Supercritical CO_2 dried chitosan: an efficient intrinsic heterogeneous catalyst in fine chemistry

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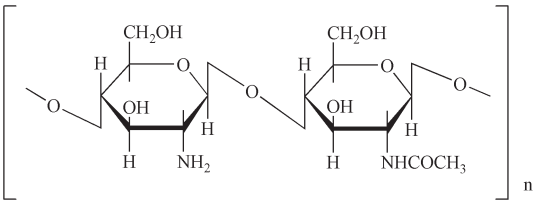
Chitosan microspheres are used as catalysts for the synthesis of monoglyceride by fatty acid addition to glycidol. Microspheres are obtained by drying gel beads of the natural polymer under supercritical CO_2 conditions, which makes the access to the polymer functional groups easy.

Chitosan is a polysaccharide derived from chitin, a linear chain of acetylglucosamine groups. It is the largest biomass polysaccharide component along with starch.[1] Chitosan is obtained by removing most of the acetyl groups from chitin. This process gives rise to amine groups, hence, chitosan can be considered as natural polyamine (Scheme 1).

The amine functionality borne by the polysaccharide framework could display intrinsic catalytic activity in acid-base catalysed reactions, providing that the reactants have easy access to these sites. In the present work, we have investigated the influence of the supercritical CO_2 drying of monosized microspheres of chitosan gel upon the accessibility of the intrinsic catalytic sites. Indeed, such a treatment has been found to have drastic effects on the texture of inorganic gels.[2–4]

Recently, Clark *et al.*[5] have reported the use of chemically modified expanded corn starches as catalysts for liquid phase organic reactions. The surface grafting of this porous materials with functionalised alkane siloxy chains bearing either sulfonic or amine and ammonium hydroxide functions yielded useful catalysts for the condensation reaction of 2-methylfurane with acetone and Knoevenagel or Michaël reactions, respectively. In order to benefit from this potentially renewable natural material, these authors have formed the expanded starch gel network by gelatinisation in hot water, followed by ageing the sample for several weeks at low temperature. Remarkably high surface areas (>100 m^2 g^{-1}) and pore volumes (>0.5 cm^3 g^{-1}) were thus obtained.

In this respect the interest of chitosan lies in its natural functionality for its possible direct use as a catalyst. Until now, all the results reported in the literature on the use of chitosan in catalysis dealt with the properties of complexation of the amino groups[6–12] or with its hydrophilic character for supported aqueous phase catalysis.[13,14]



Scheme 1 Chemical structure of chitosan.

The squid pen chitosan used here is characterised by its degree of acetylation (DA) of 10%, which is the percent of remaining acetyl groups measured by IR spectroscopy[15] and a mass of 500 000 g mol^{-1}. Beads are formed according to the procedure described in the Experimental. The SEM analysis (Fig. 1) of a diametral cutting of the beads reveals the porous and fibrous character of the materials.

The classical nitrogen sorption volumetry analysis of a microsphere degassed for 10 h at 80 °C confirms the mesoporous/macroporous texture. Isotherms are of the type I + IV in the IUPAC classification (Fig. 2). The external surface area obtained from the *t*-plot slope[16] is close to 110 m^2 g^{-1}. When chitosan is lyophilised the surface area does not exceed 1 m^2 g^{-1}.

Besides the textural analysis, the accessibility of the chitosan primary amine functions was compared with the two preparation modes, supercritical CO_2 drying *versus* lyophilisation. This was quantified by formation of the salicylaldimine Schiff base upon treatment with salicylaldehyde [17] (Scheme 2). When they entered into contact with salicylaldehyde the chitosan microspheres became yellow. Fig. 3 shows the UV-visible diffuse reflectance spectra of chitosan microspheres before and after reaction with salicylaldehyde. The spectrum of the latter sample exhibits the absorption band at 318 nm characteristic of Schiff base formation.

