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Electronic Supplementary Information

Catalytic alcoholysis of epoxides using metal-free cucurbituril-based solids

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1. Experimental

1.1. Materials and methods

Elemental analysis for C, H, and N was performed by M. Marques at the University of Aveiro with a Leco TruSpec 630-200-200 analyser. Chloride contents were quantified by using a Dionex 2000i ion chromatograph (IC) equipped with a Dionex AS4A-SC column; an isocratic elution with $NaHCO_3$ and Na_2CO_3 (3.4 mM each) was employed (detection limit 0.1 mg/L). Milli-Q grade water was used as the solvent for preparing samples. Thermogravimetric analyses (TGA) were performed under air using a Shimadzu TGA-50 system from room temperature up to ca. 800 °C with a heating rate of 5 °C min^{-1}. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were carried out on a Hitachi SU-70 microscope with an accelerating voltage of 20 kV. Samples were prepared by deposition on aluminium sample holders followed by carbon coating using an Emitech K 950 carbon evaporator. Room-temperature FT-IR spectra were recorded in the range of 300-4000 cm^{-1} with a Mattson 7000 spectrometer, using a globar source, a DTGS detector, and potassium bromide cells, with 256 scans and a resolution of 4 cm^{-1}. Raman spectra were recorded on a Bruker RFS100/S FT instrument (Nd:YAG laser, 1064 nm excitation, InGaAs detector) with 1000 scans and a resolution of 2 cm^{-1}. Solid-state $^{13}C\{^1H\}$ CP MAS NMR spectra were recorded at 100.62 MHz on a Bruker Avance 400 spectrometer, using 3.5 μs ^1H 90° pulses, a 2 ms contact time, a spinning rate of 10 kHz, and 5 s recycle delays. Chemicals shifts are quoted in ppm relative to TMS.

Glycoluril (Aldrich), paraformaldehyde, hydrochloric acid, acetone (p.a., Scharlau), styrene oxide (> 97%, Fluka), cyclohexene oxide (98%, Aldrich), cyclooctene oxide (99%, Aldrich), cyclododecene oxide (mixture of isomers, 95%, TCI), (1R, 2R)-phenylpropylene oxide (99%, Aldrich), 4-vinylcyclohexene oxide (mixture of isomers, 98%, Aldrich), R-limonene oxide (mixture of cis and trans, 97%, Aldrich), absolute ethanol (99.8%, Scharlau), and *n*-butanol (99%, Alfa Aesar) were purchased from commercial sources and used as received.

1.2. Preparation of CBs

CB6 and CB7 were prepared and purified by using a modified procedure based on those described earlier by Kim *et al.*[1] and Day *et al*.[2] Briefly, a mixture of glycoluril (300 g, 2.11 mol), paraformaldehyde (135 g, 4.48 mol), and conc. HCl (300 mL) was heated at 80 °C for 150 min and then at 100 °C for 24 h. After addition of water (2.5 L), undissolved solid (CB6+CB8) was removed by filtration, and methanol (2.5 L) was added to the filtrate to precipitate a mixture containing mainly CB5 and CB7. CB7 [in a final yield of 49 g, 12% (based on glycoluril)] was separated from CB5 through successive recrystallisations from H_2O/MeOH followed by a final recrystallisation from H_2O/acetone. Anal. Calcd for

