

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

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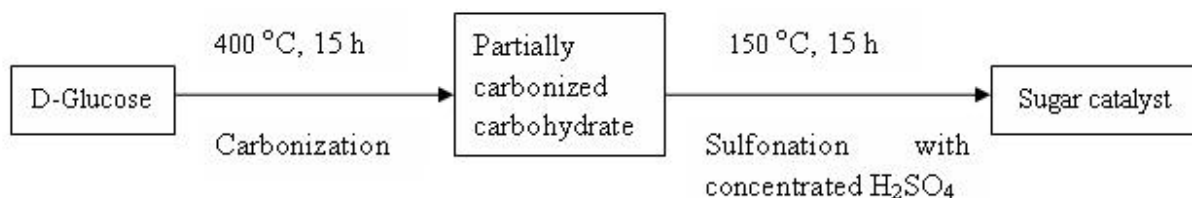
Electronic Supplementary Information (ESI)

Experimental section

Preparation of Sugar Catalysts (Fig. S1)

D-glucose powder (10 g) was heated for 15 h at 400 °C under N₂ flow to produce an incomplete carbonization. The resulting material was then ground to a powder and heated in 100 mL of concentrated H₂SO₄ (>96%) at 150 °C under N₂ flow for 15 h. The mixture was diluted with 500 mL of 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. The resulting black solids (i.e. the sugar catalyst) were dried at 60 °C *in vacuo*. The yield of the sugar catalyst is around 45% based on the used material weight.

Fig. S1 Preparation of a novel sugar catalyst (solid acid catalyst) suitable for esterification reactions.



Characterization of sugar catalyst prepared from D-glucose

1. X-ray diffraction (XRD)

XRD analysis was performed using a Rigaku D/max- system. The catalyst surface was scanned by monochromatic Cu K α radiation ($\lambda = 0.18415$ nm) at 30 kV and 30 mA. The angle (2θ) was measured in steps of 0.02° with a dwell time of 1 s, between 2° and 60° .

2. Fourier transformed infrared spectroscopy (FT-IR)

FTIR spectra were recorded on a Bruker Vector 33 FTIR spectrometer in the region 4000 – 400 cm^{-1} . The samples were prepared as KBr pellets.

3. Elemental analysis (EA)

The elemental analysis of the catalyst was conducted on an Elementar vario EL & CHN-O-RAPID apparatus. The absolute errors were $\leq 0.1\%$ (CHS) and $\leq 0.2\%$ (O), respectively.

4. Brunauer-Emmett-Teller (BET) analysis

The specific surface area (BET) of the catalysts was determined on a Micromeritics Flowsorb 2310 instrument. The catalyst was pre-treated at 120°C under vacuum for over 2 h to desorb contaminating molecules (mainly water) from the catalyst surface. For the determination of BET surface area, the value of p/p_0 in the range $0.2 < p/p_0 \leq 1$ was used, and krypton was used as the adsorbing gas. The specific surface area of the sugar catalyst was calculated from adsorption isotherms using the standard BET equation. The absolute errors were $\leq 1\%$.

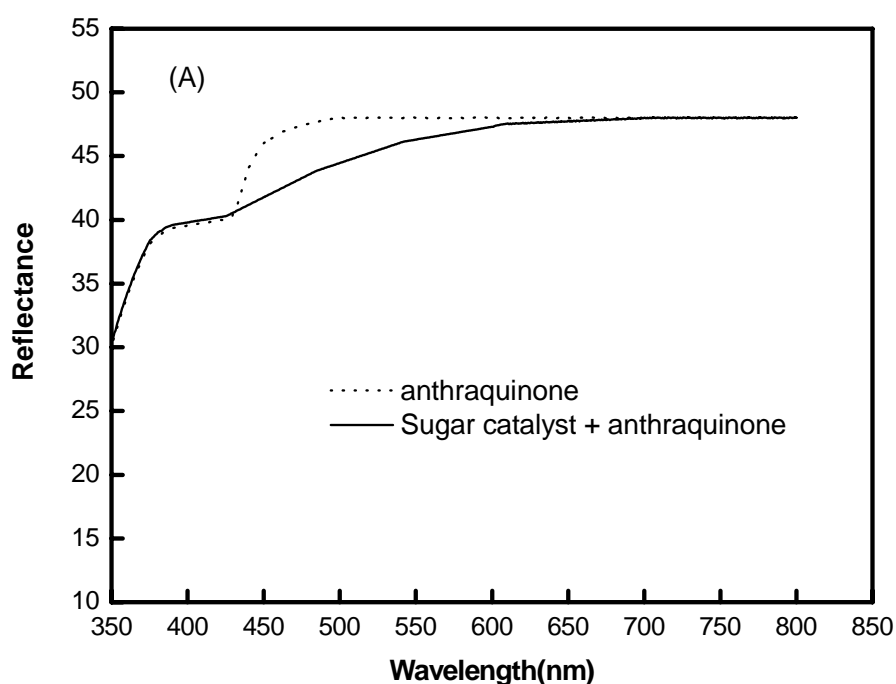
5. Thermogravimetric analysis (TGA)

