ARTICLE TYPE

Catalytic Nanoreactors in Continuous Flow: Hydrogenation inside Single-walled Carbon Nanotubes using Supercritical CO$_2$

Thomas W. Chamberlain,[*a] **James H. Earley,**[a] **Daniel P. Anderson,**[a] **Andrei N. Khlobystov**[a,b] **and Richard A. Bourne**[*c]

One nanometre wide carbon nanoreactors are utilised as the reaction vessel for catalytic chemical reactions on a preparative scale. Sub-nanometre ruthenium catalytic 10 **particles which are encapsulated solely within single-walled carbon nanotubes offering a unique reaction environment are shown to be active when embedded in a supercritical CO$_2$ continuous flow reactor. A range of hydrogenation reactions were tested and the catalyst displayed excellent stability over** 15 **extended reaction times.**

Nanoparticles of transition metals (MNPs) have been demonstrated to be excellent candidates for catalysis due to their remarkable chemical and physical properties.[1] As nanoparticles are intrinsically thermodynamically metastable the stabilisation of 20 MNPs is vitally important to prevent leaching and sintering of the metal during catalysis. Immobilising the active nanoparticles on solid supports such as alumina,[2] silica,[3] zeolites,[4] amorphous carbon[5] and graphene[6,7] and utilising the resultant materials as heterogeneous catalysts is an effective method to tackle these 25 problems. Recently, carbon nanoreactors in which MNPs are located on the inside and/or the outside of multi-walled carbon nanotubes (MWNTs) have been proposed as catalyst support materials.[8-12] The cylindrical shape and high chemical and thermal stabilities of carbon nanotubes make them ideal catalyst 30 supports and nanoreactors, stabilising the metal nanoparticles and providing a unique local environment leading to new products.[8] One significant challenge facing the development of carbon nanoreactors is the scaling down of the nanoreactor channel by one or two orders of magnitude, from 10-100 nm in the case of 35 MWNT, to a size closer to that of the reactant molecules. This decrease in reactor size to generate a more extremely confined reaction environment is predicted to enhance the effect that the carbon nanoreactor sidewalls have on chemical reaction pathways. Additionally such extreme confinement should 40 improve the stability of the catalyst: a narrower nanoreactor should prevent sintering and leaching further, thus improving the reactivity and recyclability of the catalytic MNPs.

Single-walled carbon nanotubes (SWNTs) have been proposed as the ideal nanoreactor, possessing a diameter of 1-2 nm which is 45 commensurate in size to typical organic reactants.[8] The diameter of SWNTs (crystallographic diameter 1.5 nm and van der Waals
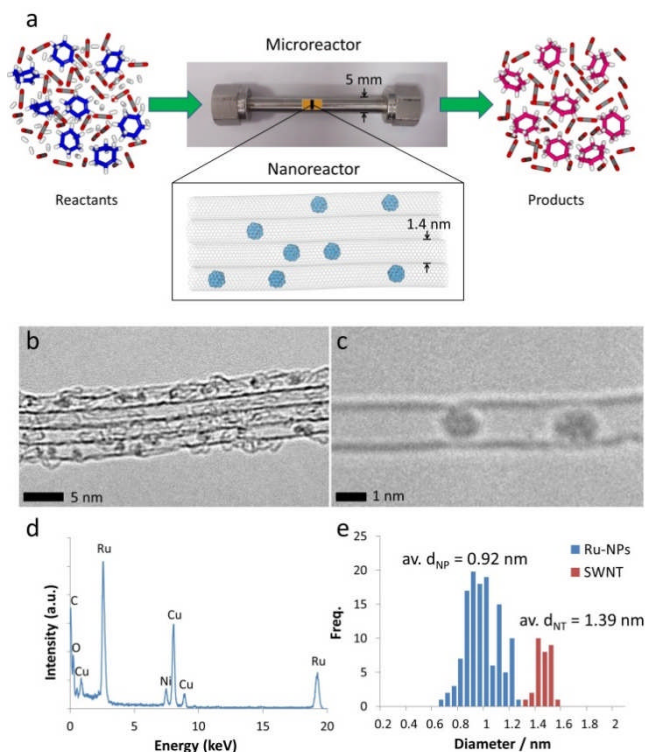

