Journal of Catalysis 314 (2014) 56-65

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Extra-small porous Sn-silicate nanoparticles as catalysts for the synthesis of lactates



JOURNAL OF CATALYSIS

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ARTICLE INFO

Article history: Received 6 December 2013 Revised 28 February 2014 Accepted 24 March 2014

Keywords: Sn-silicates Porous materials Nanoparticles Lactate synthesis

ABSTRACT

A series of Sn-MCM-41 nanoparticles (XS-Sn-MCM-41) with a diameter ranging from 20 to 140 nm and very high specific surface area were successfully prepared and tested as heterogeneous catalysts for the conversion of the triose sugar dihydroxyacetone to ethyl lactate. Characterization of the materials indicated that the physicochemical properties of the nanoparticles can be significantly affected by different synthesis parameters, including the metal loading, the sequence of adding the Si and Sn precursors into the synthesis mixture, the preparation time and temperature. Most of the XS-Sn-MCM-41 catalysts displayed higher activity compared to conventional Sn-MCM-41 with large particle size in the conversion of dihydroxyacetone into ethyl lactate. The superiority of the best XS-Sn-MCM-41 catalyst in terms of conversion and turnover number is correlated to its high amount of accessible acid sites, which in turn is ascribed to a combination of different physicochemical features such as high surface area, particles morphology and coordination of the tin atoms in tetrahedral framework sites. The best catalyst can be reused in consecutive runs without loss of activity.

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1. Introduction

Heterogeneous catalysts play a crucial role in many processes for the production of bulk and fine chemicals, including the thriving area of the conversion of renewables. The development of improved catalysts can originate from the identification of new active species but also from a tailored design of the structural and morphological features of the catalytic materials. Mesoporous silicas such as MCM-41 or SBA-15 are a widely studied class of materials with a great potential for catalytic applications due to the reduced diffusion limitations of reactants and products compared to microporous solids, e.g. zeolites. Further control of the diffusivity within these materials can be achieved by tuning the dimension and organization of the mesopores. A less-explored strategy to improve the accessibility of the active sites consists in reducing the particle size of the catalyst to the nanoscale. This can bring about dramatic enhancements in the efficiency of the catalysts [1-4]. Indeed, it has been shown by fluorescence microscopy that for particles in the micrometer range, most of the catalytic activity stems from sites located at the external rim of the

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particle [5]. In this work, we show that the catalytic performance of mesoporous Sn-silicates in the conversion of dihydroxyacetone to ethyl lactate can be significantly improved by preparing the catalysts in the form of nanoparticles. The selected reaction is relevant in the context of the conversion of renewables to added-value compounds.

For many years, petrochemical processes based on the use of fossil resources for the production of chemicals, polymers and fuels have been a mainstay of the world industry [6]. However, due to the limitation of fossil resources and the increasing concerns about environmental pollution issues, the industrial society has to find renewable feedstocks that are able to satisfy the energy needs and the production of chemicals while minimizing the negative impact on the environment [7–9]. Biodiesel, defined as methyl esters obtained from lipids (e.g. vegetable oils and animal fats), is a renewable and environmentally acceptable alternative to petroleum-based diesel fuel [10]. The manufacturing of biodiesel yields glycerol as the main co-product, in an amount equivalent to approximately 10 wt% of the produced biodiesel [10]. The continuously increasing biodiesel market led to an oversupply in the production of glycerol, which caused a drop in its commercial value and generated a shift in its role from end-of-the chain product to raw material. Therefore, new solutions for the effective utilization of glycerol are being extensively investigated. Among the catalytic processes for converting glycerol and its derivatives to valuable



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products, an attractive route is provided by the synthesis of lactic acid/lactates from trioses, *i.e.* glyceraldehyde (GLY) and dihydroxy-acetone (DHA) [11–17]. The trioses can be obtained from glycerol either by fermentation or by catalytic oxidation [18–21]. Compared to the present method to produce lactic acid and lactates, which is based on the microbial fermentation of glucose and sucrose and requires extensive neutralization, purification and separation processes [22–24], this catalytic route is greener and more efficient. Lactic acid and the related alkyl lactates have important applications as green solvents and precursors for the synthesis of polylactates, which is increasingly employed as a biodegradable plastic material, and in various other industrial areas related to chemicals, food, pharmaceuticals, and cosmetic products [8,25,26].

It was recently reported that porous structured silicas with metallic elements (e.g. Ti, Sn) partially substituting Si as single sites are active and selective catalysts for the conversion of trioses to lactic acid or alkyl lactates [14.27]. The catalytic activity originates from the acidity of the materials: namely, a combination of Lewis acid sites and mild Brønsted acid sites is the key factor to obtain high conversion and excellent selectivity toward the lactate product. Brønsted acid sites catalyze the conversion of dihydroxyacetone (or glyceraldehyde) into pyruvic aldehyde by dehydration and rearrangement, while Lewis acid sites catalyze the conversion of the formed pyruvic aldehyde into the desired lactate (Scheme 1). Strong Brønsted acidity should be avoided as it favors the formation of undesired acetal side-products [13,14,16,28,29]. Sn-MCM-41, possessing such combination of Lewis acid sites and mild Brønsted acid sites, was identified as an excellent heterogeneous catalyst for the conversion of dihydroxyacetone to ethyl lactate [14]. Here, we introduce the synthesis of novel extra-small (XS) Sn-silicate mesoporous particles with the typical structure and pore size of MCM-41 and particle diameter ranging from 20 to 140 nm. These materials are expected to present an attractive combination of active and highly accessible sites, leading to improved activity in the title reaction.

