Supporting information

Catalytic Nanoreactors in Continuous Flow: Hydrogenation inside Single-walled Carbon Nanotubes using Supercritical CO_2

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Experimental

1. Experimental set up

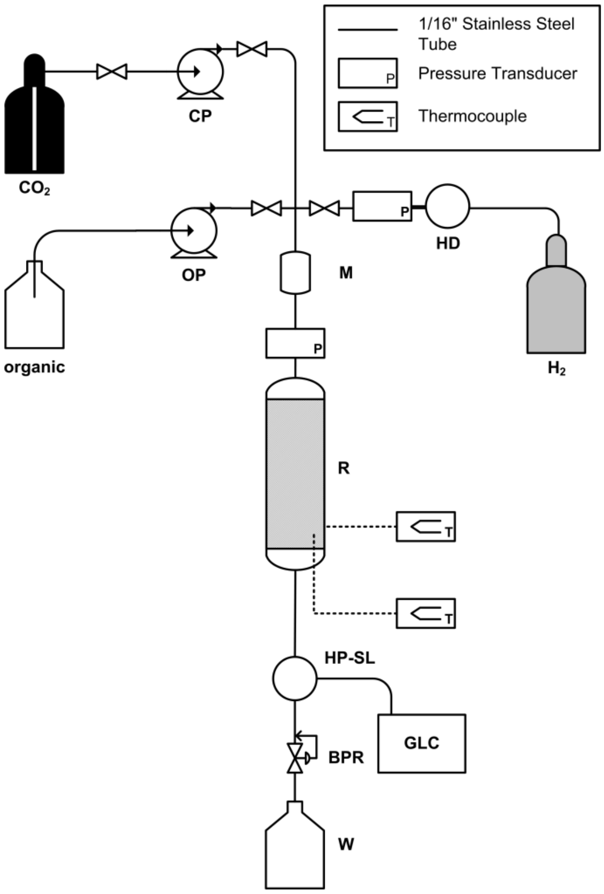

Figure S1. Schematic of flow reactor used for supercritical carbon dioxide hydrogenations. The components are labelled as follows: CP, chilled CO_2 pump; HD, H_2 dosing unit; M, mixer; OP, organic pump; PH, preheater and mixer; R, ¼ inch sand packed reactor containing ca. 20mg of RuNPs@SWNT catalyst; HP-SL, high pressure sample loop; BPR, back pressure regulator; GLC, gas liquid chromatograph; W, organic waste.

The supercritical CO_2 flow reactor was set up as previously reported.[1] In a typical experiment, the reactor (82 mm long with an internal diameter of 3.5 mm) was half filled with sand, 20 mg of catalyst was then loaded and the rest of the reactor bed was filled with sand and then sealed into the apparatus. The CO_2 pump was then initiated until the required pressure was reached (100 bar at 1 mL/min CO_2 flow rate). The reactor was then heated to the reaction temperature and the reactant pumped into the system at the desired flow rate. 2 Molar equivalents (w.r.t. the reactant) of H_2

were then dosed into the system using a Rheodyne valve. The product stream of the cyclooctene reaction was analysed online using a high pressure sample loop connected to a Shimadzu GC-14 fitted with a SPB-5 with He as the carrier gas. The GC oven was held at 40 °C with a carrier gas flow rate of 211 mL/min a column pressure of 98 kPa and a split ratio of 30. Butyraldehyde and cinnamaldehyde experiments were analysed using a SPB-1701 column with a He carrier gas. The GC oven was ramped from 60 °C-270 °C at 15 °C/min. He flowed at 250 mL/min with a split ratio of 250, this gave a column pressure of 96 kPa.

2. Molecular modelling

Consideration of the relative sizes and shapes of the reactant and product molecules and the SWNT carbon nanoreactor channel (Figure S2) reveals that though all of the molecules studied can fit inside the channel. The commensurate size of the reactants and nanotube means that there will be significantly more interaction with the nanotube sidewall compared to previous studies which use much wider multi-walled carbon nanotubes (typical d_{NT} = 10-100 nm).

