Journal of Materials Chemistry

COMMUNICATION

In situ synthesis of magnetically recyclable graphene-supported Pd@Co core–shell nanoparticles as efficient catalysts for hydrolytic dehydrogenation of ammonia borane†

Jun Wang,[ab] **Yu-Ling Qin,**[a] **Xiang Liu**[b] **and Xin-Bo Zhang**[*a]

Graphene supported Pd@Co core–shell nanocatalysts with magnetically recyclability were synthesized *via* the *in situ* synthesis strategy utilizing the distinction in reduction potentials of the two precursors with appropriate reductant. The as-synthesized catalysts exerted satisfied catalytic activity (916 L mol^{-1} min^{-1}) and recycle stability for hydrolytic dehydrogenation of ammonia borane.

Hydrogen, as an ideal alternative to petrochemical energy, has attracted widespread research concerns and interests.[1] Among many significant barriers toward establishing hydrogen as a viable resource, exploring efficient hydrogen storage materials remains a daunting challenge.[2] Currently chemical hydrides have attracted a great deal of attention because of their high gravimetric and volumetric storage capacity.[3] Among them, ammonia borane (NH_3BH_3, AB) has the advantages of the high hydrogen content (19.6 wt%) and high stability under the ambient conditions, which make it one of the most compelling candidates for chemical hydrogen storage applications.[4] Therefore, development of efficient, economical and stable catalysts is highly desired to further improve the kinetic properties under moderate conditions for the practical application of this system.[5] To date, not only noble and non-noble metal-based catalysts but also their composites have shown the high efficacy to catalyze the hydrolytic dehydrogenation of AB.[6] Investigations of these catalysts have revealed that the catalytic performance is highly dependant on the dispersion of the active metals.[7] To solve this problem, many techniques have been designed for restraining the agglomeration of nanocatalysts, such as, stabilizing nanoparticles (NPs) with surfactants, coating NPs with inert shells, and contriving the microreactors.[8] Graphene, as an exciting material, has many merits of large theoretical specific surface area, high intrinsic mobility, high thermal and electrical conductivity, and thus is applied in fields such as physics, chemistry as well as materials science.[9] Hence, it is understandable to use graphene as the substrate to anchor NPs with good

dispersion. In addition, the rational structure designs of nanocatalysts have also been convinced to enhance the catalytic activity.[10] Accordingly, the cooperative effect can be expected between graphene and nanostructures to facilitate the reaction.

Herein, we report the *in situ* synthesis of magnetically recyclable graphene-supported Pd@Co core–shell NPs (Pd@Co/graphene) utilizing the distinction in reduction potentials of the two precursors with AB as the reducing agent at ambient conditions. Interestingly, compared with its alloyed (PdCo/graphene) and graphene-free (Pd@Co) counterparts, the as-synthesized nanocatalysts exert the most excellent catalytic activity and recycle stability toward the hydrolytic dehydrogenation of AB at ambient conditions.

Briefly, the *in situ* synthetic and catalytic procedure was achieved by adding AB into the precursor solution containing Na_2PdCl_4, $Co(NO_3)_2$, and graphene oxide (GO). And the gas generated was measured volumetrically.

