Preparation of a sugar catalyst and its use for highly efficient production of biodiesel†

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Novel solid acid catalysts for esterification have recently been described that are made by incomplete carbonization of carbohydrates followed by sulfonation. Herein, such a 'sugar catalyst' is prepared from D-glucose and its catalytic properties and structure are investigated in detail. This type of sugar catalyst is, for the first time, applied for the effective production of biodiesel from waste oils. Our results indicate that sugar catalysts are highly effective, minimally polluting and re-usable catalysts that are highly suited to the production of biodiesel from waste oils with a high acid value.

The price of fossil diesel has soared in recent years and the available reserves of this important fuel will eventually be exhausted if large-scale use continues. Biodiesel is a renewable alternative to fossil diesel that is composed of monoalkyl esters of fatty acids. Waste oils, which are available cheaply, are an attractive starting material that can help in improving the economical feasibility of biodiesel. However, they are challenging due to the presence of considerable amounts of free fatty acids (FFAs), which interfere with the transesterification process and must first be converted into their corresponding esters through esterification. Reported catalysts for the production of biodiesel have included homogeneous strong bases[1] such as alkali metal hydroxides and alkoxides, homogeneous acids[1c,2] such as H_2SO_4 and enzymes such as lipases.[3] However, alkaline catalysts are generally corrosive to equipment and also react with FFAs to form unwanted soap by-products that require expensive separation.[1b] Homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems.[2f] Although the lipases are generally effective and non-polluting, they are usually expensive and there are problems associated with both FFAs and short chain alcohols (such as methanol and ethanol), which denature the lipase to some extent as well as substantially decreasing the operational stability of the enzyme. In addition, glycerol, which is one of the products of the reaction, is easily absorbed onto the surface of the lipase and has a serious negative effect on the enzyme.[4] Therefore, the development of solid acid catalysts, which have recently gained much attention in view of their ease of separation and lack of corrosion or toxicity problems, is a desirable goal.[2f,5,6]

Unfortunately, the inorganic-oxide solid acids such as zeolite and niobic acid have low densities of effective acid sites and readily lose their activities under harsh conditions.[7,8] Although strong acidic ion-exchange resins such as amberlyst and nafion have abundant sulfonic acid groups ($-SO_3H$) that function as strong acid sites, these resins are expensive and their catalytic activities are still much lower than that of sulfuric acid. In addition, such resins show low operational stability and their catalytic activity is lost after a few cycles of re-use.[6,9,10] Sulfated zirconia, on the other hand, is an efficient solid acid catalyst,[9,11] but is expensive because zirconium is a rare and costly metal. Besides, high temperatures are required both for the calcination which is necessary for preparation of sulfated zirconia and for reactivation of the catalyst.

Only recently have carbon-based solid acid catalysts been reported as promising catalysts for esterification reactions. Such a catalyst can be cheaply produced by incomplete carbonization of sulfopolycyclic aromatic hydrocarbons (such as sulfonate derivatives produced by reaction of naphthalene and anthracene with H_2SO_4)[12] or sulfonation of incompletely carbonized D-glucose.[13] Unfortunately, the former is a soft material and its aromatic molecules are leached out during liquid-phase reactions above 100 °C or when higher fatty acids are used as reactants, thus resulting in a rapid deactivation of the catalyst. However, sugar-derived solid acid catalysts, known as sugar catalysts, are physically robust and there is no leaching of SO_3H groups during use and so these catalysts exhibit a high and stable activity during the esterification reactions. In this paper, we describe the preparation of a solid acid catalyst from D-glucose (Fig. S1 in the ESI†), and use the resulting sugar catalyst for efficient production of biodiesel from higher fatty acids and especially waste oils with a high acid value. The physical and chemical properties of the D-glucose-derived catalyst are also characterized.

D-Glucose powder (10 g) was heated for 15 h at 400 °C under N_2 flow to produce an incomplete carbonization. The resulting material was then ground to a powder and heated in 100 mL of concentrated H_2SO_4 at 150 °C under N_2 flow for 15 h. The mixture was diluted with distilled water and the black precipitate was collected by filtration and washed repeatedly with hot distilled water (>80 °C) until impurities such as sulfate ions were no longer detected in the wash water.[13] The resulting black solids (i.e. the sugar catalyst) were dried at 60 °C in vacuo and were subsequently evaluated for the catalytic activity in biodiesel production as described below.