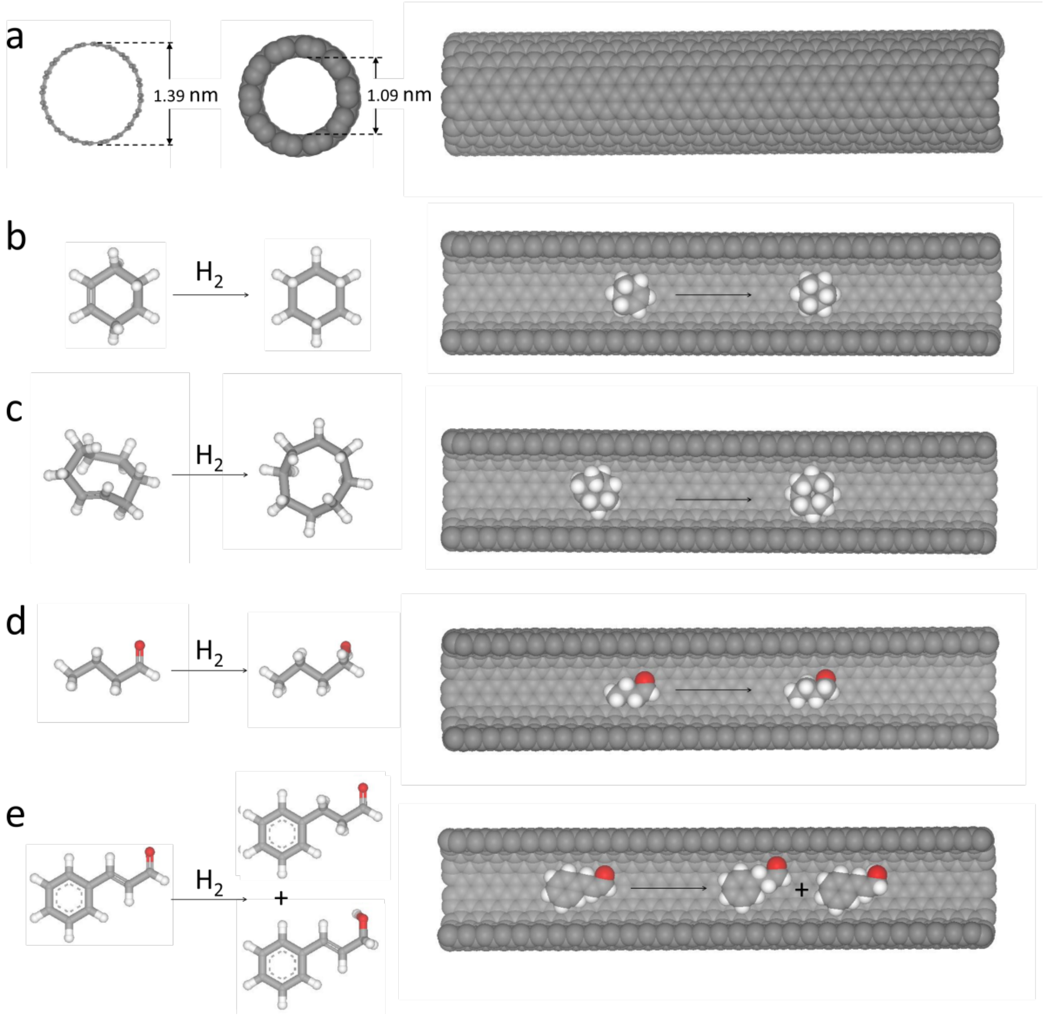

Figure S2. Molecular diagrams showing; a) the crystallographic (1.39 nm) and the van der Waals internal diameter (1.09 nm) of a [10,10]SWNT, b-e) the relative van der Waals radii of the reactant and products for the hydrogenation reactions of b) cyclohexene, c) cyclooctene, d) butryaldehyde and e) cinnamaldehyde inside a [10,10]SWNT (drawn to scale relative to the nanotube) revealing that all molecules fit snuggly inside the carbon nanoreactor cavity. The front sidewall of the nanotube is removed for clarity in b-e.

3. Catalyst Synthesis

The catalyst was prepared as follows: SWNT (arc-discharge, Helix Material Solutions Inc., US) were annealed at 380 °C for 20 minutes to open their termini and remove any residual amorphous carbon from the internal cavities, a 20 % weight loss was observed. $Ru_3(CO)_{12}$ (5% by wt. of nanotubes) was mixed with the SWNT, sealed under vacuum (10^{-5} mbar) in a quartz ampoule and heated at 130 °C for 3 days. The sample was then cooled rapidly to room temperature, washed repetitively with tetrahydrofuran (50 mL) to remove residual $Ru_3(CO)_{12}$ from the nanotube surface, filtered through a PTFE membrane (0.2 µm pore), and then heated at 600 °C in a quartz ampoule under Ar for 2 hours to form RuNPs inside nanotubes.

4. TEM characterisation of the RuNPs@SWNT catalyst post reaction

The RuNPs@SWNT catalyst was recovered after being reaction at 110 °C for 24 hours. HRTEM revealed that no significant change had occurred to the structure of the catalyst with discrete ~1 nm Ru nanoparticles observed throughout the carbon nanotubes, Figure S2. There is some evidence of amorphous material deposited on the outside of the nanotubes as a result of the hydrogenation process.