2. Experimental

2.1. Materials

The chemicals: cetyltrimethylammonium bromide (CTAB purity \geq 99%), sodium hydroxide (NaOH purity \geq 97%), tetramethylammonium hydroxide (TMAOH 25.0%), tetraethylorthosilicate (TEOS purity \geq 99.999%), absolute ethanol (EtOH purity \geq 99.5%), hexamethyldisilazane (HMDS purity \geq 99%), and tin chloride pentahydrate (SnCl₄·5H₂O purity \geq 98.0%) were all purchased from Sigma–Aldrich.



Scheme 1. Conversion of dihydroxyacetone to alkyl lactate (R = alkyl group) in an alcohol solution.

2.2. Synthesis of the XS-Sn-MCM-41 catalysts

The general protocol for the synthesis of the XS-Sn-MCM-41 catalysts is inspired by a previously reported method for the preparation of Ti-MCM-41 nanoparticles [1]. A basic aqueous solution (NaOH 2.0 M) was added to a solution of CTAB in milli-Q water and stirred at 800 rpm during 30 min. In a first approach, half of the total amount of TEOS was added to the solution, followed by the addition of SnCl₄·5H₂O previously dissolved in 1.0 mL of absolute ethanol and finally by the other half of TEOS. In an alternative approach, TEOS and SnCl₄·5H₂O were mixed together prior to their addition to the solution. In all cases, TEOS and SnCl₄·5H₂O were added in a dropwise manner. The molar ratio in the synthesis of sample XS-Sn-MCM-41-A is 1 TEOS:0.0135 SnCl₄·5H₂O:0.33 NaOH:0.125 CTAB:0.90 EtOH: 1212 H₂O. For the other materials of the XS-Sn-MCM-41 series, the concentration of SnCl₄·5H₂O (Table 1) was varied while keeping all other concentrations fixed at the values given above. The mixture was stirred at 800 rpm for either 2 h or 24 h at room temperature. An additional thermal treatment at 70 °C for 3 h was performed for a number of samples (Table 1). The resulting solid was washed three times with ultra-pure water and ethanol and dried at 60 °C for 16 h. Finally, the solid was calcined in air to remove the organic template (8 h at 550 °C, heating rate of 3 °C min⁻¹). For comparison, Sn-MCM-41 with larger particles (denoted as Sn-MCM-41-LP) was synthesized as described previously by using cetyltrimethylammonium bromide (CTAB) as template [14]. The molar ratio in the synthesis mixture is 1 SiO₂:0.02 SnO₂:0.31 (CH₃)₄N(OH)·2 SiO₂:0.6 CTAB:38 H₂O. After hydrothermal treatment in a Teflon-lined autoclave for 14 h at 140 °C, the obtained solid was filtered, washed with deionized water, dried at 60 °C and finally calcined in air for 6 h at 550 °C with a heating rate of 1 °C min⁻¹. In order to increase the hydrophobicity of a selected XS-Sn-MCM-41 sample, a silylation process was carried out by treating the calcined sample with a solution of hexamethyldisilazane (HMDS, Aldrich) in toluene under argon atmosphere, under vigorous stirring at 110 °C for 2 h [30-32]. A HMDS/SiO₂ molar ratio of 0.25 was employed to achieve a good degree of silvlation of the material. The sample was then filtered, washed thoroughly with drv toluene, and finally dried at 110 °C.

2.3. Characterization of the XS-Sn-MCM-41 catalysts

Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai 10 with an accelerating voltage of 80 kV. Nitrogen adsorption-desorption isotherms of the as-synthesized and silvlated materials were measured at 77 K with a volumetric adsorption analyzer (Micromeritics Tristar 3000). The pore size distributions were calculated from the adsorption isotherm using the Barrett-Joyner-Halenda (BJH) method [33]. The Brunauer-Emmet-Teller (BET) method was applied to calculate the specific surface area [34]. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert diffractometer with Cu Ka radiation (λ = 1.54178 Å). Scanning electron microscopy (SEM) analysis was carried out on a Philips XL30 FEG scanning electron microscope. Energy-dispersive X-ray (EDX) spectroscopy was performed using an acceleration voltage of 7.5 kV and a working distance of 8 mm. The elemental composition was calculated as the average of the results from different spots selected randomly on the surface of the catalysts. The Si environment and the coordination of the Sn atoms were studied by ²⁹Si and ¹¹⁹Sn Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra measured on a VARIAN 400 and a Bruker 500 spectrometer, respectively. ¹¹⁹Sn MAS-NMR spectra were measured at the resonance frequency of ¹¹⁹Sn (186.5 MHz). The samples were packed in a 3.2 mm Chemagnetics rotor and measured with a spinning frequency of 8000 Hz. 21,000 scans were accumulated with a recycle delay of 40 s and a pulse length of 2.0 $\mu s.$ The resonance frequency of $^{29}\mbox{Si}$ was of

