. Ramanathan, D. Klomp, J. A. Peters, U. Hanefeld, J. Mol. Catal. A Chem. 260 (2006) 62–69.
- [4] S. Tolborg, I. Sádaba, C. M. Osmundsen, P. Fristrup, M. S. Holm, E. Taarning, ChemSusChem 8 (2015) 613–617.
- [5] L. Li, X. Collard, A. Bertrand, B. F. Sels, P. P. Pescarmona, C. Aprile, J. Catal. 314 (2014) 56–65.
- [6] F. Jérôme, Y. Pouilloux, J. Barrault, ChemSusChem, 1 (2008) 586–613.
- [7] K. S. Arias, M. J. Climent, A. Corma, S. Iborra, ChemSusChem, 7 (2014) 210–220.
- [8] U. Ciesla, F. Schüth, Microporous Mesoporous Mater. 27 (1999) 131–149.
- [9] A. Taguchi, F. Schüth, Microporous Mesoporous Mater., 77 (2005) 1-45.
- [10] T. Blasco, A. Corma, M. T. Navarro, J. Pérez Pariente, J. Catal. 156 (1995) 65–74.
- [11] K. M. Reddy, I. Moudrakovski, A. Sayari, J. Chem. Soc. Chem. Commun. (1994) 1059-1060.
- [12] T. Takeguchi, J.-B. Kim, M. Kang, T. Inui, W.-T. Cheuh, G. L. Haller, J. Catal. 175 (1998) 1–6.
- [13] E.-P. Ng, J.-Y. Goh, T. C. Ling, R. R. Mukti, Nanoscale Res. Lett. 8 (2013) 120.
- [14] D. P. Sahoo, D. Rath, B. Nanda, K. M. Parida, RSC Adv. 5 (2015) 83707–83724.
- [15] G. De Cremer, M. B. J. Roeffaers, E. Bartholomeeusen, K. Lin, P. Dedecker, P. P. Pescarmona, P. A. Jacobs, D. E. De Vos, J. Hofkens, B. F. Sels, Angew. Chemie Int. Ed. 49 (2010) 908–911.
- [16] A. J. H. P. van der Pol, A. J. Verduyn, J. H. C. van Hooff, Appl. Catal. A, Gen. 92 (1992) 113–130.
- [17] U. Wilkenhöner, G. Langhendries, F. van Laar, V. G. Baron, D. W. Gammon, P. A. Jacobs, E. van Steen, J. Catal. 203 (2001) 201–212.
- [18] X. Liu, H. Sun, Y. Yang, J. Colloid Interface Sci. 319 (2008) 377–380.
- [19] S. Inagaki, Y. Aratani, Y. Sekine, E. Kikuchi, M. Matsukata, Stud. Surf. Sci. Catal. 158 (2005) 533–540.

- [20] X. Tang, S. Liu, Y. Wang, W. Huang, E. Sominski, O. Palchik, Y. Koltypin, A. Gedanken, Chem. Commun. (2000) 2119–2120.
- [21] Y. Chen, X. Shi, B. Han, H. Qin, Z. Li, Y. Lu, J. Wang, Y. Kong, J. Nanosci. Nanotechnol. 12 (2012) 7239–49.
- [22] X. Collard, L. Li, W. Lueangchaichaweng, A. Bertrand, C. Aprile, P. P. Pescarmona, Catal. Today 235 (2014) 184– 192.
- [23] X. Collard, P. Louette, S. Fiorilli, C. Aprile, Phys. Chem. Chem. Phys. 17 (2015) 26756–26765.
- [24] H. Chen, Y. P. Peng, K. F. Chen, C. H. Laia, Y. C. Lin, J. Environ. Sci. (China) (2015) 1–12.
- [25] D. P. Debecker, M. Stoyanova, F. Colbeau-Justin, U. Rodemerck, C. Boissière, E. M. Gaigneaux, C. Sanchez, Angew. Chemie - Int. Ed. 51 (2012) 2129–2131.
- [26] N. Godard, A. Vivian, L. Fusaro, L. Cannavicci, C. Aprile, D. P. Debecker, ChemCatChem 9 (2017) 1-9.
- [27] D. P. Debecker, M. Stoyanova, U. Rodemerck, F. Colbeau-Justin, C. Boissière, A. Chaumonnot, A. Bonduelle, C. Sanchez, Appl. Catal. A Gen. 470 (2014) 458–466.
- [28] F. Colbeau-Justin, C. Boissière, A. Chaumonnot, A. Bonduelle, C. Sanchez, Adv. Funct. Mater. 24 (2014) 233–239.
- [29] (a) W. N. P. van der Graaff, C. H. L. Tempelman, E. A. Pidko, E. J. M. Hensen, Catal. Sci. Technol. 7 (2017) 3151-3162; (b) X. Yang, L. Wu, Z. Wang, J. Bian, T. Lu, L. Zhou, C. Chen, J. Xu, Catal. Sci. Technol. 6 (2016) 1757-1763.
- [30] L. Li, C. Stroobants, K. Lin, P. A. Jacobs, B. F. Sels, P. P. Pescarmona, Green Chem. 13 (2011) 1175–1181.
- [31] Y.-D. Chiang, H.-Y. Lian, S.-Y. Leo, S.-G. Wang, Y. Yamauchi, K. C. W. Wu, J. Phys. Chem. C 115 (2011) 13158– 13165.
- [32] T. Matsoukas, E. Gulari, J. Colloid Interface Sci. 124 (1988) 252–261.
- [33] N. K. Plugotarenko, A. N. Korolev, V. V. Petrov, T. N. Nazarova, Inorg. Mater. 43 (2007) 1010–1014.
- [34] A. Corma, M. T. Navarro, L. Nemeth, M. Renz, Chem. Commun. (2001) 2190–2191.
- [35] M. Piumetti, B. Bonelli, M. Armandi, L. Gaberova, S. Casale, P. Massiani, E. Garrone, Microporous Mesoporous Mater. 133 (2010) 36–44.
- [36] F. Cavani, N. Ballarini, A. Cericola, Catal. Today 127 (2007) 113–131.
- [37] P. P. Pescarmona, K. P. F. Janssen, C. Delaet, C. Stroobants, K. Houthoofd, A. Philippaerts, C. De Jonghe, J. S. Paul, P. A. Jacobs, B. F. Sels, Green Chem. 12 (2010) 1083–1089.
- [38] C. Cossement, J. Darville, J. Gilles, J. B. Nagy, Magn. Reson. Chem. 30 (1992) 263–270.
- [39] Q. Cai, Z. S. Luo, W. Q. Pang, Y. W. Fan, X. H. Chen, F. Z. Cui, Chem. Mater. 13 (2001) 258–263.