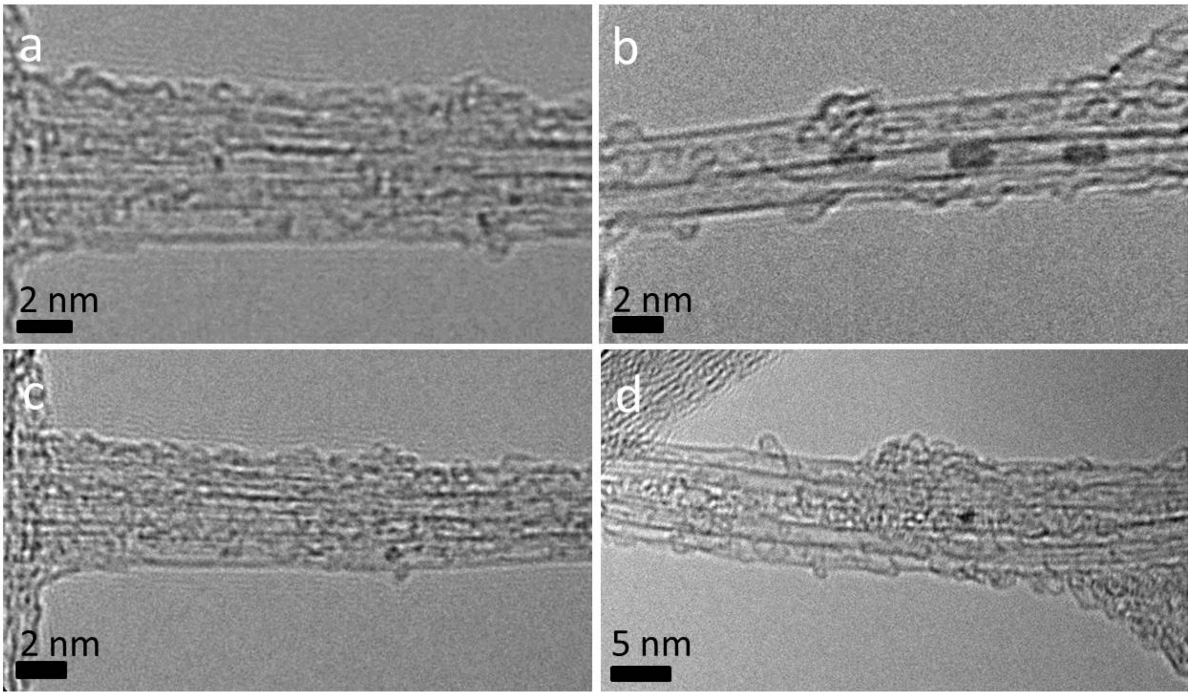

Figure S3. a-d) HRTEM images of the RuNPs@SWNT catalysts after 24 h of hydrogenation reaction at 110 °C. ~1 nm RUNPs can still be clearly seen within the nanotubes with no sintering of the nanoparticles or degradation of the nanotubes observed.

5. TOF calculations.

Turnover frequencies (TOFs) in molecules per active site per minute were calculated for both catalysts as follows:

Catalyst	RuNPs@SWNT (5% by wt. Ru)	Ru/C (5% by wt. Ru)
Active Ru Surface area/m^2 g^{-1}	0.45-12.64[a]	24.00[b]
Surface area in 20 mg of catalyst	0.0091-0.25	0.48
Active sites in 20 mg of catalyst	1.03 x 10^{17}-2.84 x 10^{-18}[c]	5.39 x 10^{18}[c]
Cyclooctane molecules produced /min^{-1}	8.93 x 10^{19}[d]	5.5927 x 10^{20}[e]
TOF/molecules per active site min^{-1}	867.5-31.5	103.8

[a] The active Ru surface area of the RuNPs@SWNT catalyst was calculated by assuming all nanoparticles to be 0.9 nm in diameter (average d_{NP} = 0.92 ± 0.13 by TEM) and to consist of 60 Ru atoms.[2] The mass of ruthenium metal within the RuNPs@SWNT catalyst, 1 mg, means that there will be 9.93 x 10^{16} Ru nanoparticles in 20 mg of catalyst. By treating the nanoparticle as a perfect spheres the surface area of an individual Ru nanoparticle was calculated to be 2.54 nm^2 and the surface area occupied by an individual Ru atom on the nanoparticle surface was approximated to be 0.89 nm^2.[3] In the ideal case in which all ruthenium nanoparticles within the catalyst will be accessible this gives an active ruthenium surface area of 0.25 m^2 for 20 mg of catalyst. However if the transport of reactants through the nanotube channel is inhibited by the presence of the confined Ru nanoparticles this could lead to some of the metal nanoparticles being inaccessible. In the most extreme case imaginable only the Ru nanoparticles at the ends of the nanotubes will be accessible and therefore catalytically active. In this case, taking into account that the number of nanotubes within 20 mg of RuNPs@SWNT can be approximated as 3.60 x 10^{15} (assuming that all carbon nanotubes are [10,10]SWNT with an average nanotube length of 1500 nm and Mw of 3176470 g/mol)[4] and the fact that only half of the surface of the nanoparticles located at the open ends of the nanotubes are accessible, the active Ru surface area = 2(3.60 x 10^{15}) x 0.5(2.54 nm^2) = 0.0091 m^2 for the RuNPs@SWNT. Realistically the active Ru surface area of the RuNPs@SWNT catalyst will be somewhere in between these two extreme values as the C_{60} filling experiment reveals that the majority of Ru nanoparticles are accessible in the RuNPs@SWNT catalyst. [b] Supplied by Alfa Aesar. [c] This assumes that the surface of the Ru nanoparticles is a 1:1 mix of 001 and 100 crystallographic planes.[3] [d] Calculated at 50 % conversion of cyclooctene at 50 °C at 0.03 ml/min of reactants. [e] Calculated at 31 % conversion of cyclooctene at 50 °C at 0.3 ml/min of reactants.