Unexpectedly, the as-synthesized Pd@Co/graphene (Pd/Co = 0.1/0.9) exerts quite satisfactory catalytic activity toward hydrolytic dehydrogenation of AB, with which the complete evolution of 3 equiv. of hydrogen takes only 3.5 min (Fig. 1a), which is faster than that of many active catalysts reported.[5–8,10] For comparison,
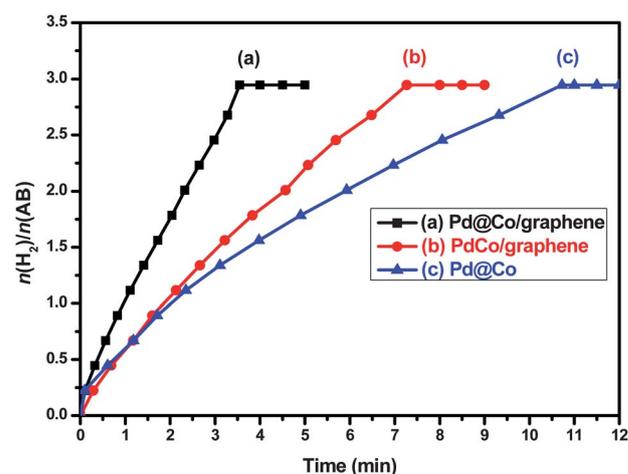
Fig. 1 Time plots of catalytic dehydrogenation of AB over (a) Pd@Co/graphene, (b) PdCo/graphene, and (c) Pd@Co nanocatalysts (Pd/Co = 0.1/0.9) at ambient conditions. Catalyst/AB = 0.02 (molar ratio).

[a]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 130022 Changchun, China. E-mail: xbzhang@ciac.jl.cn
[b]School of Chemical and Material Engineering, Jiangnan University, 214122 Wuxi, China
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2jm32229c

PdCo/graphene and Pd@Co nanocatalysts with the same ratio of Pd/Co are also prepared and applied to catalytic decomposition of AB (Fig. 1b and c). It can be seen that their catalytic activities are both inferior to that of Pd@Co/graphene, which confirms that the cooperative effect between graphene and nanostructures are favourable for AB decomposition. Yet, the catalytic performance of PdCo/graphene is better than that of Pd@Co nanocatalysts, highlighting that graphene, anchoring NPs to suppress agglomeration, is the dominant factor to facilitate AB decomposition in contrast to the role of nanostructures in our system.

The microstructures of the three samples are characterized by transmission electron microscopy (TEM) (Fig. 2). The NPs of the three samples are roughly spherical in shape and $\sim$7 nm in size. The high resolution TEM (HRTEM) images indicate that the samples, except for the crystalline core in Fig. 2B, are basically amorphous, which had been reported to result in high concentration of active sites for the catalytic reactions.[7a] A distinct contrast of core and shell metals for the in situ synthesized NPs reduced by AB can be observed clearly, and the dark cores are Pd and the gray shells are Co (Fig. 2B and F). Therefore, it can be concluded that Pd is initially reduced by AB and subsequently acted as the active sites helping for the reduction of Co which cannot be directly reduced by AB,
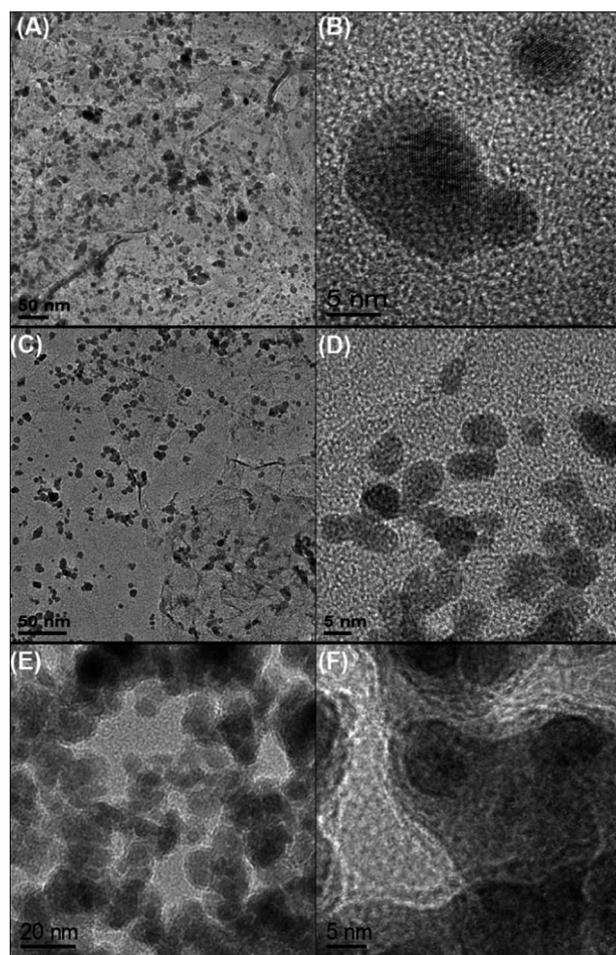
reasonably forming the Pd@Co core–shell structure.[10,11] In contrast, a relative stronger reduction agent, $NaBH_4$, instead causes the formation of PdCo alloy NPs (Fig. 2D) with inferior catalytic activity, indicating both the relative reduction potentials of the metal ions and the reduction ability of the reductant are the key factors for the in situ synthesis strategy to obtain core–shell NPs. Above all, it can be seen from Fig. 2A and C that the NPs reduced by either AB or $NaBH_4$ were well dispersed with the aid of graphene, owing to the functional groups on the GO surface (Fig. S1†). By contrast, severe agglomeration of graphene-free Pd@Co nanocatalysts is observed (Fig. 2E), which hinders the active sites of the catalysts in exerting their activities efficiently, highlighting the efficacy of graphene again.

