

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Nano Ru catalysts supported on carbon nanotubes for cellobiose conversion to sugar alcohols: Effects of CNT channel size

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Maofei Ran^{a,b,c}, Wei Chu^{b*}, Yan Liu^{c*}, Armando Borgna^c

Ruthenium (Ru) nanoparticles (NPs) were supported on the interior surface of carbon nanotubes (CNTs) with different inner diameter to study effects of CNT channel size on the cellobiose conversion. It was found that the reducibility and catalytic activity of Ru/CNT-in sample was enhanced with the decrease of carbon channel size and Ru/CNTs-in catalysts showed significantly higher catalytic activities than that of Ru/CNTs-out sample. The confinement effect of CNT channel was gradually enhanced with the decrease of the nanotube channel size (inner diameter). The encapsulation of Ru NPs inside the CNT channels improved the Ru reducibility and decreased the leaching of catalytic sites.

1. Introduction

The catalytic routes to fine chemicals and fuels from renewable biomass resources have attracted considerable attention over the last few years [1-3]. The efficient utilization of biomass has great potential for reducing greenhouse gas emissions. Attentions have been paid to the conversion of cellulose selectively to fuels and useful chemicals due to cellulose is the major component of plant biomass [4-6]. However, as cellulose possess robust crystalline structure composed of β -1,4-glycosidic bonds of D-glucose, it is difficult to be directly utilized under mild conditions [4]. The structure of cellobiose is close to that of the soluble oligosaccharide released in hydrothermal or acidic treatments of cellulose. Therefore, studies on catalytic conversion of cellobiose are important for the basic understanding of catalyst requirements for the efficient utilization of cellulose [7-9].

Supported ruthenium (Ru) catalysts are well known as efficient catalysts for a wide range of hydrogenation reactions [10], including the hydrogenation of cellobiose [9-12]. The catalytic support plays an important role in many reaction processes, determining the catalyst structure and catalytic performance [13-15]. Chen et al [12] reported that Ru supported on metal-organic frameworks (MOFs) exhibits excellent catalytic performance on conversion of cellobiose. This was resulted from the higher Ru dispersion, better hydrogenation capacity and higher acid site density of MOF. Carbon nanotubes (CNTs) have been used as good catalyst support for

a large number of catalytic reactions due to their unique properties [16-21]. Recently, the active phases were reported to be selectively loaded on the interior or exterior surface using supercritical CO₂, ultrasonication-assisted impregnation, and other methods [10,12]. Theoretical studies reveal that the deviation of CNT graphene layers from planarity causes p-electron density to shift from the concave inner surface to the convex outer surface, leading to an electron-deficient interior surface and an electron-enriched exterior surface [22-25]. This may bring forth an unexpected and interesting performance in catalytic reactions. Bao et al. reported that the negligible activity in ammonia synthesis over Ru catalyst supported on CNTs interior surface results from the lower electron densities of CNT interior surface [25]. In our early study, Ru catalyst supported on CNTs inner surface showed a better catalytic performance on conversion of biomass [26].

In this work, the effects of CNT channel sizes of Ru/CNT catalysts on the conversion of cellobiose have been investigated. The catalytic activity, redox ability and structure of catalysts with Ru nanoparticles dispersed on the interior surface with different inner diameters CNTs (Ru/CNTs-in-x) are compared to those dispersed on the exterior CNT surface (Ru/CNTs-out). It was found that Ru/CNTs-in catalysts showed significantly higher catalytic activities than those of Ru/CNTs-out for the conversion of cellobiose to sugar alcohols. Furthermore, the catalytic activity of Ru/CNT-in catalysts increased with the decrease of carbon channel sizes, indicating that the confinement effect, which benefits the high catalytic performance, decreases as the CNT diameter is increased

2. Experimental section

2.1. Catalyst Preparation.

The CNTs with inner diameters of 3-6 nm, 4-9 nm and 6-13 nm were prepared by a method reported previously [27], which

a College of Chemistry & Environment Protection Engineering, Southwest University for Nationalities, Chengdu, Sichuan 610041, People's Republic of China.

b College of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China.

c Institute of Chemical and Engineering Sciences (ICES), A*STAR, 627833, Singapore.

* Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available See DOI: 10.1039/x0xx00000x

were named as CNTs-6, CNTs-8 and CNTs-12. 1.5 g raw CNTs samples were refluxed in 150 ml concentrated HNO_3 for 14 h at 140 °C in an oil bath, which led to the opened and shortened nanotubes. The mixture was then filtered and washed with deionized water, followed by drying for 12 h at 60 °C. Such CNTs with opened end-caps (CNTs-in) was used to prepare Ru/CNTs-in catalyst. 41 mg RuCl_3 dissolved in 20 ml acetone used as the precursor salts of Ru. Then, 980 mg CNTs-in was immersed into the acetic solution to prepare Ru/CNTs-in catalysts. The catalyst was obtained by introduction of RuCl_3 acetic solution into CNT channels utilizing the capillary forces of CNTs assisted by ultrasonication for 3 h and stirring overnight. Subsequently, the mixture was evacuated in a rotary evaporator at 40 °C. Lastly, the catalyst was held in oven for 12 h at 110 °C, denoted as Ru/CNTs-in-6, Ru/CNTs-in-9 and Ru/CNTs-in-12 separately. The nanotubes with closed end-caps (CNTs-out) were obtained by refluxing raw CNTs in 5 M nitric acid at 110 °C for 5 h. This treatment removed amorphous carbon and other impurities while keeping the nanotube caps intact. Ru/CNTs-out-6 catalyst was prepared using the same impregnation procedure on the CNTs-out with inner diameters of 3-6 nm. The loadings of Ru in Ru/CNTs-in and Ru/CNTs-out catalysts were both 2.0 wt%.

2.2. Catalyst Characterization.

Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2000 FX microscope at 200 kV. The samples were ultrasonically dispersed in ethanol and placed onto a carbon film supported on a copper grid. The metal particle size distributions were obtained by measuring 200 particles randomly taken from TEM images over a wide area of the specimen. The reducibility of catalyst was studied by temperature-programmed reduction in H_2 (H_2 -TPR). H_2 -TPR was performed on a Thermo TPD/R/O 1100 catalysts analyzer instrument. Typically, 50 mg of catalyst sample loaded in a quartz reactor was pretreated in Ar gas for 2 h at 200 °C, and then H_2 -TPR was performed in a 5% H_2/He flow by heating the sample up to 850 °C at a rate of 10 °C/min.

2.3. Catalytic reaction tests.

The Ru/CNT catalysts were activated by reduction in a pure H_2 stream at 450 °C for 4 h before reaction. The reaction condition was carried out from literature [26]. The conversion of cellobiose was performed with a batch-type high-pressure autoclave reactor. Typically, the reduced catalyst (50 mg) and cellobiose (171 mg) were added into a Teflon-lined stainless steel reactor (100 ml) pre-charged with H_2O (20 ml), and then the autoclave was heated at 185 °C for 3 h after pressurization with H_2 to 5 MPa at RT. After the reaction, the solid catalyst was separated by centrifugation, and the liquid products were analyzed by a HPLC (Agilent, RI detector, Aminex HPX-87H column (10 μm , 7.8 \times 300 mm), mobile phase: 12 mmol H_2SO_4 aqueous solution). The conversion of cellobiose was calculated as follows: conversion (%) = (initial mol of $\text{C}_6\text{H}_{10}\text{O}_5$ unit in cellobiose - mol of $\text{C}_6\text{H}_{10}\text{O}_5$ unit in cellobiose after reaction) /

(initial mol of $\text{C}_6\text{H}_{10}\text{O}_5$ unit in cellobiose) \times 100. The yield of sugar alcohols was calculated as follows: yield (%) = (mol of sorbitol and mannitol in products) / (initial mol of $\text{C}_6\text{H}_{10}\text{O}_5$ unit in cellobiose) \times 100.