$C_{42}H_{42}N_{28}O_{14}\cdot 11H_2O\cdot 0.1HCl\cdot 0.5(CH_3COCH_3)$ (1393.8): C, 37.48; H, 4.85; N, 28.14; Cl, 0.25. Found: C, 37.46; H, 4.83; N, 28.08; Cl, 0.26. TGA (Fig. S1) revealed a weight loss of 16.5% up to 250 °C (calcd, for loss of $11H_2O$, 0.1 HCl, and $0.5(CH_3COCH_3)$: 16.6%). FT-IR (cm^{-1}): *v* = 3450 (s, br), 2998 (w), 2929 (w), 1728 [vs, *v*(CO)], 1639 (sh), 1475 (vs), 1421 (s), 1376 (s), 1323 (s), 1294 (m), 1234 (vs), 1192 (s), 1152 (m), 1027 (w), 990 (sh), 968 (s), 826 (sh), 806 (vs), 760 (m), 675 (m), 630 (w), 449 (w), 368 (m). Raman (cm^{-1}): *v* = 2948 (s), 2915 (w), 1757 (w), 1742 (m), 1419 (m), 1380 (m), 1327 (w), 1283 (w), 1228 (w), 1201 (w), 1185 (sh), 1135 (w), 1043 (w), 1009 (vw), 971 (w), 916 (sh), 899 (m), 829 (s), 785 (w), 752 (m), 655 (m), 440 (vs), 381 (w), 362 (w), 337 (w), 287 (w), 266 (w), 186 (s), 115 (s). ^{1}H NMR (400 MHz, D_2O): δ= 4.21 (d, 14H, *J* = 15.4 Hz), 5.50 (s, 14H), 5.76 (d, 14H, *J* = 15.4 Hz). $^{13}C\{^1H\}$ CP MAS NMR: δ = 156.3 (CO), 71.4 (CH), 52.8 (CH_2), 28.2 (acetone).

The solid mixture of CB6 and CB8 (260 g) was mixed with 3 M HCl (3 L) during 1 h. The solution was filtered off and mixed with acetone to precipitate pure CB6, which was filtered, washed with acetone and dried (136 g, 33%). Anal. Calcd for $C_{36}H_{36}N_{24}O_{12}\cdot 7H_2O\cdot 0.1HCl\cdot 0.8(CH_3COCH_3)$ (1173.0): C, 39.32; H, 4.72; N, 28.66. Found: C, 39.42; H, 4.53; N, 28.55. TGA (Fig. S1) revealed a weight loss of 14.3% up to 250 °C (calcd, for loss of $7H_2O$, 0.1 HCl, and $0.8(CH_3COCH_3)$: 15.0%). FT-IR (cm^{-1}): *v* = 3461 (br), 3000 (w), 2932 (w), 1737 [vs, *v*(CO)], 1645 (sh), 1475 (vs), 1415 (s), 1376 (s), 1326 (s), 1292 (m), 1234 (vs), 1189 (s), 1147 (m), 1027 (w), 967 (s), 820 (sh), 799 (vs), 758 (s), 675 (m), 629 (w), 452 (w), 370 (m). Raman (cm^{-1}): *v* = 2993 (w), 2943 (m), 1766 (w), 1740 (w), 1712 (w), 1417 (m), 1382 (m), 1327 (w), 1285 (w), 1233 (w), 1208 (w), 1185 (w), 1125 (w), 1047 (w), 1008 (w), 971 (w), 916 (w), 894 (w), 826 (s), 788 (w), 752 (m), 652 (w), 442 (vs), 402 (w), 362 (w), 342 (w), 286 (w), 207 (s), 125 (s). $^{13}C\{^1H\}$ CP MAS NMR: δ = 155.2 (CO), 70.3 (CH), 52.1 (CH_2), 28.6 (acetone).

1.3. Catalytic tests

The catalytic reactions were carried out under air with magnetic stirring in a closed borosilicate reaction vessel (10 mL capacity), which was immersed in a temperature-controlled oil bath. Before use, CB7 was dried under vacuum (0.1 bar) for 1 h at 40 °C. Typically, the reactor was loaded with CB7 (21 mg) and solvent (2.0 mL of absolute ethanol or *n*-butanol), and then preheated for 10 min at the desired reaction temperature. The substrate (820 μmol) was preheated in a similar fashion and then added to the mixture; the reaction time was counted from this instant. The evolution of the reaction was monitored using a Varian 3800 GC equipped with a BR-5 (Bruker) capillary column (30 m x 0.25 mm; 0.25 μm) and a flame ionisation detector, using H_2 as the carrier gas. The reaction products were identified by GC-MS [Trace GC 2000 Series (Thermo Quest CE Instruments) – DSQ II (Thermo Scientific)], equipped with a capillary DB-1 type column (30 m x 0.25 mm; 0.25 μm) and using He as carrier gas. Cyclododecane epoxide was used as an internal standard.