Fig. 1. a) Schematic diagram of the hydrogenation of cyclohexene (blue) to cyclohexane (pink) using bundles of RuNPs@SWNT catalytic 50 nanoreactors (shown in the expanded box) in a continuous flow scCO$_2$ milliscale reactor. TEM images of b) a bundle of RuNPs@SWNTs and c) an individual RuNPs@SWNT both showing that the Ru metal is located solely within the internal nanotube cavities. d) EDX spectroscopy confirms the presence of Ru metal in the nanotubes (Cu and Ni peaks are 55 due to the specimen holder and metal catalyst used for nanotube fabrication respectively). e) RuNP and SWNT diameters were measured by TEM.

internal diameter ~ 1nm) is large enough that typical reactant molecules (van der Waals diameter ~0.4-0.8 nm) can fit inside 60 the nanotube but narrow enough that they will be influenced by the proximity of the nanotube sidewalls (see ESI file). However significant practical transport issues exist in accessing such narrow nanotube channels which have prevented SWNTs from being utilised in catalytic reactions to date.

In this Communication, we introduced the Ru metal into the carbon nanotubes in the gas phase using a volatile $Ru_3(CO)_{12}$ precursor following the procedure described to produce W, Re and OsNPs inside SWNTs.[13] Thermal treatment leads to the decomposition of the ruthenium carbonyl to generate NPs whose size are controlled by the nanotube diameter. CO gas generated by carbonyl decomposition inside the SWNT prevents the metal NPs sintering to form rods. When formed the naked RuNPs are stabilised by adhesion to the internal nanotube sidewall and the CO gas is vented from the nanotube leaving the internal channel ready to accommodate reactant molecules. TEM shows very small RuNPs with a narrow diameter distribution ($d_{NP} = 0.92 \pm 0.13$ nm). The internal channel of the SWNT acts as a template to nanoparticle formation enabling precise control of the NP size. As the NP size is closely linked to the catalytic activity,[14] varying the diameter of the SWNT to template NPs of different sizes could be utilized to modulate the catalytic properties of the NPs.

The RuNPs@SWNT catalyst was immobilised in a high pressure milliscale reactor packed with a mixture of the catalyst and sand (Fig.1a). Reaction performed over the reaction bed using a gaseous mixture of cycloalkene and H_2 led to negligible (<5%) conversion.. This is in contrast to previous work reported for MWNT based nanoreactor catalysts reporting high yields for a wide variety of gas phase reactions.[8] The reduced conversion in SWNT is most likely as a result of mass transfer limitations due to the much narrower diameter of SWNTs ($d_{NT} = 1.39 \pm 0.05$ nm). However the conversion of reactions using RuNPs@SWNT increased significantly when supercritical carbon dioxide (scCO$_2$) was added as a reaction solvent. This is most likely due to the negligible surface tension and low viscosity of scCO$_2$ enabling it to deliver molecules into very narrow nanotubes.[15] In addition, scCO$_2$ is a highly effective medium for hydrogenation as H_2 is fully miscible with scCO$_2$.[16-18] It has also be shown to be a suitable solvent for non-polar organic molecules being utilized in a number of continuous flow reactions over a variety of heterogeneous supported metal catalysts.[19,20]

For example, the catalyst efficiently converted cyclooctene to cyclooctane in yields up to 80% at temperatures above 160 °C despite low amounts of available catalyst (1 mg of Ru metal in 20 mg of Ru@SWNT) relative to the flow rate of organic substrate (0.03 mL/min), Fig. 2a. For the hydrogenation of cyclooctene the temperature of the fixed catalyst bed was cycled and showed good stability over a series of temperature cycles at constant flow rates for a number of hours (Fig. 2a). Following this process the catalyst bed was held at fixed temperature of 110 °C for 11 hours for the hydrogenation of cyclooctene with no loss in activity observed. TEM of the RuNPs@SWNT catalyst after 24 h of reaction revealed that the structure remained unaltered confirming the stability of the catalyst (ESI file). Unconfined RuNPs would be unstable under these conditions and undergo fast coalescence and Ostwald ripening drastically reducing their activity.

