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New materials based on renewable resources: chemically modified expanded corn starches as catalysts for liquid phase organic reactions

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Catalytically active chemically modified expanded corn starches have been developed with site loadings and activities comparable or superior to traditional materials.

Starch is the second largest biomass on the planet and as such represents one of the most important renewable resources for the future needs of a sustainable society.[1,2] Recent examples of its successful exploitation in non-food applications include as a filler in the production of blends for use as substitutes for purely fossil-based plastics[3] and as a feedstock in the manufacture of polylactic acid. The application of starch as a material in areas such as composites, adsorbents and catalyst supports is restricted by its naturally low surface areas (<1 m^2 g^{-1}) and pore volumes (<0.1 cm^3 g^{-1}). It is known however, that the structure of starch can be opened up by gelatinisation.[4] Here we report a family of new materials based on chemically modified expanded corn starches with remarkably high surface areas and pore volumes and with useful catalytic properties.

For the expansion process, the starch is initially gelatinised by heating in water at 100–130 °C. This causes the starch granules to first swell and then collapse to a gel. If the gel is simply dried at this stage, no increase in surface area is achieved. Instead, by keeping the gel at 5 °C a process of retrogradation occurs creating a gel network. The time necessary to achieve the full retrogradation depends on the type of material used and is typically between two and three weeks for normal corn starch or one day for high amylose-content corn starch. Precipitation and washing this gel with ethanol retains a rigid porous gel network with surface areas and pore volumes of >100 m^2 g^{-1} and >0.5 cm^3 g^{-1} respectively. Even higher values can be achieved with high amylose corn starch (up to 180 m^2 g^{-1}), although the expanded material is less stable to water. In comparison, for potato starches the best we have been able to achieve is a surface area of 40 m^2 g^{-1}. The role of the ethanol is to remove water from the gel without collapsing the pore structure. This requires a liquid which is miscible with water but has a lower surface tension. We have found that ethanol is the most effective for this purpose although other alcohols give similar if smaller effects. It is important to note that the entire expansion process requires water, heat and ethanol (and time!) only and the solvents are fully recoverable and reusable. The ordinary expanded corn starches will collapse over long periods of time in atmospheres of high humidity or actually in water (*e.g.* stirring in water for 24 h at r.t. reduces the surface area to <1 m^2 g^{-1}) although simple protection from moisture gives them almost indefinite storage time.

Once expanded, the natural high functionality of starch makes it an excellent candidate for chemical surface modification so as to alter properties of the material such as hydrophobicity and adhesion, and, as we will show here, to enhance its activity in heterogeneous catalysis.

In order to evaluate the potential of these materials as a catalyst support we have prepared both solid acids and bases through chemical modification of expanded corn starch (ECS). We have studied three ways to introduce sulfonic acid functions onto ECS: (i) direct reaction with $Cl(CH_2CH(OH)CH_2SO_3Na$ and NaOH; (ii) reaction with chlorosulfonic acid and pyridine, and (iii) reaction with $(MeO)_3Si(CH_2)_3SH$ followed by oxidation with hydrogen peroxide. All of these effectively introduced sulfonic acid functions whilst maintaining an expanded starch structure, although some loss of surface area was normally observed. For example, as shown in Fig. 1, in the silane-peroxide route, the decrease in surface area was monitored for each stage of the synthesis (the chemical modification was confirmed by infrared and X-ray photoelectron spectroscopy). The methodology best serves as an illustration of the remarkable robustness of the ECS. Refluxing in toluene followed by treatment with 50% aqueous hydrogen peroxide have little effect on the structure of the material. The thermal stabilities of the chemically modified materials are also good. For instance, for the ECS-SO_3H material, no significant decomposition occurred below 200 °C. The acid functionalised materials are active catalysts. As a test we evaluated the ECS-SO_3H material in the reaction of 2-methylfuran with acetone to form the bisfurylalkane—a reaction previously used to test the activity of a synthetic high surface area silica modified with sulfonic acid groups.[5] We found that, under equivalent conditions, the ECS-SO_3H materials performed as well as the silica materials (Table 1). Moreover, if the ECS-SO_3H is simply filtered and washed at the end of the reaction, its appearance as well as reactivity are unchanged. The importance of the high surface area can be demonstrated by comparing the activity of the water-destructured material which affords <0.5% yield of product under the same reaction conditions.

In order to test the suitability of ECS as a material for heterogeneous base catalysis we have prepared a series of materials containing primary aminoalkyl, tertiary amino alkyl and quaternary ammonium hydroxide functions (Fig. 2). All three functions can be successfully introduced at high loadings on the ECS without significant loss in surface area although the ammonium hydroxide material was somewhat problematic. All of the materials proved to be active in the Knoevenagel reaction

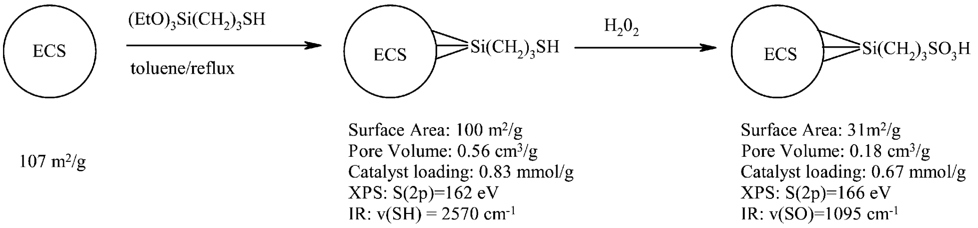

Fig. 1 Monitoring the formation of one form of sulfonic acid modified corn starch.

