Core–shell structured microcapsular-like $Ru@SiO_2$ reactor for efficient generation of CO_x -free hydrogen through ammonia decomposition[†]

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Received 17th March 2010, Accepted 19th May 2010 First published as an Advance Article on the web 14th June 2010 DOI: 10.1039/c0cc00430h

The core-shell structured microcapsular-like Ru@SiO₂ reactor is proved to be the most efficient material known to date for CO_x -free hydrogen production *via* ammonia decomposition for fuel cells application. The very active Ru core particles can retain good stability even at high temperatures (up to 650 °C) thanks to the protection of the inert SiO₂ nano-shell.

The processes such as steam reforming, partial oxidation, and autothermal reforming of methane are the conventional approaches to H₂ production. However, the level of residual CO is unacceptable for current proton-exchange membrane fuel cells (PEMFCs). In order to make use of the CO-containing H₂, one should eliminate residual CO by oxidation of CO in high hydrogen concentration, which adds substantial cost and complexity to obtain CO_x -free H₂. Choudhary *et al.*¹ also reported another way to generate CO-free hydrogen by the reversible cyclic stepwise steam reforming of methane. The catalytic decomposition of ammonia has attracted much attention because of the need of producing CO_{y} -free hydrogen for PEMFCs.² It is considered as an economical method, and NH₃ storage and delivery can be more readily handled.³ Many metals, alloys, and compounds with noble metal characters have been tested for this reaction.⁴ The invention of a carbonbased Ru catalyst that was commercialized in the mid-1990s can be considered as a breakthrough, but the details have not been disclosed.5

In the last decade, core-shell structured materials have attracted wide attention for their unique structural features and physicochemical properties.⁶ By having a nano-material encapsulated in a stable but porous shell, one can have the stability and compatibility of the material enhanced; in the mean time, there could be a change of electron charge, reactivity and functionality of the enwrapped materials.⁷ Nanoparticles (NPs) coated with silica have been studied in fields such as biology, optics, electronics, magnetism, sensing and catalysis.⁸ In this communication, we report the synthesis of core-shell structured Ru submicroparticles (SMPs) for ammonia decomposition. By employing ethylene glycol as the reducing agent in the preparation media,⁹ the metallic colloids can be directly obtained. Under the refluxing temperature the metallic colloids grow to the Ru^0 SMPs which are served as the Ru^0 cores in the core-shell structures. For the first time, it is found that the space developed between the core and the internal wall of the shell inside the microcapsular-like $Ru@SiO_2$ reactor has a critical effect on reactivity.

The Ru SMPs were synthesized through a solvent-thermal procedure. Typically, 2.0 g RuCl₃ was added to 100 ml ethylene glycol. After stirring the mixture for 1 h at 313 K, a homogeneous black-brown solution was formed. The solution was transferred to a three-neck flask and refluxed at 453 K for 3 h. The as-generated grey precipitate was collected by centrifugation and washed three times with distilled water and ethanol. Hereinafter, the solid powder dried at 313 K overnight in vacuum is denoted as Dried-SMPs, and the Dried-SMPs calcined in air at 773 K for 4 h as Calcined-SMPs.

The core–shell structures were prepared *via* a sonicationassisted Stöber process.¹⁰ Typically, Dried-SMPs of 0.95 g (or Calcined-SMPs of 1.17 g) were added to 100 ml absolute ethanol and the mixture was sonicated for 30 min in an ultrasound bath (KQ-100DE, 40 kHz, 100W). Then 20 ml NH₃·H₂O and 420 µl tetraethylorthosilicate (TEOS, 98%, the molar ratio of Si/Ru = 0.2) were added under sonication. After 1 h, the product was collected by centrifugation, washed twice with distilled water and ethanol, and dried at 313 K for 6 h. The samples so obtained are denoted as Dried-SMP@SiO₂ and Calcined-SMP@SiO₂, respectively. The catalysts subject to *in situ* reduction in a 25% H₂/Ar (v/v) flow at 823 K for 2 h are denoted as Dried-SMP-R@SiO₂ and Calcined-SMP-R@SiO₂.

 N_2 adsorption-desorption measurement was performed on an ASAP-2020 instrument at 77 K. XRD analysis was conducted on a Philips X'Pert MPD Pro X-ray diffractometer, with Cu-K α radiation ($\lambda = 0.1541$ nm) in the 2 θ range of 10-80°. Scanning electron microscopy (SEM) measurements were carried out on a S-4800 scanning microscope whereas TEM images were taken on JEOL JEM-1010/2010 transmission electron microscopes operated at 80 or 200 kV.