Table 1

Physicochemical properties of the XS-Sn-MCM-	41 materials.
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Entry	Sample	Si/Sn ratio		Temperature and time of the synthesis	BET $(m^2 g^{-1})$	Average pore) size (nm)	Pore volume $(cm^3 g^{-1})$	Internal pore volume (cm ³ g ⁻¹) ^b	Average size of the nanoparticles (nm) ^c
		In the reaction mixture	In the final material ^d	2					,
1	XS-Sn-MCM-41-A	74	65 (63 ^e)	2 h RT	1111	2.3	0.84	0.77	118 ± 21
2	XS-Sn-MCM-41-B	41	27	2 h RT	1042	2.3	1.09	0.62	35 ± 11
3	XS-Sn-MCM-41-C	41	28 (31 ^e)	2 h RT + 3 h 70 °C	946	2.3	1.13	0.59	39 ± 13
4	XS-Sn-MCM-41-D	41 ^a	24	2 h RT + 3 h 70 °C	896	2.3	1.14	0.58	71 ± 31
5	XS-Sn-MCM-41-E	41 ^a	32	24 h RT	804	2.3	1.31	0.47	72 ± 28
6	XS-Sn-MCM-41-F	28 ^a	22	2 h RT + 3 h 70 °C	858	2.3	1.20	0.52	76 ± 25
7	Sn-MCM-41-LP ^f	50	54	2 h 30 RT + 14 h 140 °C	729	2.5	0.76	0.46	285 ± 83
8	Silylated XS-Sn- MCM-41-A	-	n.d.		1074	1.7	0.62	0.54	

n.d. = not determined.

^a TEOS and SnCl₄·5H₂O were mixed together before addition.

^b Calculated for p/p_0 from 0.0 to 0.8.

^c Expressed as 'average ± standard deviation', calculated by measuring 45 randomly selected particles in the TEM images.

^d Determined by EDX.

e Determined by ICP-OES.

^f Data taken from [14].

79.46 MHz. The samples were packed in a 4 mm zirconia rotor and measured with a spinning frequency of 8000 Hz. 4.14×10^{6} scans were accumulated with a recycle delay of 6 s and a pulse length of 2.0 µs (30°). Tetramethylsilane (TMS) was used as shift reference. The ²⁹Si MAS-NMR spectrum of the silvlated sample was recorded on a Bruker AMX300 spectrometer (7.0 T). At this field, the resonance frequency of ²⁹Si is 59.6 MHz. The sample was packed in a 4 mm Zirconia rotor and measured with a spinning frequency of 5000 Hz. 4000 scans were accumulated with a recycle delay of 60 s and a pulse length of 5.0 µs. Tetramethylsilane (TMS) was used as shift reference. Diffuse reflectance UV-Vis spectra were collected on a Varian Cary 5000 UV-Vis-NIR Spectrophotometer with a Harrick single-beam Praying Mantis Diffuse Reflectance collection system. Elemental analyses of selected catalysts were performed by dissolving 50 mg of the sample in a mixture of 0.5 mL of aqua regia and 3 mL of 40% aqueous HF. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Jobin Yvon Ultima instrument) was employed to analyze the obtained solutions. Analysis of the acid properties of the XS-Sn-MCM-41 catalysts was carried out by adsorption and temperature programmed desorption (TPD) of pyridine monitored by Fourier Transform infrared spectroscopy (FTIR). In a home-made vacuum infrared cell with ZnSe windows, a self-supporting wafer of the sample (about 15 mg) was initially dried under vacuum at 400 °C for 1 h, and then cooled down to 50 °C. During the cooling process, reference spectra were recorded at 350, 250, 150 and 50 °C. Afterward, the wafer was saturated with about 25 mbar of pyridine vapor at 50 °C for 10 min and then evacuated again for 30 min to fully remove physisorbed pyridine. Finally, the evacuated sample containing chemisorbed pyridine was subjected to TPD at 150, 250 and 350 °C for 30 min, with a heating rate of 4 °C min⁻¹, and the IR spectra were recorded in situ at these temperatures. The amounts of acid sites were determined from the integral intensity of characteristic bands (1450 cm⁻¹ for Lewis acid sites, and 1545 cm⁻¹ for Brønsted acid sites) using the molar extinction coefficients of Emeis [35].

2.4. Catalytic tests

The catalytic reactions were carried out in a multiple-well parallel reaction block [14]. In a typical experiment for the conversion of dihydroxyacetone (DHA) to ethyl lactate, 0.180 g of DHA $(2.00 \times 10^{-3} \text{ mol}, \text{ in the form of } 1,3\text{-dihydroxyacetone dimer})$ and 0.0215 g of decane $(1.50 \times 10^{-4} \text{ mol}, \text{ as GC internal standard})$ were dissolved in 3.92 g ethanol (as solvent and reactant) at 45 °C for 30 min. Then, the selected amount of catalyst (50, 100 or 200 mg) was added to the solution at room temperature. This reaction mixture was heated at 90 °C under vigorous stirring (1200 rpm) for the selected reaction time. At the end of the test, the catalyst was separated by centrifugation and the solution was analyzed by gas chromatography (GC) on a Trace GC Ultra from Interscience; more details about the GC analyses can be found in previous reports [14]. Recyclability tests were performed by separating the catalyst from the reaction mixture by centrifugation followed by washing with ethanol. The washing procedure was repeated five times. Finally, the catalyst was dried overnight at 100 °C. Alternative approaches involved a calcination step for 2 h (either at 300 °C or at 500 °C, with a heating rate of 2 °C min⁻¹) after the washing step.