The extreme confinement imposed by the narrow nanotubes efficiently stabilises the nanoparticle catalyst and also provides a unique reaction environment. Interestingly, the activity of the confined catalyst is reduced as compared that of the traditionally used Ru/C catalyst due to the spatial restriction in SWNT

nanoreactor: the turnover frequency (TOF, number of product molecules formed per active Ru atom, see ESI file for details) of the RuNPs@SWNT and Ru/C (20 mg of the commercially available catalyst, 5% by wt. Ru) catalysts for the hydrogenation of cyclooctene at 50 °C were measured to be 32 min^{-1} and 103 min^{-1} respectively. The reduction in catalyst activity in nanoreactors is less severe than expected under the conditions of extreme spatial confinement in RuNPs@SWNT due to the fact that scCO$_2$ is an ideal solvent able to access the catalyst in SWNT narrow channel.
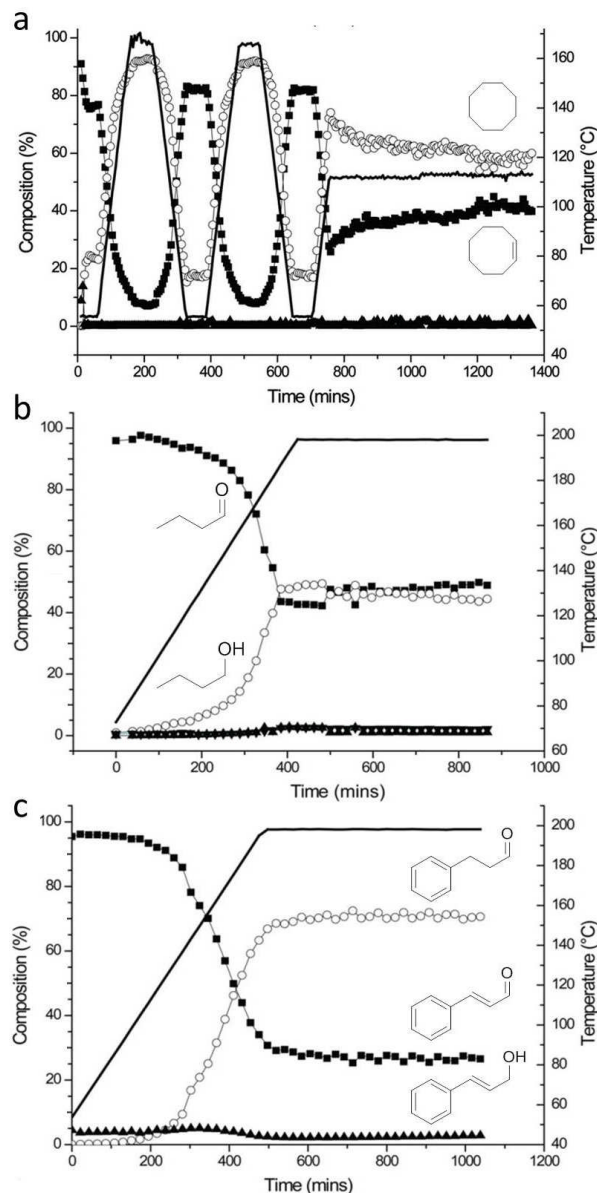

Fig. 2. Reaction kinetics for the reduction of (a) cyclooctene (■) to cyclooctane (○) and other products (▲), (b) butryaldehyde (■) to butanol (○) and small amounts of other products (▲) and then changing the feedstock solution for the reduction of (c) cinnamaldehyde (■) to hydrocinnamaldehyde (○) and cinnamyl alcohol (▲). The reactor internal temperature is shown as the solid line in all plots. Flow rates were as follows; 1mL/min CO$_2$, 0.03mL/min organic substrate, 0.06mL/min H$_2$ under 100bar pressure.