6. Cyclohexene hydrogenation

The hydrogenation of cyclohexene was performed with the freshly synthesised RuNPs@SWNT catalyst, Figure S3. The catalyst efficiently converted cyclohexene to cyclohexane in yields up to 75% at temperatures above 125 °C and showed good stability towards cycling of the reaction temperature. The high initial activity observed is most likely due to small amounts of material deposited on the external surfaces of the nanotubes, it is proposed that this materially aggregates to form large Ru particles which adhere less strongly to the convex surface of the nanotube and are washed from the support during the first temperature ramp resulting in consistent activity over the remaining temperature cycles.

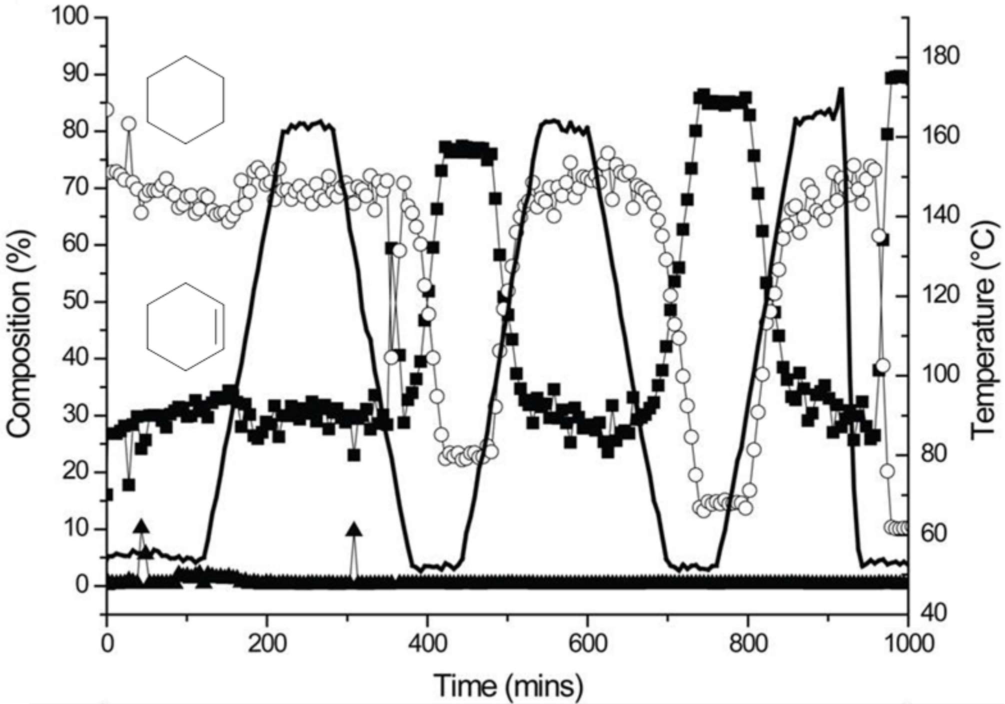

Figure S4. Reaction kinetics showing the catalytic activity of RuNPs@SWNT for the reduction of (a) cyclohexene (■) to cyclohexane (○) and other (▲) products. The temperature is shown as a solid line.

References

1 J. G. Stevens, R. A. Bourne and M. Poliakoff, *Green Chemistry*, 2009, **11**, 409-416.

2 T. W. Chamberlain, T. Zoberbier, J. Biskupek, A. Botos, U. Kaiser and A. N. Khlobystov, *Chem. Sci.*, 2012, **3**, 1919-1924.

3 R. A. D. Betta, *Journal of Catalysis*, 1974, **34**, 57-60.

4 Supplied by Helix Material Solutions, Inc. US.