High-grade biodiesel can be produced by esterification of oleic acid, one of the constituent fatty acids of the triglycerides of vegetable oils, with short chain aliphatic alcohols (methanol or ethanol). In order to rationally evaluate the activity of sugar

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catalyst in this reaction, a comparative study was made between the D-glucose-derived sugar catalyst and three typical solid acid catalysts (sulfated zirconia, amberlyst-15 and niobic acid). The reaction used was the esterification of oleic acid (10 mmol) with methanol (100 mmol) at 80 °C. As can be seen in Fig. 1, the sugar catalyst showed a much higher esterification activity than either sulfated zirconia (67 µmol min^{-1} *vs.* 21 µmol min^{-1}) or amberlyst-15 (67 µmol min^{-1} *vs.* 7 µmol min^{-1}), and gave a markedly enhanced yield of methyl oleate after 5 h (95% *vs.* 85% or 15%). Niobic acid, which is a solid acid catalyst, manifested no significant catalytic activity (<1.5 µmol min^{-1}) towards the esterification of oleic acid with methanol. Surprisingly, the solid acid catalyst sulfated zirconia exhibited much lower esterification activity than the sugar catalyst although the former has a substantially larger BET surface area (214 ± 0.08 m^2 g^{-1}) than the latter (4.13 ± 0.03 m^2 g^{-1}), which suggests that the surface of the greater part of the micropores in sulfated zirconia do not participate in the esterification reaction. The main reason for the unexpected result might be that the acid sites of sulfated zirconia were fewer than those of the sugar catalyst prepared from D-glucose, which is the subject of ongoing investigation in our laboratory. In order to compare the sugar catalyst with a homogeneous acid catalyst, the esterification of oleic acid with methanol was also conducted using concentrated H$_2$SO$_4$ as the catalyst. In spite of its slightly higher esterification activity than the sugar catalyst (78 µmol min^{-1} *vs.* 67 µmol min^{-1}), the concentrated H$_2$SO$_4$ as a liquid acid catalyst cannot be readily recycled, and it presents a threat to the environment and the operator's health, especially when it is employed on a large scale. Although H$_2$SO$_4$ is used during the preparation of the sugar catalyst, the catalyst itself is relatively non-toxic and can be re-used many times. It therefore represents a greener solution to biodiesel production than concentrated H$_2$SO$_4$.

The esterifications of other higher fatty acids such as palmitic acid and stearic acid with methanol were also successfully conducted with the D-glucose-derived sugar catalyst. As depicted in Fig. 2, the yield of fatty acid methyl ester clearly increased with increasing reaction time up to 5 h, and subsequently showed no significant improvement. After 5 h, the yield of the methyl ester
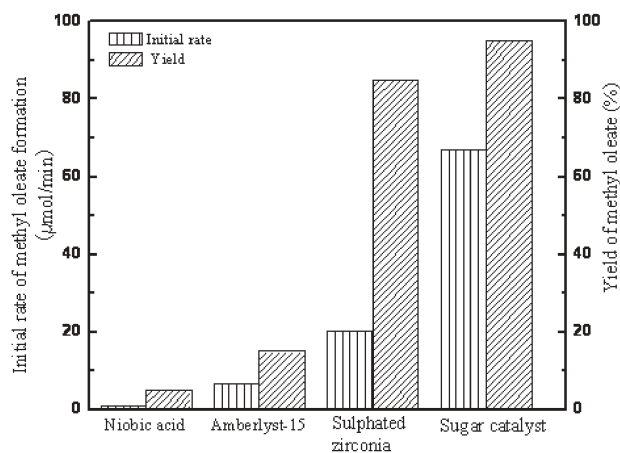
Fig. 1 Initial rate of methyl oleate formation and the yield during esterification of oleic acid by the D-glucose-derived sugar catalyst and other catalysts. Reaction condition: 10 mmol oleic acid; 100 mmol methanol; 0.14 g catalyst; 80 °C; reflux system.
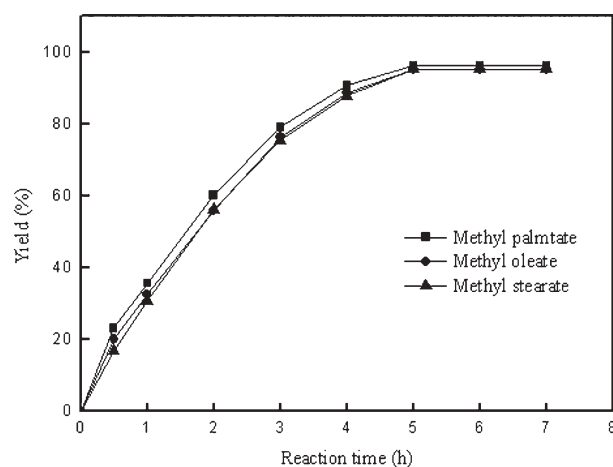