Quantitative GC analysis of the remaining salicylaldehyde in the solution gives the fraction of reacted amino groups, which corresponds to the accessible sites. The measurements were done in two different solvents, cyclohexane and ethanol, in order to take advantage of the possibility of swelling the polymer. The results are reported in Table 1. These data clearly demonstrate that the method of drying has a dramatic effect on the texture of the polymer and therefore on the accessibility of the surface functional groups. The use of a protic solvent known to be a good swelling agent for the polysaccharide framework strongly increases this effect.

Evaluation of the catalytic activities of the chitosan samples prepared by different methods is crucial to provide absolute

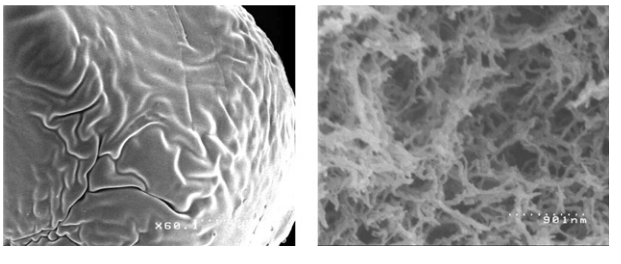


Fig. 1 SEM images of a microsphere of chitosan after $scCO_2$ drying: (A) external surface, (B) diametral cut.

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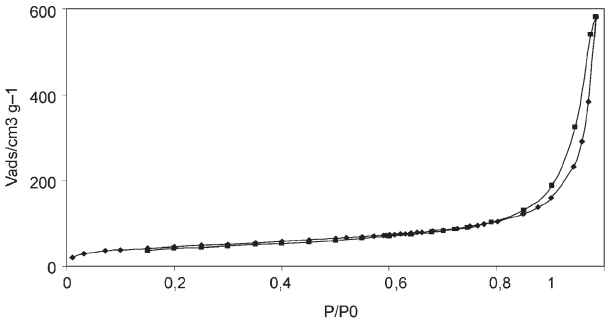
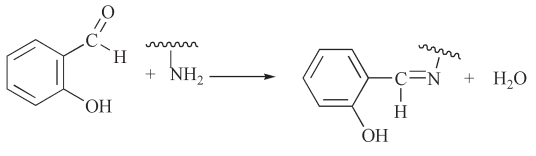


Fig. 2 Nitrogen sorption/desorption isotherm of chitosan beads.

proof of the potential of biopolymers as heterogeneous catalysts. In this respect, we have investigated the application of chitosan as a catalyst for fatty acid addition to glycidol, leading to monoglyceride formation (Scheme 3). Although monoesters of fatty acids and glycerol are useful emulsifiers in most processed fatty or oily foods, as well as in cosmetic and pharmaceutical products, very few results have been previously reported on this kind of reaction in the literature. To the best of our knowledge, only three papers deal with the use of amine or quaternised ammonium salts under homogeneous conditions.[18–20] Under heterogeneous conditions, we have previously shown that primary or tertiary amines grafted onto silica successfully catalysed this reaction in refluxing toluene as solvent.[21] More recently, Jaenicke *et al.*[22,23] have studied the use of stronger heterogeneised organic bases such as guanidine grafted on silica. However, these materials suffer from a detrimental decrease in the catalytic activity when they are reused.

Table 2 shows the results of the catalytic activity of the chitosan microspheres compared to amino-functionalised silica. The temperature has to be lower than 120 °C due to the thermal stability of this natural polymer. Thus the reactions were performed at 70 °C in toluene. The catalytic activity of $scCO_2$ dried chitosan in the lauric acid addition to glycidol compared to the inactivity of lyophilised chitosan emphasises the major role played by the drying mode upon the polymer framework structure, and, indeed, confirms the site accessibilty.

It is noteworthy that this natural polymer exhibiting a large mesoporosity displays a comparable catalytic performance to that of amine-functionalised silica. But in contrast to the latter, this solid is stable under basic conditions, a property that opens up the field of application of this natural heterogeneous basic catalyst.



Scheme 2 Salicylaldimine Schiff base formation.