Catalytic testing was carried out in a continuous-flow quartz reactor (catalyst: 0.1 g, 60–80 mesh) under pure NH₃ (flow rate: 50 ml min⁻¹; GHSV_{NH3}: 30 000 ml/(h g_{cat})). Before the reaction, the catalyst was reduced *in situ* in a 25% H₂/Ar (v/v) flow at 823 K for 2 h before being exposed to a flow of pure ammonia. The reactivity was evaluated in the 623–923 K range, and acquisition of activity data was conducted after establishment of a steady state at a particular temperature. Product analysis was performed using an on-line gas

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 $[\]dagger$ Electronic supplementary information (ESI) available: N_2 adsorption–desorption data, $H_2\text{-}TPD$ and $H_2\text{-}TPR$ profiles. See DOI: 10.1039/ c0cc00430h

chromatograph (GC-122) equipped with a thermal conductivity detector and a Poropak Q column, using He as a carrier gas. NH_3 conversion in a blank reactor was found to be <1.0% at 823 K.

It was observed that the BET surface areas, pore volumes and pore size distribution of the two catalysts were similar (ESI[†]). The reaction was thought to be not diffusion limited, because the silica shells were thin (~ 50 nm) and rather porous.

The experimental procedures for the silica coating of Ru cores and the following in situ hydrogen reduction of core-shell structures are exactly identical for the two catalysts. Moreover, the catalytic reaction has been conducted over the core-shell structured Ru@SiO2 catalyst at 500-650 °C in a period of 60-80 h and there is no loss of catalytic activity observed. The porosity of the silica shell and the particle size of the Ru cores are essentially maintained even subject to high temperature process. According to our preparation strategy of core-shell structures, one can infer that in the case of Calcined-SMP@SiO₂ although there is structure expansion due to air-calcination of Ru⁰ to RuO₂ and structure contraction because of the following reduction of RuO_2 to Ru^0 , the Ru⁰ core particles are similar in size in the two catalysts. Most importantly, the measured metal surface areas of the two catalysts are identical on the basis of per unit mass of catalyst (ESI[†]), suggesting that the accessible active metal surfaces are precisely comparable.

From Fig. 1, one can see that the dried SMPs are essentially in the form of metallic Ru (JCPDS No. 01-1253), while the calcined ones are a mixture of Ru and RuO₂ (JCPDS No. 21-1172). After reduction, both Dried-SMP-R@SiO₂ and Calcined-SMP-R@SiO₂ show identical patterns of metallic Ru, having crystallinity higher than that of Dried-SMP@SiO₂. No silica signal was observed over the samples, indicating that the SiO₂ shells are amorphous.

The SEM images of Dried-SMPs show the Ru particles are spherical in shape and 100–300 nm in size (Fig. 2). The SEM image of higher magnification indicates that the SMPs are made up of smaller Ru NPs (10–20 nm).

Shown in Fig. 3 are the TEM images of the samples of Fig. 1. It is found that for Dried-SMP@SiO₂ (A) and Calcined-SMP@SiO₂ (B) the core and shell are in close contact. As for



Fig. 2 SEM images of Dried SMPs.

Dried-SMP-R@SiO₂ (A-R), still there is no void between SiO₂ and Ru. However, the TEM image of Calcined-SMP-R@SiO₂ (B-R) shows that there is space developed between the core and the internal wall of the shell. Of the four samples, the cores are enclosed in uniform SiO₂ shells of 30–50 nm thickness. The presence of stable silica shells can also effectively prevent the Ru cores from aggregation; as a consequence, the Ru⁰ particle size can be essentially retained.

Fig. 4 shows the temperature dependence of NH_3 conversion over the Dried-SMP-R@SiO₂ and Calcined-SMP-R@SiO₂ catalysts. The results show that Calcined-SMP-R@SiO₂ is significantly more active than Dried-SMP-R@SiO₂. Over the former, 100% NH_3 conversion is achieved at 823 K while NH_3 conversion is only 78.8% at 823 K over the latter. The observation suggests that the pre-calcination of the unwrapped cores has a critical effect on catalyst activity.