Fig. 2 Esterification of higher fatty acids with methanol catalyzed by the D-glucose-derived sugar catalyst. Reaction condition: 10 mmol palmitic acid, oleic acid or stearic acid; 100 mmol methanol; 0.14 g sugar catalyst; 80 °C; reflux system.

product was high (⩾95%) for the sugar catalyst-catalyzed esterification of all three higher fatty acits (Fig. 2). Palmitic acid gave slightly faster initial rate of esterification than oleic acid and stearic acid. Among the three fatty acids tested, the initial rate of the esterification decreased slightly with increasing the carbon-chain length of the fatty acids, possibly resulting from the steric hindrance effect of the carbon chains.

Presently one bottleneck for biodiesel production is the high cost of the feedstock. Therefore, the production of biodiesel directly from vegetable oils and greases is obviously uncompetitive. The introduction of waste oils for biodiesel production is, in contrast, very competitive and promising.[16] The D-glucose-derived sugar catalyst was therefore also tested for the production of biodiesel from waste oils with a high acid value (27.8% FFAs). Such high acid-value oils are unsuitable for conversion to biodiesel with alkaline catalysts because the FFAs form unwanted soap byproducts in the presence of alkali. Enzyme catalyzed conversion of such materials is not favourable either, owing to denaturation of the enzymes under acidic conditions. Fig. 3 illustrates the profiles of biodiesel production from waste oils with a high acid value catalyzed by the three typical solid acid catalysts (sulfated zirconia, amberlyst-15 and niobic acid) and the sugar catalyst prepared during this study. A remarkable enhancement in the reactivity and the yield was observed with sugar catalyst as compared with the other solid acid catalysts examined. The D-glucose-derived catalyst afforded a high yield of above 90% .

For evaluation of the operational stability of the sugar catalyst, the catalyst was recovered for further reaction by filtration, extensive washing with *t*-butanol (until no trace of reaction solution was left from the previous esterification), and drying *in vacuo*. It was found that the sugar catalyst still retained a remarkably high proportion (93%) of its original catalytic activity in the methyl oleate formation reaction, even after more than fifty cycles of successive re-use. Thus the sugar catalyst had excellent operational stability.

The physical and chemical properties of the D-glucose-derived sugar catalyst were also investigated. As can be seen in Fig. 4, the X-ray diffraction (XRD) pattern of the sugar catalyst exhibited a
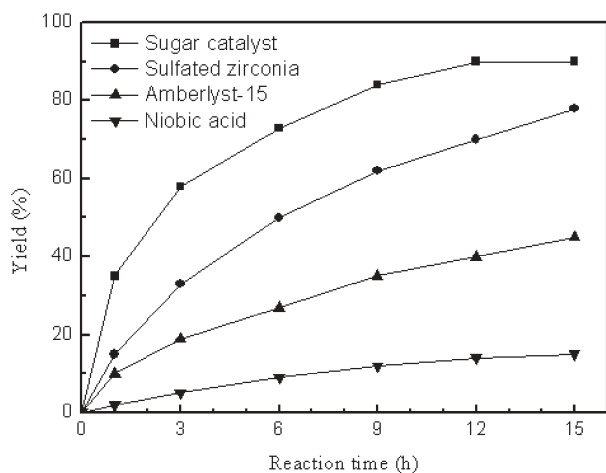
Fig. 3 Profiles of the production of biodiesel from waste oils with a high acid value by the D-glucose-derived sugar catalyst and other solid acid catalysts. Reaction condition: 5.0 g waste oil (27.8% FFAs); 5.54 g methanol; 0.5 g catalyst; 80 °C; reflux system.