In addition to olefins, the catalyst also exhibited good activity towards carbonyl hydrogenation, RuNPs@SWNT successfully reduced butyraldehyde to butanol (ca. 50% conversion at 200 ºC, see Fig. 2b). It was also possible to selectively reduce cinnamaldehyde to hydrocinnamaldehyde (ca. 70% conversion, >99% selectivity, Fig. 2c). Interestingly at 60 ºC, the major product was cinnamyl alcohol, but at relatively low conversion (<6%). In the case of cinnamaldehyde no doubly reduced products were observed (i.e. phenylpropanol). In both cases the reduction proceeded smoothly with negligible reduction in yields when held at the upper reduction temperature of 200 °C.
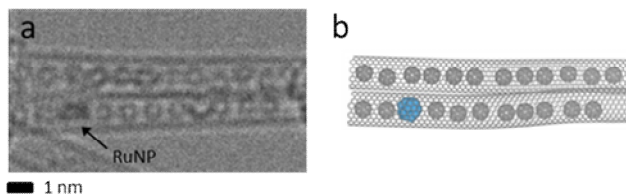

Fig. 3. a) TEM image of two nanotubes of the RuNPs@SWNT catalyst after exposure to C_{60}. b) Structural diagram showing the positions of the C_{60} molecules (grey) and the RuNP (blue) inside the carbon nanotubes.

To illustrate that the size and shape of the RuNPs themselves do not impede reactants from being able to reach a portion of the RuNPs within these structures and to confirm that hydrogenation takes place solely inside the nanoreactors, the RuNPs@SWNT catalyst was exposed to gaseous C_{60}. TEM was subsequently utilised to confirm the encapsulation of the fullerene molecules and the extent to which they could penetrate the internal channels of the catalyst (Fig. 3). As the 1 nm sized C_{60} spheres fit snuggly into the nanotube channel they prevent access of any substrate molecules to the internal RuNPs. In a control experiment the resultant (C_{60} + RuNPs)@SWNT material was used in a test hydrogenation reaction of cyclooctene and showed no activity confirming that the catalysis occurs solely via RuNPs located inside the nanotubes. The fact that the C_{60} molecules can penetrate through to RuNPs within the nanotube (Fig. 3a) visually demonstrates the accessibility of the metal centres in RuNPs@SWNT to organic reactants during preparative hydrogenation in a flow of scCO2.

Conclusions

We have successfully combined the concept of carbon nanotube nanoreactors with supercritical continuous flow technology, which demonstrate the potential for the utilisation of fixed bed carbon nanoreactors. This is the first example of catalysis within SWNT, which not only provide precise control of catalyst size but also preventing sintering of the RuNPs leading to enhanced stability. Due to the extreme spatial confinement the RuNP@SWNT catalyst showed a lower TOF for the reduction of cyclic alkenes in comparison to a Ru/C catalyst, but no drop in activity or change in structure of the RuNPs observed over 24 hours at 110 °C. The development of a methodology to utilise nanoreactors of dimensions commensurate with molecular reactants and products provides the potential for the formation of new species which are impossible to form without this unique reaction environment. Future work will also investigate the optimal nanotube length in order to maximise catalyst turnover frequency.

Notes and references

ᵃ School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK.. Fax: +44 (0)115 9513563; Tel: +44 (0)115 9513234; E-mail: thomas.chamberlain@nottingham.ac.uk
ᵇ Nottingham Nanotechnology and Nanoscience Centre, University of Nottingham, University Park, Nottingham, NG7 2RD, UK Fax: +44 (0)115 9513563; Tel: +44 (0)115 9513917; E-mail: andrei.khlobystov@nottingham.ac.uk
ᶜ Institute for Process Research and Development, School of Process, Environmental & Materials Engineering, University of Leeds, Leeds, LS2 9JT, UK Fax: +44 (0)113 3436565; Tel: +44 (0)113 3430109; E-mail: R.A.Bourne@Leeds.ac.uk

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