In situ measurement of the metal surface exposure of Ru cores has been performed by means of *in situ* H₂ reduction followed by H₂-TPD. The measured H₂-TPD peak areas of Calcined-SMP-R@SiO₂ and Dried-SMP-R@SiO₂ are proved to be identical, suggesting that the metal surface area of the two catalysts is the same. The desorption profiles of the two catalysts also matched quite well in the range of 50-350 °C, indicating that the pre-calcination had a slight impact on the nature of the Ru cores. This experimental evidence suggests that neither the metal surface area nor the chemical nature of the Ru cores can be notably modified by the oxidation/reduction pre-treatments. Based on the characterization results of (HR)TEM and H₂-TPD, one can conclude that the difference in catalytic activity is mainly due to the variation in catalyst



Fig. 1 XRD patterns of (A): Dried-SMP@SiO₂; (A-R): Dried-SMP-R@SiO₂; (B): Calcined-SMP@SiO₂, and (B-R): Calcined-SMP-R@SiO₂.



Fig. 3 TEM images of (A): Dried-SMP@SiO₂; (A-R): Dried-SMP-R@SiO₂; (B): Calcined-SMP@SiO₂, and (B-R): Calcined-SMP-R@SiO₂.



Fig. 4 Temperature dependence of ammonia conversion over the Dried-SMP-R@SiO₂ and Calcined-SMP-R@SiO₂ catalysts.

structures and particularly in the local reaction environment around Ru cores.

According to the XRD result (Fig. 1) and TPR profiles (ESI[†]), the core of Dried-SMP@SiO₂ is originally Ru⁰, and there is little shrinkage of core volume during H₂ reduction because there is no removal of lattice oxygen. As a result, little space is created between the core and the shell. On the other hand, the core of Calcined-SMPs is the mixture of Ru and RuO₂, and the RuO₂ core component can be completely transformed into metallic particles. In view of the (HR)TEM images of the Dried-SMP@SiO₂ and Calcined-SMP@SiO₂, one can find that the shell layers and core particles are closely contacted. Owing to the removal of lattice oxygen of the RuO₂ core, there is core shrinkage and hence the space between the core and shell, resulting in "microcapsular-like" structures (Fig. 2, B-R).

The unique environment around the Ru cores can function as a microcapsular-like reactor¹¹ in which the reactant molecules are enriched (confinement effect). A similar phenomenon has been reported recently over the carbon nanotube encapsulated Fe nanoparticles.¹² The consequence is enhanced adsorption and catalytic reaction on the core surfaces (Scheme 1). In other words, despite there being a decline in exposure of surface metal atoms (per unit mass of catalyst), the core–shell catalysts are catalytically more active than the naked metal NPs or conventional supported ones.

We acknowledge the financial support of the RGC, HKSAR (RGC 200107).



Scheme 1 Illustration of enhanced adsorption and reaction in a microcapsular-like reactor: (A-R) Dried-SMP-R@SiO₂; (B-R) Calcined-SMP-R@SiO₂.