The thermal stability of the catalysts was examined by TGA using Netzsch TG 209 F1. The catalysts were detected at a heating rate of $10^\circ\text{C min}^{-1}$ with 10 mg sample under a flow of air from 25°C to 800°C .

6. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS)

The acid strength of the sugar catalyst was examined by ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) on a Shimadzu UV-2501PC spectrophotometer. A mixture of the sugar catalyst (0.2 g) and BaSO_4 powder (a reference material for DRS measurement, 1.0 g) was evacuated at 150°C for 1 h to remove adsorbed water. In an Ar-filled glove box, the mixture was packed into a sealable quartz cell, and benzene (with or without the color-producing reagents *p*-nitrotoluene and anthraquinone) was then added to the cell. The DRS of the mixture in each benzene solution was measured without exposure to air. The DRS of the color-producing reagent in the presence of the sugar catalyst was obtained by subtracting the spectrum for the mixture in pure benzene from that of the mixture in the benzene solution solving the color-producing reagent. The DRS for each color-producing reagent was also observed in a similar manner using BaSO_4 in benzene with and without the color-producing reagent.

Fig. S2 shows the UV-vis DRS spectra for the sugar catalyst coated with the color-producing reagents after subtraction of the reflection due to the sugar catalyst. The spectra for the color-producing reagents are also shown for comparison. A broad absorption band appears at 450-600 nm in the spectrum for the sugar catalyst with anthraquinone, attributable to the yellow coloration of anthraquinone in strong acid ($\text{pK}_a \leq -8.2$), corresponding to concentrated H_2SO_4 of greater than 90 wt%. The yellow coloration of *p*-nitrotoluene ($\text{pK}_a \leq -11.4$) is not observed, indicating that the pK_a of the sugar catalyst is in the range of approximately -11 to -8, comparable to that of concentrated H_2SO_4 .



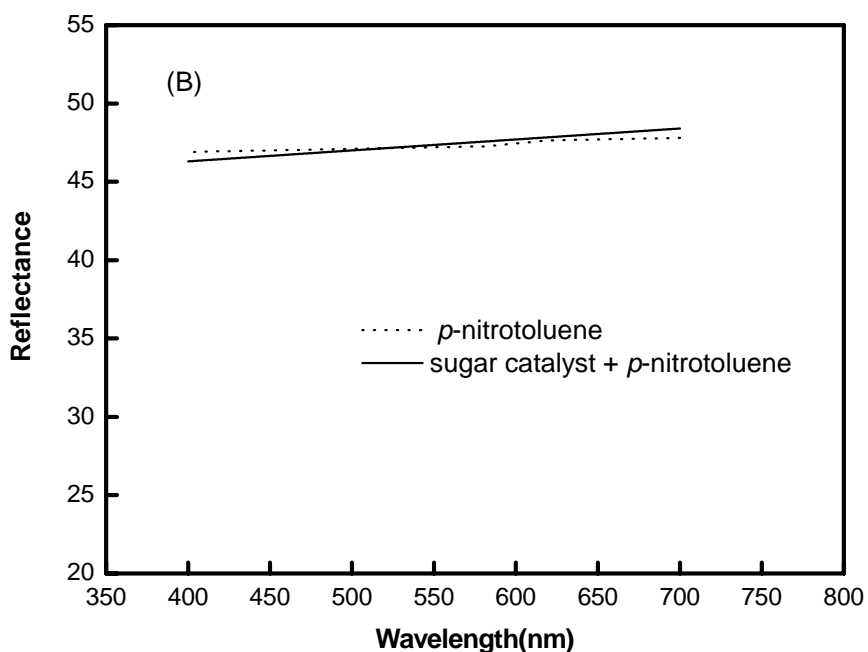


Fig. S2 UV-vis DRS spectra of sugar catalyst with (A) anthraquinone and (B) *p*-nitrotoluene. The dot lines are reflections of anthraquinone and *p*-nitrotoluene

4. Scanning electron microscopy (SEM)

SEM pictures (Fig. S3) were taken using a FEI Quanta 400 FEG with an acceleration voltage of 20 kV. Catalyst samples were goldcoated prior to scanning.