For the recycling tests, after a 1 h batch run the solid phase was separated from the reaction mixture by centrifugation, washed with ethanol (3 × 1 mL), dried at room temperature overnight followed by a further treatment under vacuum (0.1 bar) for 1 h at 40 °C, and then reused in a catalytic batch run.

Contact tests (CTs) were performed by mixing CB7 with ethanol at 35 or 55 °C for 1 h. Afterwards, the mixture was centrifuged, and the liquid phase was separated and filtered through a 0.22 μm PTFE membrane. It was then transferred to a separate reactor and preheated at the desired reaction temperature for 10 min. Subsequently, styrene oxide (StyOx) was added in order to have a StyOx:ethanol molar ratio equivalent to that used under the typical reaction conditions. The filtration test (FT) was carried out as follows: after 10 min of StyOx reaction in the presence of CB7 (using typical catalytic conditions) at 35 °C, the mixture was centrifuged, and the liquid phase was filtered using a

0.22 µm PTFE membrane, and left to react at 35 °C for a further 4 h.

To determine acid contents (5% error), acid-base titrations were performed in triplicate by mixing CB*n* (25 mg) with ethanol or Milli-Q grade water (20 mL) at 35 °C. The resultant mixtures were titrated with 0.001 M NaOH.

2. Additional characterisation data

Thermogravimetric (Fig. S1), $^{13}C\{^{1}H\}$ CP MAS NMR (Fig. S2) and FT Raman (Fig. S3) data for as-prepared CB6 and CB7 were in agreement with published results.[3-5]

References

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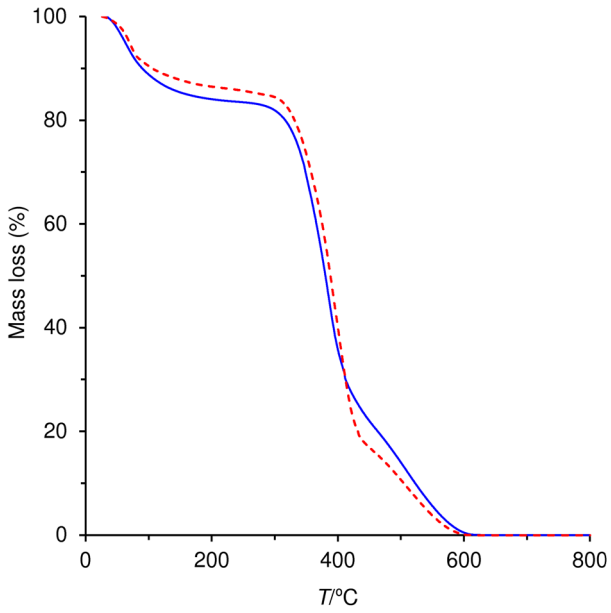

Fig. S1 Thermogravimetric analysis traces for the synthesised CB6 (– – –) and CB7 (———) samples.