3. Results and discussion

3.1 Morphology of the CNT and Ru/CNT samples

TEM micrographs of the synthesized CNTs with different inner diameters are shown in Fig. 1. The inner diameter distributions were obtained by measuring 200 nanotubes randomly taken from TEM images over a wide range of the specimen. It can be seen from images that the samples CNTs-6, CNTs-8 and CNTs-12 shows high purity, uniform nanotubes, indicating the CNT samples with high aspect ratios [28]. Their inner diameters vary between 3-6 nm, 4-9 nm and 6-13 nm, respectively.

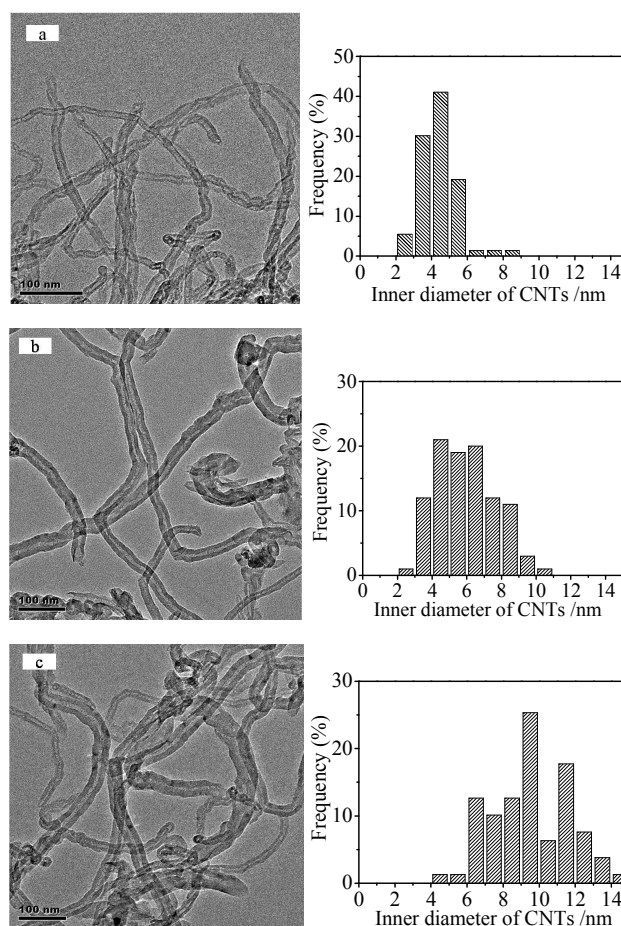


Fig. 1 TEM images of CNT samples with different inner diameters. a: CNTs-6, b: CNTs-8, c: CNTs-12

The morphologies of Ru nanoparticles in the reduced Ru/CNT catalysts were displayed in TEM images (Fig. 2). The dark spots represented Ru metal particles are well dispersed on the interior or exterior surface of nanotubes. As displayed in the

Fig. 2a, 2b and 2c, most of Ru particles are located inside the tubes of Ru/CNTs-in-6, Ru/CNTs-in-8 and Ru/CNTs-in-12, which is attributed to the tubular morphology of opened end-cap carbon nanotubes prepared by concentrated nitric acid treatment. The capillary forces were induced during the impregnation process [29]. The Ru particles have almost the same distributions from 2-4 nm, indicating that the CNT channel diameter is not a crucial factor for the Ru particle sizes. Ru particles of Ru/CNTs-out-6 are homogeneously dispersed on the exterior surface of nanotubes (Fig. 2d) due to RuCl₃ solution can only contact with the outside surface of nanotubes with the closed end-caps.