broad diffraction peak ($2\theta = 10$–$30°$) and a weak diffraction peak ($2\theta = 35$–$50°$), which can typically be attributed to amorphous carbon.[14] This indicates that the sugar catalyst had an amorphous structure, which may be important in the catalyst's activity during esterification reactions. In contrast, catalysts prepared by sulfonation of familiar carbon materials such as graphite, carbon black, graphitized carbon fibre, activated carbon and glassy carbon, displayed no catalytic activity in the esterification reaction.[15]

Fig. 5 depicts the FT-IR spectra of the sugar catalyst before and after sulfonation. The strong peak at around 1712 cm^{-1} and the weak peak at around 1207 cm^{-1} could be typically assigned to the stretching modes of SO$_3$H groups which are the "active sites" of the sugar catalyst. The FT-IR spectra clearly demonstrate that the sugar catalyst after sulfonation contains SO$_3$H groups. In addition, the higher the SO$_3$H group content in the material, the higher its catalytic activity. Elemental analysis (EA) of the sugar catalyst showed that the sulfur content was 4.7% (by mass) and that the catalyst had the elemental composition of CH$_{1.14}$S$_{0.03}$O$_{0.39}$. All sulfur atoms in sulfonated sugar catalysts have previously been

Fig. 4 XRD pattern of sugar catalyst prepared from D-glucose.
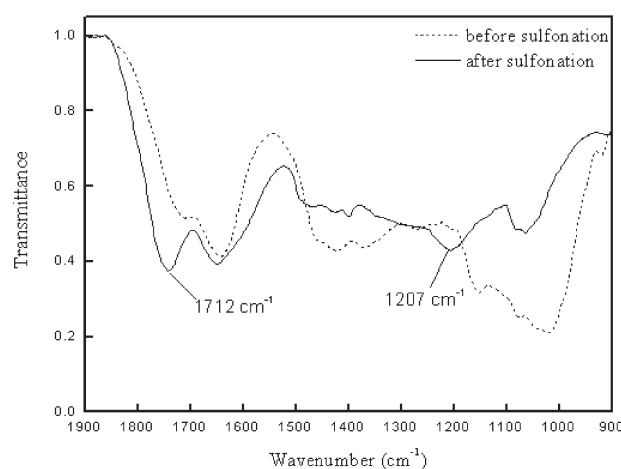

Fig. 5 Comparison of FT-IR spectra of sugar catalyst prepared from D-glucose before and after sulfonation.

shown to be present as SO$_3$H groups.[15] Thus, the mass content of SO$_3$H groups was calculated to be about 11.9% based on the sulfur content, and the acid site concentration of the sugar catalyst was calculated to be around 1.5 mmol g^{-1} according to the SO$_3$H group content. Analysis by means of ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS; Fig. S2 in the ESI†) indicated that the acid strength (pK_a) of the sugar catalyst was in the range of -11 to -8, which is comparable to that of concentrated H$_2$SO$_4$.

Additional information about the sugar catalyst was provided by scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis. As is evident from the SEM image in Fig. S3 (ESI†), the particles of the sugar catalyst reached micrometre dimensions and did not significantly aggregate. The large surface area of the sugar catalyst almost certainly contributes to its catalytic activity. The BET surface area of the sugar catalyst prepared under the conditions described in the ESI† was found to be 4.13 ± 0.03 m^2 g^{-1} based on calculations from adsorption isotherms using the standard BET equation, and was much larger than that of other sugar catalysts prepared under different carbonization temperatures and times, as well as with different duration and temperature of sulfonation (data not shown).