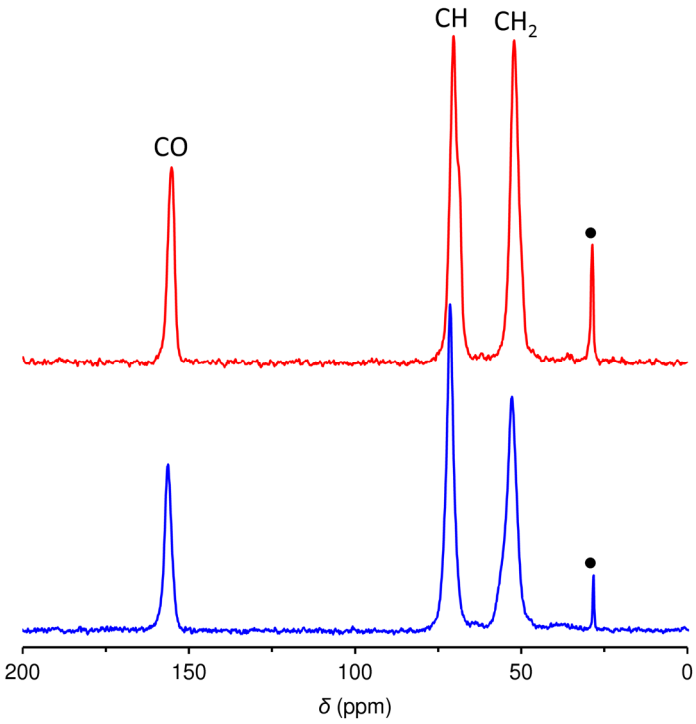

Fig. S2. $^{13}C\{^{1}H\}$ CP MAS NMR spectra of the synthesised CB6 (—) and CB7 (—) samples. The signal labelled with the filled circle is due to acetone.

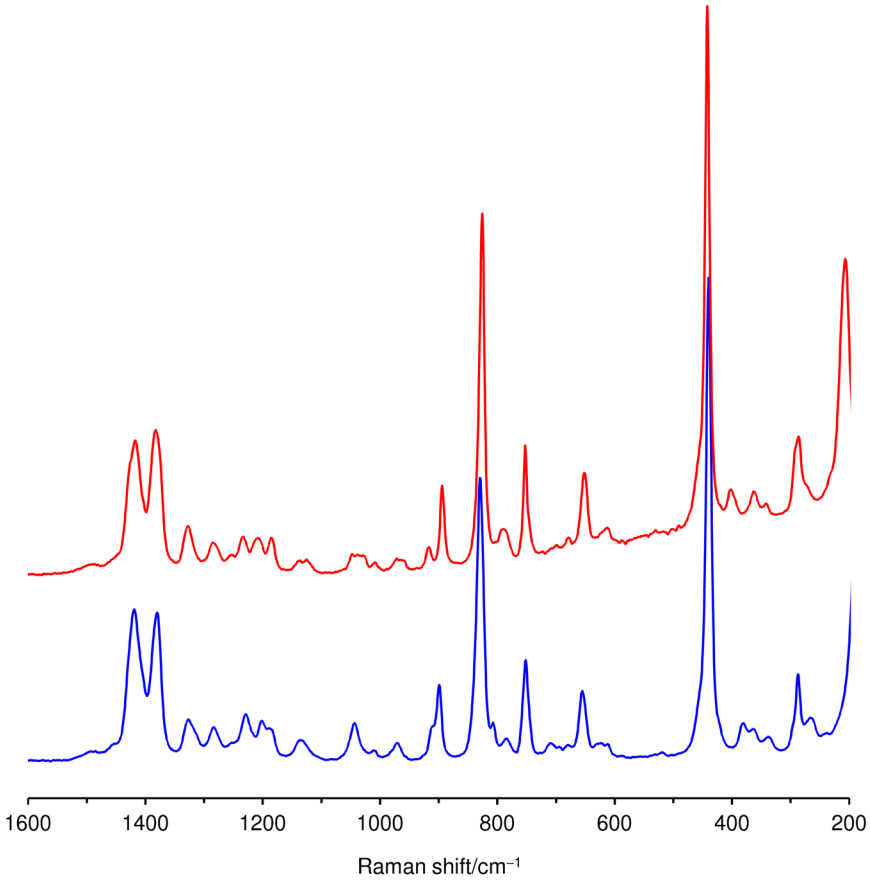

Fig. S3. Selected region of the FT-Raman spectra of the synthesised CB6 (—) and CB7 (—) samples.