Table 1 Evaluation of solid acid catalysts in the reaction of 2-methylfuran (0.9 g) with acetone (1.6 g) to form the bisfurylalkane (BMP). 0.9 g of catalyst was used

Catalyst	Surface area/m^2 g^{-1})	Pore volume/cm^3 g^{-1}	Loading/mmol g^{-1}	BMP yield (%)
ECS-$CH_2CH(OH)CH_2SO_3H$	4.1	0.03	0.57	3.0
ECS≡Si-$(CH_2)_3SO_3H$	30.7	0.18	0.67	37.3
ECS≡Si-$(CH_2)_3SO_3H$[a]	30.7	0.18	0.67	52.6
ECS-SO_3H	32.0	0.17	0.81	27.2
Silica≡Si-$(CH_2)_3SO_3H$[b]	400	0.19	1.0–1.5	52–85

[a] 1.8 g of catalyst used. [b] Reference 5

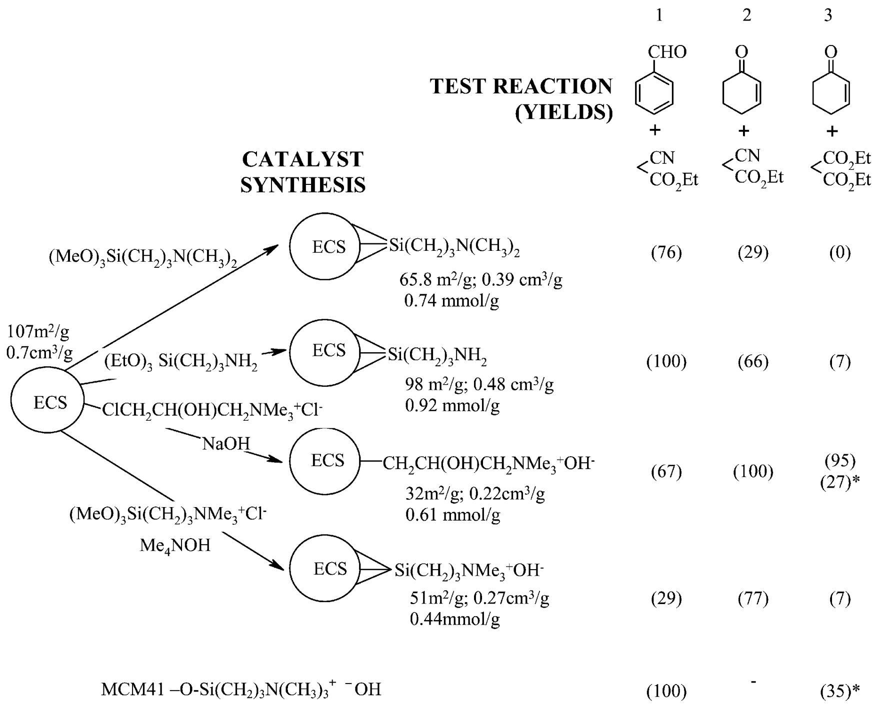

Fig. 2 Synthetic routes to solid bases from expanded corn starch (surface areas, pore volumes and functional loadings are given). Catalyst activity was tested for three reactions: 1st was carried out for 2 h at 60 °C and the 2nd and 3rd reactions were carried out for 24 h at 80 °C. The results are compared to silica supported bases from literature (ref. 7). *Reactions carried out for 2 h at 80 °C. The results are compared to silica supported bases from literature (ref. 7. *Reactions carried out for 2 h at 80 °C.

of benzaldehyde with ethylcyanoacetate with the ECS-NH_2 performing particularly well (100% conversion of benzaldehyde after 2 h in a reaction with 4 mmol of benzaldehyde and 5 mmol of ethyl cyanoacetate using 0.04 g of catalyst in 2.5 ml of ethanol at 60 °C). Extending the tests to the Michael reaction of cyclohexenone with ethyl cyanoacetate (8 mmol of cyclohexenone, 8 mmol of ethyl cyanoacetate and 0.06 g of catalyst in 2 ml of ethanol at 80 °C for 24 h) differentiates between the materials with the ECS-NH_2 and ECS-$N(CH_3)_2$ giving lower yields of 66% and 29% respectively, while the more active quaternary ammonium hydroxide functionalised materials (ECS-$CH_2CH(OH)CH_2NMe_3^+OH^-$) gave 100% conversion (a similar conversion can also be achieved in the reaction of cyclohexenone with diethylmalonate where the other catalysts are inactive). Once again the performance of the novel starch solid bases compares reasonably well with those of other solid bases[6] but the results are especially important in further demonstrating the potential of using expanded corn starch as a base material for making porous and versatile organophilic heterogeneous catalysts.

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Notes and references

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