The thermal stability of the sugar catalyst was examined by thermogravimetric analysis (TGA) under a flow of air at a heating rate of 10 °C min^{-1}. As shown in Fig. 6, the sugar catalyst before sulfonation displayed a slight weight loss (about 3%) over a temperature range of 25–380 °C, possibly due to the loss of a small amount of water in the H$_2$SO$_4$-untreated catalyst. The catalyst after sulfonation exhibited a marginal weight loss over the temperature range of 25–275 °C, but showed a rapid weight loss between 275 and 325 °C. The sample weight remained almost constant from 325 to 380 °C. The H$_2$SO$_4$-treated sugar catalyst underwent a total weight loss of about 15%, which equals the total content of SO$_3$H groups (around 11.9%) and water (around 3%). These results clearly indicate that the rapid weight loss of the sugar catalyst upon heating can be attributed to the thermal decomposition of the SO$_3$H groups that are the active sites of the catalyst, which was confirmed by elemental analysis of the catalyst after heating (data not shown). This conclusion is further supported by
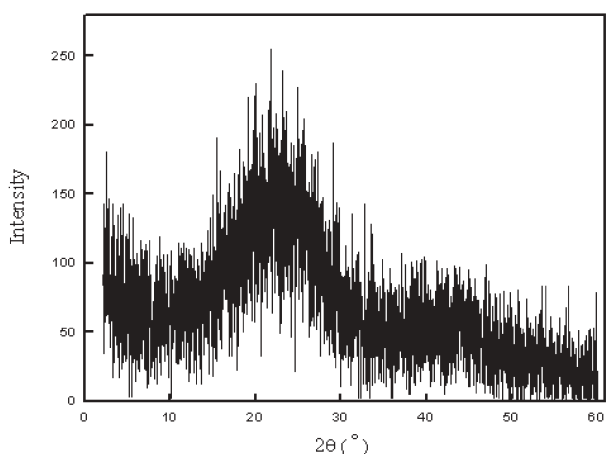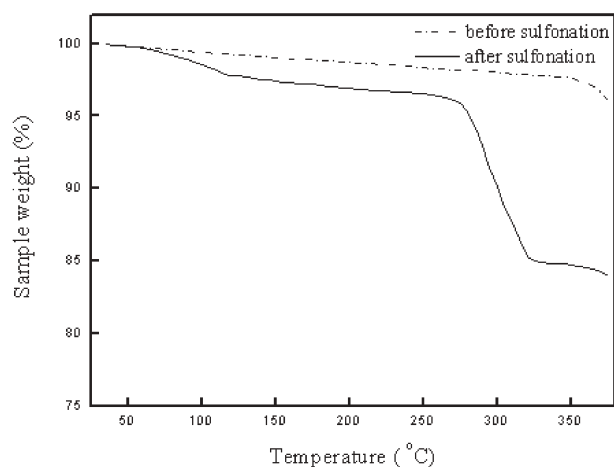
Fig. 6 TGA of sugar catalyst prepared from D-glucose before and after sulfonation.

the observation that the sugar catalyst exhibited no significant esterification activity after being incubated at 275–325 °C for 1 h. Nonetheless, the sugar catalyst that we prepared worked excellently at a temperature as high as 275 °C, while the previously reported H_2SO_4-treated carbon nanotube worked only below 230 °C.[17] In addition, the H_2SO_4-treated carbon nanotube manifested no esterification activity towards higher fatty acids such as oleic acid, palmitic acid and stearic acid, but the sugar catalyst exhibited high esterification activity towards these compounds (Fig. 2). These results clearly indicate that the sugar catalyst is superior to the H_2SO_4-treated carbon nanotube with respect to thermal stability and esterification activity towards long-chain fatty acids.

In summary, our results support the conclusions that sugar catalysts have much higher catalytic activity than other solid acid catalysts and as such are very promising to replace sulfuric acid and other catalysts as a green catalyst for efficient production of biodiesel from higher fatty acids and especially waste oils with a high acid value. In addition, it is possible that environmentally benign, recyclable sugar catalysts may find wide applications in reactions where concentrated H_2SO_4 or other acids are currently used as catalysts.

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