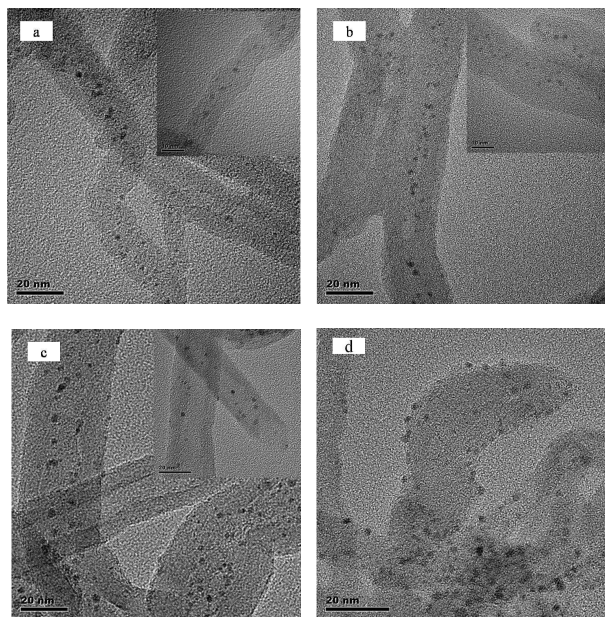


Fig. 2 TEM images of Ru based catalysts supported inside the CNTs with different inner diameters, a: Ru/CNTs-in-6, b: Ru/CNTs-in-8, c: Ru/CNTs-in-12, and outside the CNT. d: Ru/CNTs-out-6

3.2 Reducibility of the Ru/CNT catalysts

The reducibility of Ru/CNT catalysts was analysed by TPR, as shown in Fig. 3. It can be seen that the blank CNTs yield almost no H₂ consumption below 350 °C. An intense H₂ consumption peak appears at the temperature range of 150-300 °C for all the Ru/CNTs catalysts. The peak can be attributed to the reduction of Ru³⁺ to Ru⁰ species [25, 30, 31]. It is noteworthy that the reduction temperatures of Ru/CNTs-in catalysts increased with the carbon channel sizes, i.e. the reduction peaks of Ru/CNTs-in-6, Ru/CNTs-in-8 and Ru/CNTs-in-12 showed at 195 °C, 215 °C and 221 °C, respectively. The reduction temperatures of Ru species in Ru/CNTs-in are lower than that of Ru/CNTs-out i.e. 230 °C, in well agreement with those reported in literatures [25, 29, 32]. The interior surface of CNTs is electron-deficient while the exterior surface is electron-enriched. This electron density loss can be partially compensated through the interaction with the encapsulated metals [28], which would destabilize metal nanoparticles and facilitate the reduction. However, the confinement effect of CNT channels was gradually weakened with the increase of nanotube diameters, resulting from a decrease of

interactions between the encapsulated metal and CNT surface. It could be the reason behind the change of reduction temperatures.

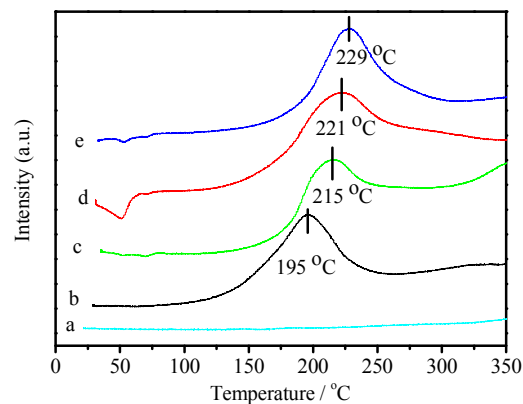


Fig. 3 TPR patterns of Ru based catalyst supported inside the CNTs with different inner diameters. a: blank CNTs, b: Ru/CNTs-in-6, c: Ru/CNTs-in-8, d: Ru/CNTs-in-12, e: Ru/CNTs-out-6

3.3 Catalytic Performances of Ru/CNT Catalysts in Conversion of Cellobiose

The catalytic performance of Ru supported on CNTs with different channel sizes were analysed in the conversion of cellobiose to sugar alcohols. The reaction scheme in the carbon-nanotube reactor with Ru active sites was proposed in Figure 4. In this hypothesis, cellobiose diffuses into the CNT channel and interacts with Ru active sites to produce sugar alcohols (sorbitol and monitol) [33].