Due to the small amount of Pd, the X-ray diffraction (XRD) pattern of the in situ synthesized Pd@Co/graphene (Fig. S2†) has no obvious diffraction peak, implying that the sample is almost in an amorphous state, which is in good agreement with the HRTEM image. The relative change in the D to G peak intensity ratio before and after the reduction in the Raman spectra (Fig. S3a and S3c†) confirms the reduction of GO during the in situ synthetic and catalytic process. Comparatively, the capability of AB alone for GO reduction (Fig. S3b†) is weak, revealing that the presence of metal nanocatalysts facilitates the reduction of GO.

To investigate the Pd/Co ratio-dependent effect toward AB decomposition, the Pd/Co ratio is varied from 0 to 1.0 with the molar ratio for catalysts to AB as a constant of 0.02 (Fig. S4†). Due to the absence of Pd NPs, the precursor of Co cannot be inductively reduced, resulting in no activity toward catalytic dehydrogenation of AB. Unexpectedly, with the increase of Pd content, the catalytic activities of the as-synthesized catalysts decrease gradually. Even worse, when the Pd/Co ratio increases to 0.9/0.1, AB cannot be catalytic decomposed completely. And only 82% of H_2 is released over graphene supported pure Pd NPs, revealing the negative effect of as-synthesized Pd on the hydrogen selectivity. The results above may be attributed to more active sites deriving from the higher amorphous Co contents.[7a] Moreover, the catalytic activities of Pd@M/graphene (Pd/M = 0.1/0.9, M = Fe and Ni) nanocatalysts are also examined (Fig. S5†). For the more negative reduction potential of Fe^{2+}, the zero-valent Fe is not obtained using AB as the reductant in the presence of Pd NPs, making the as-prepared catalysts show no obvious catalytic activity for AB decomposition within 13 min. Although the reduction potential of Ni^{2+} is similar to that of Co^{2+}, the combination of Pd with Ni displays inferior catalytic activity and hydrogen selectivity toward the dehydrogenation of AB at ambient conditions.

The stability or recycling ability is of great importance for the practical application of catalysts. In this sense, the recycling stability is evaluated in terms of the turnover frequency (TOF) for Pd@Co/graphene as well as PdCo/graphene and Pd@Co nanocatalysts (Fig. 3). With the highest initial TOF of 916 L mol^{-1} min^{-1},[5–8,10] the catalytic activity of Pd@Co/graphene has no serious decrease (3% decrease) after 5 cycles, indicating the superior recycle stability. Although the initial TOF of PdCo/graphene is not too high, it remains almost stable with the presence of graphene. Pd@Co nanocatalysts with the worst initial TOF show the apparent loss in catalytic activity, confirming that graphene as the ideal substrate is benefit for catalysts to exert remarkable activities in durable lifetime. Moreover, the in situ synthesized Pd@Co/graphene is magnetic and thus can be recovered by an external magnet (Fig. S6†).

