Tin-substituted mesoporous silica molecular sieve (Sn–HMS): synthesis and properties as a heterogeneous catalyst for lactide ring-opening polymerization

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An Sn-substituted mesoporous silica molecular sieve (Sn–HMS), prepared by neutral amine surfactant assembly of silicon and tin(IV) alkoxide precursors at ambient temperature, shows exceptional promise for producing poly(L-lactic acid) with polydispersity values near 1.1.

Biodegradable lactic acid polymers have been widely used in the biomedical field,[1–4] particularly for temporary tissue fixations where good mechanical strength is required. Semicrystalline poly(L-lactic acid) (PLA) normally is formed by polymerization of the monomer in the presence of a homogeneous Lewis-acid catalyst. Tin(II) salts, such as tin(II) octoate which affords polymers with molecular masses $>100\,000$, are the most common commercial catalysts for the homogeneous polymerization of lactides and lactones. Because the catalyst remains in the polymer, however, the applications of the polymer can be limited by potential toxicological effects of the catalysts and by diminished shelf stability. Heterogeneous $SnCl_2$, and $SnBr_4$ catalysts[5] form lactide polymers with number-average molecular masses as high as 50 000, but the polydispersity values (*ca.* 2.0) are undesirably high, most likely due to intramolecular (back-biting) and intermolecular transesterification side reactions.[6]

The present work reports our initial efforts to develop improved heterogeneous catalysts for lactide and related ring-opening polymerization catalysts based on mesoporous silica molecular sieves containing framework-substituted metal centres, particularly tin. Mesoporous MCM-41 and HMS silicas are prepared by ionic[7–9] and neutral[10–12] surfactant templating pathways, respectively. Both types of materials are characterized by large surface areas ($\geqslant 1000$ m^2 g^{-1}), high hydrocarbon sorption capacities, high thermal stabilities and large pore sizes that can be tuned from 1.5 to 10 nm depending on the chain length of the surfactant alkyl group. The potential importance of these materials lies in their use as catalysts for large-molecule transformations[10–14] and as hosts for supramolecular assembly.[15] However, HMS silicas, assembled by hydrogen-bonding interactions between a neutral amine surfactant (S^0) and an alkoxide precursor (I^0),[10–12] offer certain advantages over electrostatically templated MCM-41 analogues. In particular, S^0I^0 templating affords mesostructures with thicker walls (1.9–3.0 nm, depending on surfactant chain length) and smaller crystallite domain sizes for improved access to the framework mesopores.[10] The latter property is especially important for enhancing the conversions of diffusion-controlled condensed-phase reactions. S^0I^0 templating also offers other advantages, particularly the ability to form stable mesostructures under ambient reaction conditions and the synthetic versatility needed to substitute framework silicon by catalytically active metals through the use of alkoxide precursors. For these reasons the neutral surfactant templating route was used in the present work to prepare metal-substituted HMS derivatives.

Tin-substituted HMS containing 1.0 mol% Sn was prepared by mixing tetraethylorthosilicate (6.83 g, 32.8 mmol) with tin(IV) isopropoxide (0.117 g, 0.03 mmol). The resulting solution was added under vigorous stirring to a solution of dodecylamine (1.24 g, 6.69 mmol) in 29 ml of ethanol and 87 ml deionized water. The resulting reaction mixture was aged for 18 h, and then the product was filtered, washed with ethanol and calcined in air at 550 °C for 6 h. The calcined product (denoted Sn–HMS) exhibited a BET surface area of 886 m^2 g^{-1}. For comparison purposes a series of M–HMS (M = Ti, Fe, Y, La) derivatives with surface areas comparable to Sn–HMS were prepared by the same procedure. Also, an Sn-doped (1.0 mol%) silica gel with a surface area of 490 m^2 g^{-1} (550 °C calcination) was prepared by a hydrolysis procedure analogous to that used to prepare Sn–HMS, except that propylamine was used in place of dodecylamine. Finally, a bulk tin oxide (surface area 20 m^2 g^{-1}) was prepared by hydrolysis of tin(IV) isopropoxide in the presence of dodecylamine.

In a typical lactide polymerization reaction 0.1 g of metal-substituted HMS or 0.001 g SnO_2 catalyst (0.67 mmol Sn) was added to 2.00 g (13.9 mmol) of lactide dimer. After reaction at 130 °C for 72 h, the lactide to PLA conversion was measured by proton NMR spectroscopy. The average molecular mass and polydispersity were determined by gel permeation chromatography (GPC).