As shown in Fig. 5, both yields to sugar alcohols and conversions of cellobiose for all the Ru/CNTs-in catalysts are significantly higher than that of Ru/CNTs-out catalyst, as reported in [34, 26]. The enhancement of catalytic activity of Ru/CNTs-in should be attributed to the confinement of Ru nanoparticles inside the CNTs to avoid leaching of activity sites and the lower electron densities of CNT interior surface. It is noteworthy that the activities decreased with the CNT channel diameters. The conversions of cellobiose for Ru/CNTs-in-6, Ru/CNTs-in-8, Ru/CNTs-in-12 are 57%, 49%, and 45% separately. That means the confinement effect of CNT channels was gradually weakened with the increase of nanotube diameters, as mentioned in the previous part, probably resulting from the decreases of interactions between the encapsulated metals and CNT surface and electron densities between CNT interior and exterior surfaces [25].

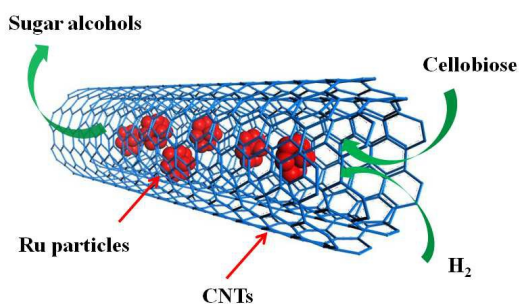


Fig. 4 Schematic diagram showing sugar alcohols production from cellobiose inside Ru-loaded carbon nanotubes.

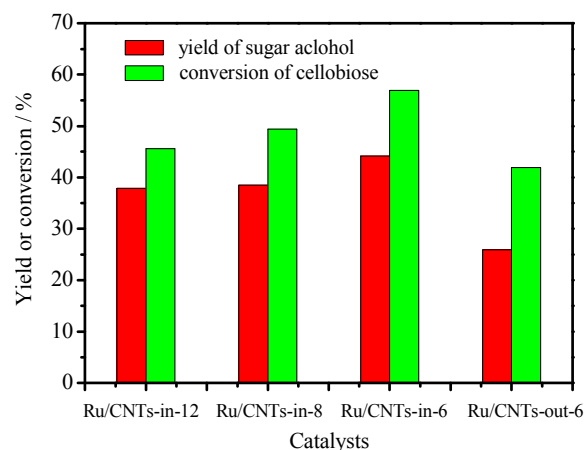


Fig. 5 Sugar alcohol yields in the conversion of cellobiose over different catalysts. Reaction conditions: cellobiose, 0.50 mmol; catalyst, 50 mg; H₂O, 20 ml; H₂, 5 MPa; temperature, 185 °C; time, 3 h.

3.4. Characterization of Ru/CNT catalysts after reaction

Dispersion and size range of Ru particles in Ru/CNT-in catalysts with different CNT diameters before and after reaction were determined by TEM. As shown in Fig. 6, 70% of the particles in Ru/CNTs-in-6 before reaction fall in the range of 1.5–3.5 nm (Fig. 6e), while those of Ru/CNTs-in-12 before reaction are in the range of 2–4 nm (Fig. 6f). The mean sizes of Ru particles in the Ru/CNTs-in-6 and Ru/CNTs-in-12 before reaction are almost same, as 2.2 nm and 2.4 nm respectively. This indicated that CNT diameters have little effects on Ru particle sizes confined in the CNT channel. After the reaction of cellobiose hydrogenation, the Ru particles in Ru/CNTs-in-6 and Ru/CNTs-in-12 (Fig. 6b and 6d) are still homogeneously dispersed on the interior surface of CNTs. More than 70% Ru particle sizes for both Ru/CNTs-in-6 and Ru/CNTs-in-12 (Fig. 6e and 6f) keep in the range of 2–4 nm, which display the similar distribution with those before the reaction. As shown in Fig. 6e and 6f, the mean diameters of Ru/CNTs-in-6 before and after reaction are 2.2 nm and 2.6 nm, while those of Ru/CNTs-in-12 are 2.4 nm and 2.7 nm respectively. The results indicated that Ru particles did not suffer severe agglomeration, which may be due to the spatial restriction of CNT channels, low reaction temperature and

the liquid phase reaction environment investigated, suggesting that it is not the particle size but the confinement which makes the difference on Ru reducibility and catalytic performance.