Leaching tests were carried out under the general reaction conditions employed for the catalytic tests (*vide supra*). The catalyst was removed from the reaction mixture after 30 min by centrifugation, followed by hot filtration at the same temperature used for the catalytic test using a plastic syringe equipped with a 25 mm HPLC syringe filter from Altech, with a pore size of 0.2 μ m. The filtrate was allowed to react for another 5 h 30 min. The products were analyzed by GC both after 30 min and at the end of the filtrate test (6 h).

3. Results and discussion

A series of Sn-MCM-41 samples with extra-small (XS) nanoparticle morphology (XS-Sn-MCM-41) was synthesized and studied as heterogeneous catalysts for the conversion of dihydroxyacetone into ethyl lactate. The synthesis methods used for preparing the XS-Sn-MCM-41 materials were inspired by a diluted solution route previously reported for Ti-MCM-41 nanoparticles [1], which allows obtaining a particle size distribution below 200 nm. Different protocols for the addition of the Si and Sn precursors (TEOS and SnCl₄·H₂O) were investigated with the aim of achieving a homogeneous distribution of tin as single site in the silicate framework and of minimizing the formation of SnO₂ domains. Different ratios between Si and Sn were also studied. Additionally, the dimension and mesoporous ordering of the XS-Sn-MCM-41 nanoparticles were optimized by varying the temperature and reaction time. A summary of the reaction conditions is presented in Table 1. For comparison, the reaction parameters used for the synthesis of standard Sn-MCM-41 particles are also reported (entry 7, Table 1).

The physicochemical features of the XS-Sn-MCM-41 materials were studied by means of a combination of characterization techniques. The complete characterization of three representative samples (A, C and E) will be discussed in detail, while the characterization data of all the other materials of the series can be found in the Supporting Information (SI). Transmission electron microscopy demonstrated the presence of small nanoparticles and proved the mesoporous nature of all samples, with the regular hexagonal organization typical of MCM-41 materials (Figs. 1 and S1 in the SI). The particle size of the XS-Sn-MCM-41 materials is substantially smaller than that of a conventional Sn-MCM-41 reference sample (Sn-MCM-41-LP), which consists of irregular particles with a typical size of few hundred nanometers (Fig. S2 in the SI). XS-Sn-MCM-41-A presents a relatively narrow particle size distribution centered at 118 nm (Table 1 and Fig. 1a). The samples prepared with higher loading of tin display an even smaller particle size: for example, XS-Sn-MCM-41-C shows particles in the range between 20 and 60 nm (Table 1 and Fig. 1b), indicating a slight change in the formation mechanism of the nanoparticles with a preference of nucleation compared to growth. This may be due to a decrease in pH value as a consequence of the increased concentration of SnCl₄ in the reaction medium: the hydrochloric acid generated upon hydrolysis of the tin precursor partially neutralizes the NaOH present in solution. Notably, TEM revealed that the additional thermal treatment of the reaction mixture and the longer reaction time (samples XS-Sn-MCM-41-C to E) favor a moderate increase in the particle size but also the formation of aggregates. Particularly, the TEM image of XS-Sn-MCM-41-E evidenced the presence of zones of condensation between the XS particles (Fig. 1c and d). Interparticle condensation was also observed, though to less extent, in samples C, D and F (Figs. 1b and S1 in the SI).

Analysis of the series of XS-Sn-MCM-41 solids by nitrogen physisorption isotherms reveals that all the prepared materials have high specific surface area and display a type IV isotherm with a step at low relative pressure corresponding to a narrow pore size distribution centered at 2.3 nm (Table 1, Figs. 2 and S3, SI). These features are characteristic of the long-range order of MCM-41 structures, in agreement with the TEM analysis. All XS-Sn-MCM-41 materials display higher specific surface area compared to the conventional Sn-MCM-41-LP. The values of surface area vary throughout the series of materials, reaching a remarkable value of 1111 m² g⁻¹ for sample XS-Sn-MCM-41-A. A slight decrease in the specific surface area was observed when increasing the amount of Sn present in the structure (Table 1, compare XS-Sn-MCM-41-A and B). A significant drop in surface area was detected for the solid prepared with a long reaction time (compare XS-Sn-MCM-41-D and E in Table 1). The decrease in surface area in the XS-Sn-MCM-41 series is accompanied by an increase in the pore volume (Table 1). This trend is attributed to the presence of large interparticle meso- and macropores, as indicated by the hysteresis loop at higher relative pressure observed in the N₂ adsorption-desorption isotherms of all the nanoparticles except XS-Sn-MCM-41-A (Figs. 2b, c and S3, SI). Accordingly, a broad signal in the range 20-70 nm is observed in the pore size distribution of samples XS-Sn-MCM-41-B to F, being particularly evident for sample E (Fig. 2c). The presence of these disordered interparticle cavities can be related to the appearance of zones of condensation between the particles as observed by TEM. These interparticle voids are expected to contribute scarcely to the surface area but relevantly to the pore volume. In order to test this hypothesis, the pore volume was recalculated by excluding the contribution of the larger pores, *i.e.* those corresponding to p/p_0 from 0.8 to 1.0 (Table 1). These values give an estimation of the internal mesopore volume and, as anticipated, follow the same trend as the surface areas. These findings suggest that after 2 h at room temperature, the nanoparticles reach their critical size, while longer synthesis time favors the aggregation of the particles.