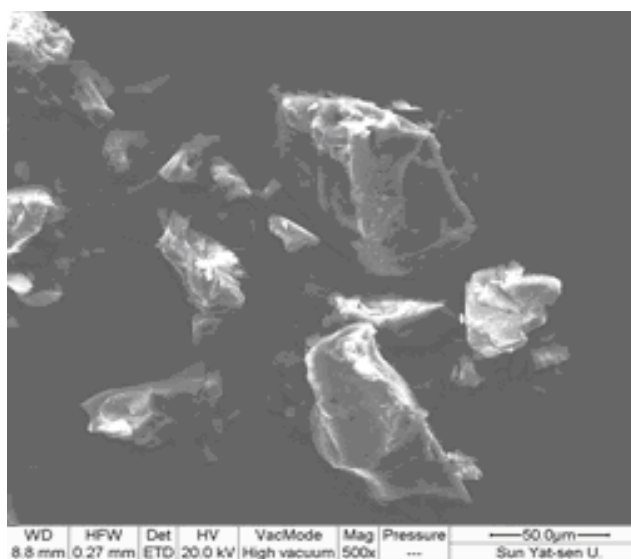


Fig. S3 SEM image of sugar catalyst prepared from D-glucose.

Esterification of oleic acid with sugar catalyst and other solid acid catalysts

In a typical experiment, the esterification of oleic acid was conducted at 80 °C by addition of 0.14 g of the D-glucose-derived sugar catalyst or other solid acid catalysts available (Sulphated zirconia, Amberlyst-15 and Niobic acid) to a stirred batch reflux system containing a methanol-oleic acid mixture (methanol: 100 mmol; oleic acid: 10 mmol). Samples (50 μL) were withdrawn at specified time intervals from the reaction mixture and centrifuged (10,000 rpm, 10 min), and then the upper layer (5 μL) in combination with *n*-hexane (200 μL) containing 1.0 mM methyl heptadecanoate (as an internal standard) was taken for GC analysis. Reaction rate did not increase with increasing reaction stirring speed, indicating that the reaction was under kinetic control and not diffusion-limited.

Esterification of other higher fatty acids with methanol catalyzed by sugar catalyst

In two typical experiments, the esterification of palmitic acid and stearic acid were conducted at 80 °C by addition of 0.14 g of the D-glucose-derived sugar catalyst to two stirred batch reflux systems, respectively. Among the two systems, one contained a methanol-palmitic acid mixture (methanol: 100 mmol; palmitic acid: 10 mmol), the other one contained a methanol-stearic acid mixture (methanol: 100 mmol; stearic acid: 10 mmol). Samples (50 μL) were withdrawn at specified time intervals from the reaction mixture and centrifuged (10,000 rpm, 10 min), and then the upper layer (5 μL) in combination with *n*-hexane (200 μL) containing 1.0 mM methyl heptadecanoate (as an internal standard) was taken for GC analysis.

Production of biodiesel from waste oils with a high acid value catalyzed by sugar catalyst and other solid acid catalysts

In a typical experiment, the transesterification of waste oils with a high acid value (27.8% free fatty acids) was conducted at 80 °C by addition of 0.50 g of the D-glucose-derived sugar catalyst or other solid acid catalysts available (Sulphated zirconia, Amberlyst-15 and Niobic acid) to a stirred batch reflux system containing a methanol-waste oils mixture (methanol: 5.54 g; waste oils: 5.00 g). Samples (50 μL) were withdrawn at specified time intervals from the reaction mixture and centrifuged (10,000 rpm, 10 min), and then the upper layer (5 μL) in combination with *n*-hexane (200 μL) containing 1.0 mM methyl heptadecanoate (as an internal standard) was taken for GC analysis.

GC Analysis

The reaction mixture was assayed with a GC 2010 gas chromatography (Shimadzu Corp., Kyoto, Japan) with a HP-5 capillary column (0.53 mm × 15 m, HP, USA) equipped with a flame ionization detector. The column temperature was hold at 180 °C for 1 min, then raised to 186 °C at 0.8 °C /min and kept for 1 min. Nitrogen was used as the carrier gas at 2 ml/min. Split ratio was 1:100 (v/v). The injector and the detector temperatures were set at 250 °C and 280 °C, respectively. The retention times for methyl heptadecanoate and methyl oleate were 5.88 and 7.64 min, respectively. The initial reaction rate was calculated from the GC data. The average error for this determination was less than 0.5%. All reported data are averages of experiments performed at least in duplicate.