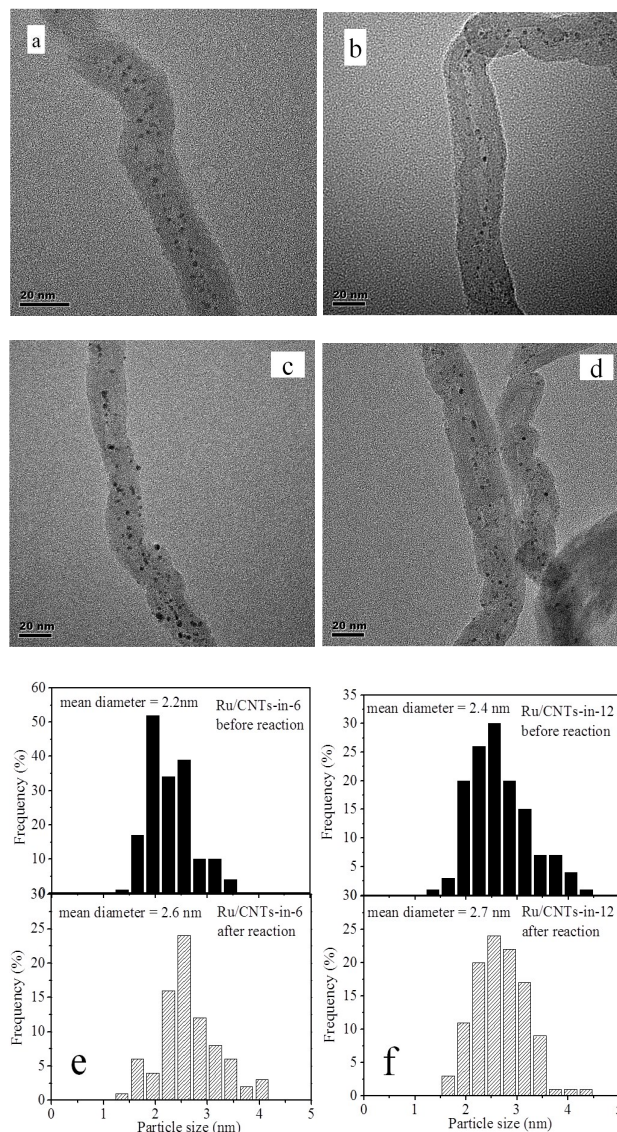


Fig. 6 TEM images and the Ru particle size distributions of the catalysts before and after reaction. (a), (b) and (e): Ru/CNTs-in-6; (c), (d) and (f): Ru/CNTs-in-12.

4. Conclusions

In summary, the investigation on effects of CNT channel sizes of Ru/CNT catalysts in conversion of cellobiose reaction shows that the reducibility of Ru and catalytic activity of Ru/CNT-in increased with the decrease of carbon channel sizes. All the Ru/CNTs-in catalysts showed significantly higher catalytic activities than that of Ru/CNTs-out. The confinement effect of CNT channel was gradually enhanced with the decrease of nanotube diameters, which

could be the reasons behind the catalytic performance of Ru/CNTs-in catalysts varied with CNT channel sizes.