In agreement with the characterization by TEM and N₂-physisorption, X-ray diffraction (XRD) analysis of XS-Sn-MCM-41-A shows the typical pattern of MCM-41 with an intense d_{100} peak and two smaller d_{110} and d_{200} signals (Fig. 3a), while for the materials characterized by smaller particles (XS-Sn-MCM-41-B to F) only a broad d_{100} peak is observed (Figs. 3b, c and S4, SI). The larger peak width observed for sample E could arise from the higher degree of aggregation between the particles observed by TEM and consequent decrease in long-range ordering.

The synthesis of mesoporous Sn-silicates proceeds through the hydrolysis of the precursors, followed by condensation with the formation of Sn–O–Si and Si–O–Si bonds (and ideally no Sn–O–Sn bond). The degree of condensation of the materials was studied by solid-state ²⁹Si NMR (Fig. 4a), which shows a broad band that can be deconvoluted into a mixture of Q³ [(SiO)₃SiOH] and Q⁴ [(SiO)₄Si] signals. The elevated contribution of Q³ compared to standard MCM-41 materials is attributed to the extra-small dimension of the XS-Sn-MCM-41 solids, which implies a high surface-to-volume ratio and thus a larger population of surface silanols.

Ideally, Sn should be incorporated as single site with tetrahedral coordination in the silica framework. The nature of the Sn sites in the XS-Sn-MCM-41 materials was studied by means of solid-state ¹¹⁹Sn NMR and UV-Vis spectroscopy. It should be noted that, although the isotopic abundance of the ¹¹⁹Sn is high (compared to ¹³C or ²⁹Si), the detection of this element by Magic Angle Spinning (MAS) NMR is hindered by its long spin-lattice relaxation time and low wt% in the prepared catalysts. Despite these intrinsic limitations and the high Si/Sn ratio of the samples, a noisy ¹¹⁹Sn signal centered at around -700 ppm could be detected for the materials displaying higher tin loading (XS-Sn-MCM-41-C and F) after 3 days of acquisition (Figs. 4b and S5, SI). This ¹¹⁹Sn signal is attributed to tetrahedrally coordinated Sn⁴⁺ ions connected to four silicon atoms through oxygen bridges within the silica framework [36,37] or to hydrated framework Sn(IV) species with an extended coordination shell including two water molecules [38,39]. Octahedrally coordinated tin in SnO₂ gives a sharp peak at around -600 ppm [40– 42]. This peak was not observed in our samples, though the poor signal-to-noise ratio of the spectra does not allow excluding the presence of small amounts of SnO₂.

Diffuse reflectance UV-Vis spectroscopy allowed highlighting further the coordination of tin in the XS-Sn-MCM-41 materials. Metal atoms that isomorphously substitute silicon atoms in the framework of MCM-41 acquire the typical tetrahedral coordination of silicate units. Therefore, their absorption in the UV-Vis region is generally easily distinguished from that due to extra-framework species. The UV-Vis spectrum of XS-Sn-MCM-41-A reveals a main absorption band centered at 208 nm corresponding to Sn⁴⁺ in tetrahedral coordination [36,43,44] (Fig. 5a), evidencing that at low metal loading the incorporation of tin in the structure is mainly achieved as single site species. Samples B and C present two additional signals at 245 and 280 nm (Figs. 5b and S6, SI). The assignment of the band at 245 nm is still a matter of debate: this signal has been attributed to distorted tetrahedral and penta-coordinated framework tin sites [44] but also to small extra-framework SnO₂ domains [38,45]. The broad absorption around 280 nm has been assigned to hexa-coordinated polymeric Sn-O-Sn type species [36,38,43]. The presence of these two additional species in samples B and C is ascribed to the higher amount of tin precursor and to the sequential method used for adding the Si and Sn precursors to the reaction mixture. On the other hand, the UV-Vis spectra of samples D to F do not exhibit the additional peaks at 245 and 280 nm, indicating that the incorporation of tin in tetrahedral coordination is more efficient if TEOS and SnCl₄·5H₂O are mixed together before being added to the reaction solution (Figs. 5c and S6, SI). Although



Fig. 1. TEM analysis of XS-Sn-MCM-41-A (a), C (b) and E (c, d).



Fig. 2. N₂ physisorption isotherms (top) and the pore size distribution (bottom) of XS-Sn-MCM41-A (a), C (b) and E (c).

UV–Vis spectroscopy evidenced the presence of Sn–O-Sn species in some of the XS-Sn-MCM-41 samples, EDX spectroscopy allows excluding the formation of large (*i.e.* >50 nm) separate domains of silicon or tin oxide, as indicated by the homogeneous distribution of tin and silicon observed in all the samples. This conclusion is further supported by the elemental mapping images recorded using SEM (Fig. S7, SI).