The powder X-ray diffraction (XRD) pattern of Sn–HMS, shown in Fig. 1, exhibited a single diffraction peak corresponding to a *d* spacing (4.2 nm) larger than the spacing observed for unsubstituted HMS prepared under the same reaction conditions. Increases in *d* spacings also were observed for the Ti-, Fe-, Y- and La-substituted HMS products. Fig. 2 presents the N_2 adsorption–desorption isotherm for Sn–HMS, along with

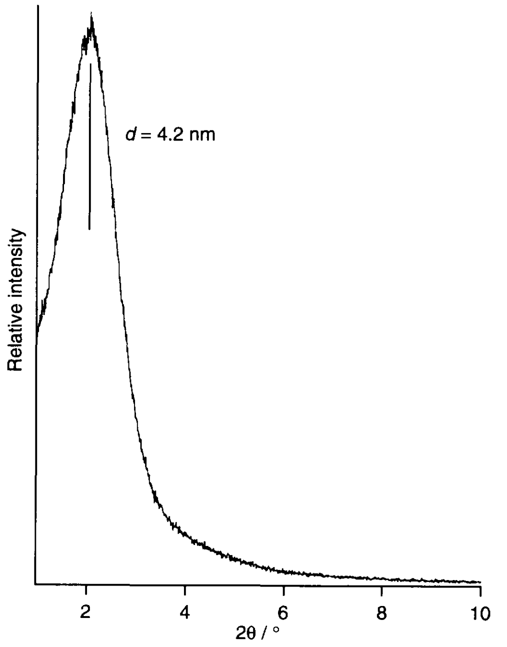

Fig. 1 X-Ray powder diffraction pattern of Sn–HMS. The pattern was measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode and Cu-Kα radiation (λ = 0.15418 nm).

the corresponding Horvath–Kawazoe (HK) pore size distribution curve. The presence of the XRD peak and the inflection point at a P/P_0 value at *ca.* 0.35 in the N_2 adsorption isotherm indicated that the 2.7 nm mesopores were a consequence of the surfactant-templated framework structure. A repeat distance of 4.8 nm between the pore centres of the hexagonal structure was calculated from the XRD data with the relationship $a_0 = 2d_{100}/\sqrt{3}$. The framework wall thickness was estimated to be 2.1 nm, as determined by subtracting the HK pore size from the repeat distance between pore centres. In comparing Sn–HMS with pure silica HMS,[10] we found that the pore size increased by 0.6 nm and the framework wall thickness increased by 0.3 nm upon the incorporation of framework tin.

As shown in Table 1, the polymerization product obtained from Sn–HMS exhibited the highest conversion (82%), the largest average molecular mass (36000) and a low polydispersity (1.1). In the case of pure tin oxide as the catalyst, the conversion was substantial (73%), but the polymerization product had a much lower molecular mass (17800) and a high polydispersity (1.7). The low activity in the case of Fe–, Y– and La–HMS and the Sn-doped silica gel may indicate the lack of a suitable dispersion of active metal centres in the host silica. Sn–HMS, however, clearly combines the reactivity of tin Lewis-acid sites with the selectivity of a regular mesopore structure in affording PLA with a reasonably high molecular mass and low polydispersity. It appears that the ordered pore structure improves average molecular mass and polydispersity values in comparison to homogeneous catalysts by imposing steric constraints on the propagating PLA chains and minimizing 'back-biting' and intermolecular transesterification reactions.

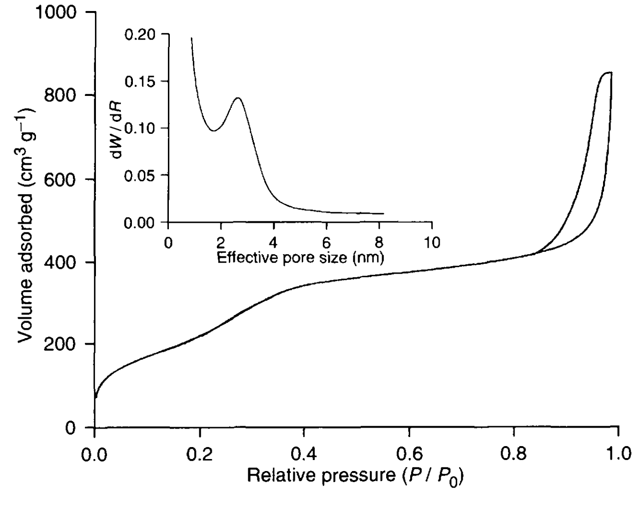

Fig. 2 Nitrogen adsorption and desorption isotherms for Sn–HMS. The isotherms were measured at 77 K on a Counter Omnisorp 360CX Sorptometer using a continuous adsorption procedure. Insert: The Horvath–Kawazoe pore size distribution curve for Sn–HMS, d*W*/d*R* is the derivative of the normalized nitrogen volume adsorbed with respect to the pore diameter of the adsorbent.

Table 1 Lactide polymerization over heterogeneous catalysts[a]

Catalyst	Conversion (%)	PLA molecular mass
Sn-HMS	82	36000
Ti-HMS	15	808
Fe-HMS	2	583
Y-HMS	0	—
La-HMS	0	—
HMS	0	—
Sn-doped Silica	22	3200
SnO_2	73	17800

[a] *Reaction conditions*: 2.00 g (13.9 mmol) lactide dimer; 0.1 g catalyst (except for SnO_2, where 0.001 g was used); T = 130 °C; reaction time 72 h.

In summary, a mesoporous tin-substituted silica molecular sieve (Sn–HMS) has been prepared by a neutral amine surfactant templating route using silicon and tin alkoxides as the reaction precursors. The framework-incorporated tin sites catalyse lactide ring-opening and provide PLA with a polydispersity near 1. Future work will focus on improving the average PLA molecular mass and on extending Sn–HMS catalysts to other ring-opening reactions.

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