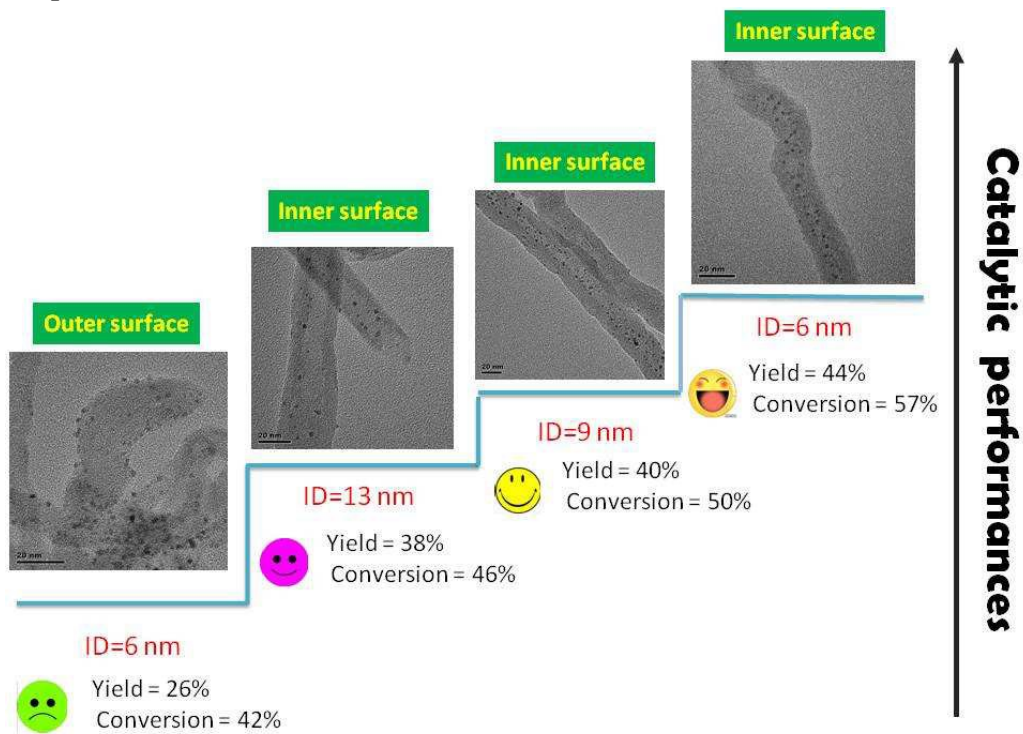
Acknowledgements

This work was supported by the National Natural Science Foundation of China (21506174), Supported by the Fund Project of Sichuan Provincial Department of Education (15ZB0481) and the Project of Postgraduate Degree Construction, Southwest University for Nationalities (2015XWD-S0703). Dr M Ran is grateful to the China Scholarship Council (CSC) for providing the Ph.D. scholarship and ICES (Singapore) for financial support. The authors thank Dr Wenjing Sun for her constant encouragements and helpful discussions