In order to verify the reproducibility of the synthesis protocol, a second batch of materials XS-MCM-41-A, C and E was synthesized and characterized by XRD, N₂-physisorption, TEM and UV-Vis spectroscopy, leading to analogous results to the first batch of materials (Fig. S8, S1).

On the basis of the characterization results discussed above, it can be expected that the XS-Sn-MCM-41 will display relevant catalytic performance in the conversion of dihydroxyacetone to ethyl lactate. Indeed, most of the studied XS-Sn-MCM-41 materials present higher conversion of dihydroxyacetone compared to conventional Sn-MCM-41 consisting of large particles (Table 2: compare entries 1–4 and 6 with entry 7). The mechanism leading to the conversion of dihydroxyacetone to ethyl lactate has been extensively discussed in the literature [14]: Brønsted acid sites catalyze the dehydration of dihydroxyacetone into the pyruvic aldehyde intermediate, followed by rearrangement into the lactate product catalyzed by Lewis acid sites (Scheme 1). In Sn-MCM-41 materials, the



Fig. 3. XRD patterns of XS-Sn-MCM-41-A (a), C (b), E (c), in the small angle region $(2\theta = 1-10^{\circ})$.



Fig. 4. Solid-state ²⁹Si MAS-NMR spectrum (a) and ¹¹⁹Sn MAS-NMR spectrum (b) of XS-Sn-MCM-41-C.



Fig. 5. Diffuse reflectance UV-Vis spectra of XS-Sn-MCM-41-A (a), C (b) and E (c).

Lewis acidity is provided by surface tin atoms tetrahedrally coordinated to the silica framework, whereas Brønsted acidity is ascribed to surface silanols located in the vicinity of tin [14.46]. In order to explain the observed catalytic results, it is useful to monitor the number and type of accessible acid sites by means of FT-IR analysis of adsorbed pyridine. The vibrations at 1455 and 1623 cm⁻¹ are characteristic of pyridine adsorbed on strong Lewis acid sites, at 1575 cm^{-1} for weak Lewis acid sites, at 1545 and 1639 cm⁻¹ for Brønsted acid sites and at 1492 cm⁻¹ for both Lewis and Brønsted acid sites (Fig. 6a) [14,47]. All the XS-Sn-MCM-41 catalysts display the required combination of Lewis and Brønsted acidity (Table 3), and the differences in catalytic performance between them can be explained in terms of their amounts of acid sites. More specifically, the lactate yield and selectivity correlate well with the amount of Lewis acid sites (Fig. 6b and c and Tables 2 and 3), in agreement with the proposed reaction mechanism.

The best catalytic results, both in terms of dihydroxyacetone conversion and of lactate yield, were obtained with XS-Sn-MCM-

41-A, which exhibits the largest amount of accessible Lewis and Brønsted acid sites among the studied catalysts (Table 3). This feature is ascribed to the high specific surface area of this material (Table 1) and to the efficient insertion of Sn in tetrahedral sites in the structure, as evidenced by the absorption band at 208 nm in the UV-Vis spectrum (vide supra). The lower catalytic activity of XS-Sn-MCM-41-B and C compared to XS-Sn-MCM-41-A, despite their higher Sn content, is mainly ascribed to the lower fraction of Sn in tetrahedral sites accompanied by the presence of catalytically inactive clusters of SnO₂ (as indicated by the UV-Vis absorptions at 245 and 280 nm). On the other hand, tetrahedral tin sites are generated more efficiently in the samples in which the Sn and Si precursor were added simultaneously during the synthesis (XS-Sn-MCM-41-D, E and F). However, this method leads to lower specific surface areas (Table 1) and to interparticle agglomeration (vide supra), which is particularly relevant for sample E. The aggregation between particles might lead to blocking of one entrance of the pores and thus reduce the accessibility of the active sites. These Table 2

Entry	Catalyst	Conv. (%) ^a	Y _{ethyl lactate} (%)	Y _{hemiacetal} (%)	Y _{acetal} (%)	S _{ethyl lactate} (%)	TON ^c
1	XS-Sn-MCM-41-A	64	44	15	5	69	104
2	XS-Sn-MCM-41-B	49	27	16	6	55	35
3	XS-Sn-MCM-41-C	51	30	16	5	59	37
4	XS-Sn-MCM-41-D	39	19	16	4	49	25
5	XS-Sn-MCM-41-E	16	6	8	2	38	13
6	XS-Sn-MCM-41-F	53	34	16	3	64	31
7	Sn-MCM-41-LP ^b	32	30	1	1	94	41
8	Silylated XS-Sn-MCM-41-A	28	26	1	1	93	n.d.

Catalytic conversion of dihydroxyacetone to ethyl lactate over XS-Sn-MCM-41 catalysts.

Conditions: 50 mg of catalyst, 2.00×10^{-3} mol DHA in ethanol. Decane (1.50×10^{-4} mol) was used as internal standard for GC analysis. n.d. = not determined.

n.a. = not determined

^a Calculated as the sum of the yields of the reaction products [14].

^b Data taken from [14].

^c TON is defined as mol of dihydroxyacetone converted per mol of Sn atoms.