Fig. 2 TEM (left) and HRTEM (right) images of (A and B) Pd@Co/graphene, (C and D) PdCo/graphene, and (E and F) Pd@Co nanocatalysts, respectively.
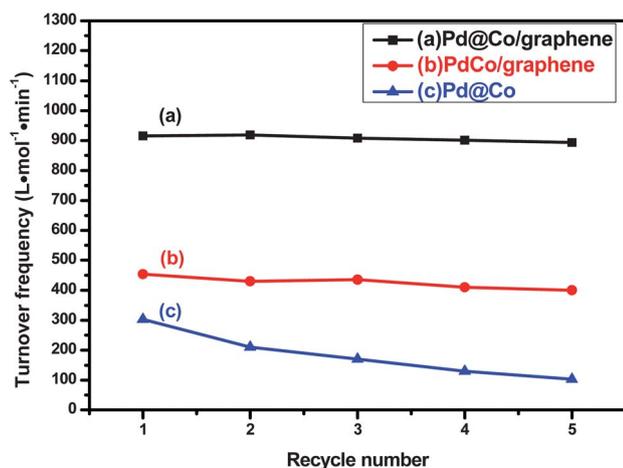
Fig. 3 Stability testing of catalytic dehydrogenation of AB over (a) Pd@Co/graphene, (b) PdCo/graphene, and (c) Pd@Co nanocatalysts (Pd/Co = 0.1/0.9) in terms of TOF at ambient conditions. Catalyst/AB = 0.02 (molar ratio).

Conclusions

In summary, the cooperative effect between graphene and nano-structures is confirmed by the *in situ* synthesized graphene supported Pd@Co core–shell nanocatalysts which possess the merits of quite satisfactory catalytic activity, durable stability and magnetically recyclability for the hydrolytic dehydrogenation of AB at ambient conditions. In addition, this synergy can be easily extended to the other graphene-based metallic systems, which are used as optical, magnetic, and electrical materials as well as heterogeneous catalysts.

Acknowledgements

Notes and references

1 *Hydrogen as a Future Energy Carrier*, ed. A. Züttel, A. Borgschulte and L. Schlapbach, Wiley-VCH, Weinheim, 2008.
2 (*a*) L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353; (*b*) P. Chen, Z. Xiong, J. Luo, J. Lin and K. L. Tan, *Nature*, 2002, **420**, 302; (*c*) C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem.*