Notes and references

- [1] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, J. R. Liotta, R. Mielenz, R. Murphy, T. Templer, Tschaplinski, *Science*, 2006, 311: 484-489.
- [2] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.*, 2007, 107: 2411.
- [3] N.M. Mubarak, J.R. Wong, K.W. Tan, J.N. Sahu, E.C. Abdullah, N.S. Jayakumar, P. Ganesan, *J Mol Catal. B*, 2014, 107: 124-131.
- [4] V. S. Vande, J. Geboers, P.A. Jacobs, B.F. Sels, *ChemCatChem*, 2011, 3: 82-94.
- [5] A. Fukuoka, P. L. Dhepe, *Angew. Chem. Int. Ed.*, 2006, 45: 5161-5163.
- [6] G. D. Wen, Y. P. Xu, Z. S. Xu, Z. J. Tian, *Catal. Comm.*, 2010, 11:522-526.
- [7] K. Fleming, D. G. Gray, S. S. Matthew, *Chem. Eur. J.*, 2001, 7: 1831-1835.
- [8] Z. C. Gernhart, A. Bhalkikar, J. J. Burke, K. O. Sonnenfeld, C. M. Marin, R. Zbasnik, C. L. Cheung, *RSC Adv.*, 2015, 5: 28478-28486.
- [9] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.*, 2006, 106: 4044-4098.
- [10] T. W. Chamberlain, J. H. Earley, D. P. Anderson, A. N. Khlobystovab, R. A. Bourne, *Chem. Commun.*, 2014, 50, 5200-5202.
- [11] Y. F. Niu, H. Wang, X. L. Zhu, Z. Q. Song, X. N. Xie, X. Liu, J. Y. Han, Q. F. Ge, *Micropor. Mesopor. Mat.*, 2014, 198: 215-222.
- [12] J. Z. Chen, S. P. Wang, J. Huang, L. M. Chen, L. L. Ma, X. Huang, *ChemSusChem*, 2013, 6, 1545-1555.
- [13] Z. X. Xu, N. Wang, W. Chu, J. Deng, S.Z. Luo, *Catal. Sci. Technol.*, 2015, 5:1588-1597.
- [14] N. Wang, Z. Xu, J. Deng, K. Shen, X. Yu, W. Qian, W. Chu, F. Wei, *ChemCatChem*, 2014, 6, 1470-1480.
- [15] J. Deng, M. Cai, W. Sun, X. Liao, W. Chu, X. S. Zhao, *ChemSusChem*, 2013, 6, 2061-2065.
- [16] B. D. Li, C. Wang, G. Q. Yi, H. Q. Lin, Y. Z. Yuan, *Catal. Today*, 2011, 164, 74-79.
- [17] N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. Liu, Y. Kou, *J. Am. Chem. Soc.*, 2006, 128: 8714-8715.
- [18] W. P. Deng, X. S. Tan, W. H. Fang, Q. H. Zhang, Y. Wang, *Catal. Lett.*, 2009, 133: 167-174.
- [19] X. S. Tan, W. P. Deng, M. Liu, *Chem. Comm.*, 2009, 46: 7179-7181
- [20] S. K. Xu, P. Zhang, H. B. Li, H. J. Wei, L. M. Li, B. J. Li, X. Y. Wang, *RSC Adv.*, 2014, 4: 7079-7083.
- [21] C. T. Hsieh, J. L. Wei, J. Y. Lin, B. H. Yang, *Diam. Relat. Mater.*, 2011, 20: 1065-1071.
- [22] X. L. Pan, Z. L. Fan, W. Chen, Y. J. Ding, H. Y. Luo, X. H. Bao, *Nature Mater.*, 2007, 6: 507-511.
- [23] H. Zhang, W. Chu, C. J. Zou, Z. Y. Huang, Z. B. Ye, L. Zhu, *Catal. Lett.*, 2011, 141: 438-444.
- [24] J. M. Planeix, N. Coustel, B. Coq, V. Brotons, P. S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier, P. M. Ajayan, *J. Am. Chem. Soc.*, 1994, 116: 7935-7936.
- [25] S. J. Guo, X. L. Pan, H. L. Gao, Z. Q. Yang, J. J. Zhao, X. H. Bao, *Chem. A. Euro. J.*, 2010, 16: 5379-5384.
- [26] M. F. Ran, Y. Liu, W. Chu, A. Borgna, *Catal. Lett.*, 2013, 143:1139-1144.
- [27] M. F. Ran, Y. Liu, W. Chu, D. Liu, C Zhang, *J Ener. Chem.*, 2014, 23: 781-788.
- [28] X. L. Pan, X. H. Bao, *Chem. Comm.*, 2008, 47: 6271-6281.
- [29] W. Chen, X. L. Pan, X. H. Bao, *J. Am. Chem. Soc.*, 2007, 129: 7421-7426.
- [30] S. K. Xu, P. Zhang, H. B. Li, H. J. Wei, L. M. Li, B. J. Li, X. Y. Wang, *RSC Adv.*, 2014, 4: 7079 -7083.
- [31] W. Chu, J. Q. Xu, J. P. Hong, T. Lin, A. Khodakov, *Catal. Today*, 2015, 256: 41-48.
- [32] W. Chen, Z. L. Fan, X. L. Pan, X. H. Bao, *J. Am. Chem. Soc.*, 2008, 130: 9414-9419.
- [33] W. P. Deng, M. Liu, X. S. Tan, Q. H. Zhang, Y. Wang, *J. Catal.*, 2010, 271: 22-32.
- [34] R. M. M. Abbaslou, A. Tavassoli, J. Soltan, A. K. Dalai, *Appl. Catal. A.*, 2009, 367: 47-52.

Graphical abstract:



The catalytic activity of Ru/CNT-in sample was enhanced with the decrease of CNT inner diameter and it was much higher than that of Ru/CNTs-out.