Fig. 6. (a) Infrared spectra of pyridine adsorbed at 150 °C over XS-Sn-MCM-41-A-F (i-vi) [L = Lewis acid sites; B = Brønsted acid sites]; (b) yield of ethyl lactate and (c) selectivity toward ethyl lactate over the XS-Sn-MCM-41 catalysts as a function of their amount of Lewis acid sites [48].

features can explain the catalytic trends observed between samples D, E and F and their lower activity compared to XS-Sn-MCM-41-A. These results indicate that the catalytic performance of the XS-Sn-MCM-41 materials in the conversion of dihydroxyacetone to lactate depends on a combination of parameters including surface area, morphology, and population of tetrahedral tin sites on the surface.

Remarkably, the highest amount of accessible acid sites and thus the best catalytic performances were obtained with the material prepared with lower tin content (XS-Sn-MCM-41-A), while higher tin loadings led to a higher fraction of poorly active or inactive Sn species, either because located in partially blocked pores or embedded within the pore walls and thus not accessible, or because in the form of SnO₂ clusters. This is reflected by the much higher fraction of Sn atoms acting as Lewis acid sites in XS-Sn-MCM-41-A (80%) compared to the other materials of the series (Table 3). The high efficiency in employing Sn to generate Lewis acid sites led to the striking superiority of XS-Sn-MCM-41-A when compared to the other catalysts in terms of turnover numbers (TON, Table 2).

All the XS-Sn-MCM-41 nanoparticle materials display lower selectivity toward ethyl lactate compared to the reference Sn-MCM-41-LP (Table 2) [14]. The selectivity in this reaction is controlled by the relative amount and strength of the acid sites of

Table 3	
Type and amount of surface acid sites of the XS-Sn-MCM-41 materials, as determined by TPD-IR of adsorbed pyridine.	

Sample	Lewis acidity (mmol g ⁻¹) ^a	Brønsted acidity $(mmol g^{-1})^a$	$L + B \pmod{g^{-1}}$	L/B ratio		$\%$ of Sn acting as Lewis $\operatorname{acid}^{\operatorname{b}}$
				at 150 °C	at 350 °C	
XS-Sn-MCM-41-A	0.197	0.094	0.291	2.1	10	80
XS-Sn-MCM-41-B	0.159	0.052	0.211	3.1	6.0	28
XS-Sn-MCM-41-C	0.164	0.068	0.232	2.4	7.0	30
XS-Sn-MCM-41-D	0.149	0.037	0.186	4.0	(∞)	24
XS-Sn-MCM-41-E	0.128	0.031	0.159	4.1	(∞)	27
XS-Sn-MCM-41-F	0.172	0.042	0.214	4.1	5.5	25

^a Calculated from the integral intensity of the corresponding bands (1450 cm⁻¹ for Lewis acid sites and 1545 cm⁻¹ for Brønsted acid sites) in the IR spectra recorded at 150 °C.

^b Calculated from the Sn content determined by EDX and the number of Lewis acid sites (mmol g⁻¹) determined by IR of adsorbed pyridine.

the catalyst, with Lewis acid sites promoting the conversion of the intermediate pyruvic aldehyde to lactate and Brønsted acid sites favoring the formation of hemiacetal and acetal side-products (vide supra). FT-IR analysis of adsorbed pyridine shows that all materials of the XS-Sn-MCM-41 series have a much higher amount (mmol g^{-1}) of Brønsted acid sites and lower ratio between Lewis and Brønsted acid sites compared to the reference Sn-MCM-41-LP (Table 3 and [47]). Analysis of the spectra measured at different temperatures indicates that pyridine is more strongly adsorbed on the Lewis compared to the Brønsted acid sites, as shown by the increase in the ratio between these two sites at higher temperatures (Table 3). This suggests the relatively mild nature of the Brønsted acid sites of these catalysts. The higher amount of Brønsted acid sites of the XS-Sn-MCM-41 materials can be attributed to a higher population of surface silanol groups due to the more defective structure of nanoparticles compared to larger particles (Q⁴/Q³ determined by ²⁹Si NMR is 1.4 for XS-Sn-MCM-41-A and 1.9 for Sn-MCM-41-LP). In order to confirm the role of the silanol groups in this reaction, sample XS-Sn-MCM-41-A was silvlated with hexamethyldisilazane [30-32]. Solid-state ²⁹Si NMR shows an increase in Q^4/Q^3 ratio in XS-Sn-MCM-41-A to 3.7 after silvlation and the appearance of a new band at 14 ppm associated with Me₃Si-(OSi) groups (Fig. S9, SI) [27], indicating the successful silvlation of the silanols with formation of trimethylsilyl groups anchored on the surface of the material. The presence of these groups also leads to a slight decrease in the specific surface area and a decrease in pore volume and average diameter (Table 1, compare entries 1 and 8). The silvlated sample gave lower dihydroxyacetone conversion compared to the untreated one, though the selectivity toward ethyl lactate was improved notably (Table 2, entry 8). This result is fully in accordance with the proposed role of silanols as Brønsted acid sites, which can catalyze the initial step consisting in the dehydration of dihydroxyacetone, but also promote the formation of the hemiacetal and acetal side-products.