Notes and references

- (a) T. V. Choudhary and D. W. Goodman, J. Catal., 2000, 192, 316; (b) T. V. Choudhary and D. W. Goodman, Catal. Lett., 1999, 93, 59.
- 2 (a) D. G. Loffler and L. D. Schmidt, J. Catal., 1976, 44, 244;
 (b) W. Arabczyk and J. Zamlynny, Catal. Lett., 1999, 60, 167;
 (c) J. L. Chen, Z. H. Zhu, Q. Ma, L. Li, V. Rudolph and G. Q. Lu, Catal. Today, 2009, 148, 97; (d) R. O. Idem and N. N. Bakhshi, Ind. Eng. Chem. Res., 1994, 33, 2047; (e) J. Zhang, M. Comotti, F. Schtüh, R. Schlögla and D. S. Su, Chem. Commun., 2007, 1916;
 (f) T. V. Choudhary, C. Sivadinaray and D. W. Goodman, Catal. Lett., 2001, 72, 197; (g) S. S. Pansare, W. Torres and J. G. Goodwin, Jr., Catal. Commun., 2007, 8, 649;
 (h) S. S. Pansare and J. G. Goodwin, Jr., Ind. Eng. Chem. Res., 2008, 47, 4063.
- 3 (a) R. Metkemeijer and P. Achard, *Int. J. Hydrogen Energy*, 1994, 19, 535; (b) R. Metkemeijer and P. Achard, *J. Power Sources*, 1994, 49, 271.
- 4 (a) W. Rarog, Z. Kowalczyk, J. Sentek, D. Skladanowski, D. Szmigiel and J. Zielinski, Appl. Catal., A, 2001, 208, 213;
 (b) M. E. E. Abashar, Y. S. Al-Sughair and I. S. Al-Mutaz, Appl. Catal. A, 2001, 236, 35; (c) X. K. Li, W. J. Ji, J. Zhao, S. J. Wang and C. T. Au, J. Catal., 2005, 236, 181; (d) M. C. J. Bradford, P. E. Fanning and M. A. Vannice, J. Catal., 1997, 172, 479;
 (e) G. Papapolymerou and V. Bontozoglou, J. Mol. Catal. A: Chem., 1997, 120, 165; (f) S. F. Yin, Q. H. Zhang, B. Q. Xu, W. X. Zhu, C. F. Ng and C. T. Au, J. Catal., 2004, 224, 384;
 (g) S. F. Yin, B. Q. Xu, W. X. Zhu, C. F. Ng, X. P. Zhou and C. T. Au, Catal. Today, 2004, 93–95, 27.
- 5 J. J. McCarroll, S. R. Tennison and N. P. Wilkinson, US Pat., 4 600 571, 1986.
- 6 (a) M. Danek, K. F. Jensen, C. B. Murray and M. G. Bawendi, *Chem. Mater.*, 1996, **8**, 173; (b) X. Peng, M. C. Schlamp, A. V. Kadavanich and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1997, **119**, 7019; (c) V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord and J. Nogues, *Nature*, 2003, **423**, 850; (d) Y. H. Deng, D. W. Qi, C. H. Deng, X. M. Zhang and D. Y. Zhao, *J. Am. Chem. Soc.*, 2008, **130**, 28; (e) J. C. Park, H. J. Lee, J. U. Bang, K. H. Park and H. Song, *Chem. Commun.*, 2009, 7345; (f) Z. F. Bian, J. Zhu, F. L. Cao, Y. F. Lu and H. X. Li, *Chem. Commun.*, 2009, **43**, 6551; (g) D. C. Niu, Y. S. Li, X. L. Qiao, L. Li, W. R. Zhao, H. R. Chen, Q. L. Zhao, Z. Ma and J. L. Shi, *Chem. Commun.*, 2008, 4463; (h) B. Y. Ahn, S. I. Soak, I. C. Baek and S.-I Hong, *Chem. Commun.*, 2006, 189; (i) L. Li, H. F. Qian and J. C. Ren, *Chem. Commun.*, 2005, 4083.
- 7 (a) K. P. Velikov, A. Moroz and A. van Blaaderen, *Appl. Phys. Lett.*, 2002, **80**, 49; (b) J. Luo, M. M. Maye, Y. B. Lou, L. Han, M. Hepel and C. J. Zhong, *Catal. Today*, 2002, **77**, 127.
- 8 (a) P. Reiss, J. Bleuse and A. Pron, *Nano Lett.*, 2002, **2**, 781; (b) F. Teng, Z. J. Tian, G. X. Xiong and Z. S. Xu, *Catal. Today*, 2004, **93–95**, 651; (c) Y. X. Li, S. Q. liu, L. H. Yao, W. J. Ji and C.-T. Au, *Catal. Commun.*, 2010, **11**, 368; (d) Y. X. Li, L. H. Yao, S. Q. Liu, J. Zhao, W. J. Ji and C.-T. Au, *Catal. Today*, 2010, DOI: 10.1016/j.cattod.2010.02.066.
- 9 (a) F. Bonet, K. Tekaia-Elhsissen and K. V. Sarathy, Bull. Mater. Sci., 2000, 23, 165; (b) P. Y. Silvert, R. Herrera-Urbina and K. Tekaia-Elhsissen, J. Mater. Chem., 1997, 7, 293; (c) Y. S. Sun, Y. D. Yin, B. T. Mayers, T. Herricks and Y. N. Xia, Chem. Mater., 2002, 14, 4736; (d) P. Y. Silvert and K. Tekaia-Elhsissen, Solid State Ionics, 1995, 82, 53; (e) F. Kim, S. Connor, H. Song, T. Kuykendall and P. Yang, Angew. Chem., Int. Ed., 2004, 43, 3673.
- 10 W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci., 1968, 26, 62.
- (a) J. Shi, N. Ren, Y. H. Zhang and Y. Tang, *Prog. Chem.*, 2009,
 21, 1750; (b) W. M. Zhang, J. S. Hu, Y. G. Guo, S. F. Zheng,
 L. S. Zhong, W. G. Song and L. J. Wan, *Adv. Mater.*, 2008, 20, 1160; (c) S. H. Joo, P. J. Young, C. K. Tsung, Y. Yamada,
 P. D. Yang and G. A. Somorjai, *Nat. Mater.*, 2009, 8, 126.
- 12 X. L. Pan and X. H. Bao, Chem. Commun., 2008, 6271.