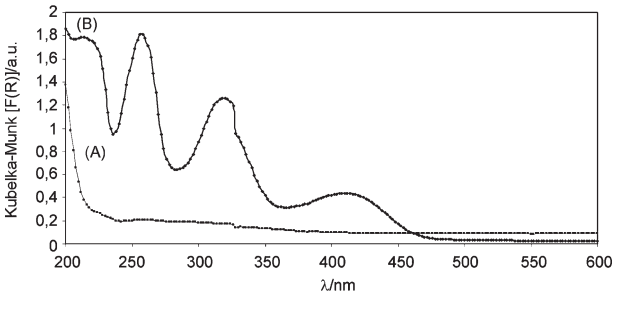
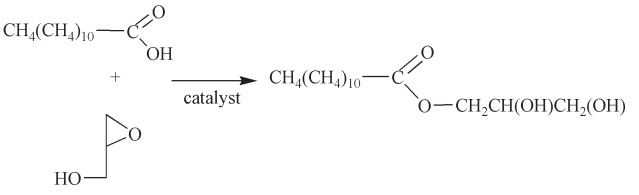


Fig. 3 UV-visible diffuse reflectance spectra of chitosan microspheres (A) before and (B) after reaction with salicylaldehyde.

Table 1 Percentage of accessible amine groups as a function of the solvent and drying mode

Solvent	Lyophilisation	$scCO_2$ drying
C_6H_{12}	4	54
EtOH	27	73

This work demonstrates the remarkable properties of chitosan as a catalyst in fine chemistry and emphasises the potential of natural biopolymers as renewable resources even though their textural or chemical composition may need to be adjusted, depending on the catalytic reactions in which they are to be used.



Scheme 3 Monoglyceride synthesis.

Table 2 Catalytic formation of α-monolaurin by lauric acid addition on glycidol

		t_r = 6 h		t_r = 24 h	
Catalyst	Run	% Conversion[a]	% Selectivity[b]	% Conversion[a]	% Selectivity[b]
None	1	0	0	0	0
Lyophilised chitosan	1	0	0	0	0
$scCO_2$	1	18	26	65	66
	2	—	—	98	71
NH_2/SiO_2[c]	1	66	45	79	89

[a] Glycidol conversion. [b] Glycidol selectivity in α-monoglyceride formation (by-product resulting from glycidol polymerisation[21]). [c] Synthesised according to ref. 21

Experimental

Preparation of $scCo_2$ dried chitosan microspheres

An aqueous solution of chitosan is obtained by dissolving 1 g of chitosan in 100 mL of a solution of acetic acid (0.055 mol·L^{-1}). This corresponds a stoechiometric amount of acid with respect to the NH_2 functional groups. Total dissolution is obtained by stirring one night at room temperature. This solution is dripped into a NaOH solution (4 N) through a 0.8 mm gauge syringe needle. The chitosan beads are stored in the alkaline solution for 2 h and then dehydrated by immersion in a series of successive ethanol–water baths of increasing alcohol concentration (10, 30, 50, 70, 90, 100%) for 15 min each. Then, the microspheres are dried under supercritical CO_2 conditions (74 bars, 31.5 °C) in a Polaron 3100 apparatus.

Quantitative GC analysis of the remaining salicylaldehyde in the solution

In a typical experiment, 33.8 mg of microspheres are put in 2.5 ml of a solution of salicylaldehyde (0.03 mol L^{-1}) in ethanol. The amount of aldehyde remaining in solution is determined by GC analysis (FID, BP20, $T_{injt.}$ = 250 °C, $T_{det.}$ = 270 °C, oven 50–250 °C, 20 °C min^{-1}) according to a calibration curve.

Catalytic test

In a typical experiment 0.5 mmol of lauric acid and 0.5 mmol of glycidol are injected in a flask containing 30 mg of chitosan beads in 4 mL of toluene. The zero time of reaction is taken as when the temperature reaches 70 °C. The amounts of reactants and products are determined by GC analysis (FID, HP5, $T_{inj} = 250$ °C, $T_{det} = 275$ °C, oven 50–250 °C, 15 °C min^{-1}) with octanol as the internal standard according to a calibration curve established with authentic samples.

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