A kinetic study was performed employing the most promising catalyst (XS-Sn-MCM-41-A), with the purpose of analyzing the formation and conversion of the various reaction intermediates and products (Fig. 7). This study was carried out with a double catalyst loading compared to the tests in Table 2. Under these conditions, the yield of hemiacetal and acetal of pyruvic aldehyde reaches a plateau after 2-4 h, after which the concentration of these two compounds starts decreasing until their almost complete disappearance after 6 h [14]. This allows reaching a total conversion of dihydroxyacetone with almost complete selectivity to ethyl lactate after 6 h of reaction. Remarkably, the loading required to achieve this degree of conversion and selectivity in 6 h at 90 °C is half of that needed to achieve a similar performance with the reference Sn-MCM-41-LP [14]. This excellent result demonstrates that XS-Sn-MCM-41-A is a superior catalyst compared to conventional Sn-MCM-41 and that the lower lactate selectivity observed at lower loading of XS-Sn-MCM-41-A (Table 2) is not a point of concern. A comparison between XS-Sn-MCM-41-A and standard Sn-MCM-41-LP. in terms of surface area and accessible acid sites. allows highlighting the importance of the reduced particle size. Both materials present the hexagonal array of pores typical of MCM-41 and display similar pore size distribution, but XS-Sn-MCM-41-A presents much higher surface area and shorter channels due to its extra-small dimensions. These features lead to a higher amount of accessible acid sites, as proved by pyridine adsorption measurements, hence leading to the observed better catalytic performance. XS-Sn-MCM-41-A is also a very good catalyst when compared to other previously reported heterogeneous catalysts for this reaction [13-16,49-51]: although the different reaction conditions prevent full comparison, the performance of our catalyst in terms of TON, TOF and productivity are highly promising (see Table S1). The attractive features of XS-Sn-MCM-41-A have a potential for other relevant applications in the conversion of renewables to added-value products [52-54].

To evaluate the reusability of XS-Sn-MCM-41-A, the catalyst was tested in several consecutive cycles employing two recycling approaches (Fig. 8). If the recycling protocol only involved washing of the catalyst with ethanol, the conversion of dihydroxyacetone drastically dropped in the second run and remained constant in the successive cycles. However, the activity could be completely restored if the sample was calcined at 500 °C for 2 h (Fig. 8). This recycling behavior is analogous to that of the conventional Sn-MCM-41-LP [14], indicating that a certain amount of residues deposits on the catalysts during the reaction and that complete restoration of the activity can be achieved only through calcination. Aiming at a more energy efficient process, an alternative



Fig. 7. Yield of ethyl lactate, diethyl acetal and hemiacetal of pyruvic aldehyde as a function of reaction time in the conversion of dihydroxyacetone over XS-Sn-MCM-41-A (100 mg, 90 $^{\circ}$ C).



Fig. 8. Recycling of XS-Sn-MCM-41-A in the conversion of dihydroxyacetone to ethyl lactate, using two different approaches.



Fig. 9. Leaching test of XS-Sn-MCM-41 catalysts in the conversion of dihydroxyacetone to ethyl lactate (200 mg of catalyst, 90 °C).

recycling approach was investigated: after each run, the sample was washed twice with ethanol and thermally treated at milder conditions ($300 \,^{\circ}$ C for 2 h). This approach was successful and allowed reusing the catalyst in five consecutive runs with only minor losses in activity (Fig. 8), indicating that a mild treatment at $300 \,^{\circ}$ C is sufficient to remove the reaction residues and fully reactivate the catalyst.

The heterogeneous nature of the studied catalysts was investigated by means of hot filtration leaching tests. After 30 min of reaction at 90 °C, the catalyst was removed from the reaction mixture by centrifugation followed by filtration at the reaction temperature. The filtrate was allowed to react for further 5 h 30 min at 90 °C. The conversion of dihydroxyacetone toward ethyl lactate after 30 min of reaction was compared with that at the end of the filtrate reaction (6 h) (Fig. 9). The slight increase in conversion is attributed to the unavoidable permeation of some of the small catalyst particles through the filter, rather than to the leaching of active species.

4. Conclusions

A series of ordered mesoporous Sn-silicate nanoparticles (XS-Sn-MCM-41) was successfully synthesized and studied as heterogeneous catalysts for the conversion of dihydroxyacetone

to ethyl lactate. This reaction provides an attracting and sustainable route for the production of valuable chemicals from renewable sources. The most active catalyst. XS-Sn-MCM-41-A. presented high turnover number and significantly improved conversion compared to conventional Sn-MCM-41 with larger particle size, and could achieve full conversion of dihydroxyacetone with virtually complete selectivity toward the desired lactate product. The excellent activity of XS-Sn-MCM-41-A is attributed to its optimal synthesis protocol: a short synthesis time at low temperature and a relatively low metal loading led to a material with small particle size (around 120 nm), exceptionally high specific surface area (1111 m² g⁻¹) and favored the incorporation of isolated tetrahedrally coordinated Sn into the silicate framework, which provide the acid sites required for the reaction. These catalytic results, together with the easy synthesis route required for the preparation of the material, make XS-Sn-MCM-41-A an extremely promising catalyst for other possible applications. XS-Sn-MCM-41-A could be recycled efficiently after regeneration by means of a mild calcination.

Acknowledgments

We acknowledge sponsoring in the frame of the following research programs: START1, CREA, Methusalem, IAP-PAI. The authors acknowledge G. Daelen for his assistance in the NMR measurements.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2014.03.012.

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