Soc. Rev., 2009, **38**, 279; (*d*) S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel and C. M. Jensen, *Chem. Rev.*, 2007, **107**, 4111.
3 (*a*) J. M. Ogden, *Annu. Rev. Energy Environ.*, 1999, **24**, 227; (*b*) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127; (*c*) J. Graetz, *Chem. Soc. Rev.*, 2009, **38**, 73; (*d*) A. Gutowska, L. Li, Y. Shin, C. M. Wang, X. S. Li, J. C. Linehan, R. S. Smith, B. D. Kay, B. Schmid, W. Shaw, M. Gutowski and T. Autrey, *Angew. Chem., Int. Ed.*, 2005, **44**, 3578.
4 (*a*) Y. S. Chen, J. L. Fulton, J. C. Linehan and T. Autrey, *J. Am. Chem. Soc.*, 2005, **127**, 3254; (*b*) H. V. K. Diyabalanage, R. P. Shrestha, T. A. Semelsberger, B. L. Scott, M. E. Bowden, B. L. Davis and A. K. Burrell, *Angew. Chem., Int. Ed.*, 2007, **46**, 8995; (*c*) Z. T. Xiong, C. K. Yong, G. T. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards and W. I. F. David, *Nat. Mater.*, 2008, **7**, 138.
5 (*a*) M. Chandra and Q. Xu, *J. Power Sources*, 2007, **168**, 135; (*b*) M. Chandra and Q. Xu, *J. Power Sources*, 2006, **156**, 190; (*c*) F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant and D. A. Dixon, *Angew. Chem.*, 2007, **119**, 760; F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant and D. A. Dixon, *Angew. Chem., Int. Ed.*, 2007, **46**, 746; (*d*) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 12048; (*e*) C. W. Yoon and L. G. Sneddon, *J. Am. Chem. Soc.*, 2006, **128**, 13992.
6 H. L. Jiang, S. K. Singh, J. M. Yan, X. B. Zhang and Q. Xu, *ChemSusChem*, 2010, **3**, 541.
7 (*a*) J. M. Yan, X. B. Zhang, S. Han, H. Shioyama and Q. Xu, *Angew. Chem., Int. Ed.*, 2008, **47**, 2287; (*b*) S. B. Kalidindi, M. Indirani and B. R. Jagirdar, *Inorg. Chem.*, 2008, **47**, 7424.
8 (*a*) C. W. Chiang, A. Wang, B. Z. Wan and C. Y. Mou, *J. Phys. Chem. B*, 2005, **109**, 18042; (*b*) K. Qian, H. Sun, W. Huang, J. Fang, S. Lv, B. He, Z. Jiang and S. Wei, *Chem.–Eur. J.*, 2008, **14**, 10595; (*c*) X. Liu, A. Wang, X. Wang, C. Mou and T. Zhang, *Chem. Commun.*, 2008, 3187; (*d*) J. M. Yan, X. B. Zhang, S. Han, H. Shioyama and Q. Xu, *Inorg. Chem.*, 2009, **48**, 7389; (*e*) H. L. Jiang, T. Umegaki, T. Akita, X. B. Zhang, M. Haruta and Q. Xu, *Chem.–Eur. J.*, 2010, **16**, 3132.
9 (*a*) A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183; (*b*) X. Li, X. Wang, L. Zhang, S. Lee and H. Dai, *Science*, 2008, **319**, 1229; (*c*) M. D. Stoller, S. J. Park, Y. W. Zhu, J. H. An and R. S. Ruoff, *Nano Lett.*, 2008, **8**, 3498; (*d*) A. A. Balandin, S. Ghosh, W. Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, *Nano Lett.*, 2008, **8**, 902; (*e*) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197; (*f*) A. Fasolino, J. H. Los and M. I. Katsnelson, *Nat. Mater.*, 2007, **6**, 858; (*g*) C. Lee, X. D. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385; (*h*) X. Huang, X. Qi, F. Boey and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 666; (*i*) X. Huang, Z. Y. Yin, S. X. Wu, X. Y. Qi, Q. Y. He, Q. C. Zhang, Q. Y. Yan, F. Boey and H. Zhang, *Small*, 2011, **7**, 1876; (*j*) X. H. Cao, Q. Y. He, W. H. Shi, B. Li, Z. Y. Zeng, Y. M. Shi, Q. Y. Yan and H. Zhang, *Small*, 2011, **7**, 1199; (*k*) Q. He, S. Wu, S. Gao, X. Cao, Z. Yin, H. Li, P. Chen and H. Zhang, *ACS Nano*, 2011, **5**, 5038; (*l*) H. G. Sudibya, Q. Y. He, H. Zhang and P. Chen, *ACS Nano*, 2011, **5**, 1990; (*m*) Q. Y. He, H. G. Sudibya, Z. Y. Yin, S. X. Wu, H. Li, F. Boey, W. Huang, P. Chen and H. Zhang, *ACS Nano*, 2010, **4**, 3201; (*n*) J. Q. Liu, Z. Y. Yin, X. H. Cao, F. Zhao, A. P. Lin, L. H. Xie, Q. L. Fan, F. Boey, H. Zhang and W. Huang, *ACS Nano*, 2010, **4**, 3987.
10 J. M. Yan, X. B. Zhang, T. Akita, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5326.
11 D. Wang and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 6280.

12470 | *J. Mater. Chem.*, 2012, **22**, 12468–12470

This journal is © The Royal Society of Chemistry 2012