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A facile one-step synthesis of polymer supported rhodium nanoparticles in organic medium and their catalytic performance in the dehydrogenation of ammonia-borane[†]

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A new type of supported rhodium nanoparticles were reproducibly prepared from $N_2H_4BH_3$ reduction of $[Rh(\mu-Cl)(1,5-cod)]_2$ without using any solid support and pre-treatment technique. Their characterization shows the formation of well dispersed rhodium(0) nanoparticles within the framework of a polyaminoborane based polymeric support. These new rhodium(0) nanoparticles were found to be the most active supported catalyst in the catalytic dehydrogenation of ammonia-borane in water at room temperature.

Today, the preparation of metal nanoparticles with high stability against bulk formation is of great importance for their potential applications in many fields,¹ including catalysis.² The majority of the protocols followed in the synthesis of metal nanoparticles include the use of surfactants or ligands that can stabilize them in the embryonic stage against agglomeration.³ Although they attain colloidal stability with the help of ligands/surfactants, they still have a tendency to form clumps and eventually to agglomerate into bulk metal during the catalytic processes.⁴ The prevention of nanoparticles agglomeration is one of the most important challenges in the field of nanocatalysis.⁵ In this context, the use of nanoparticles on solid matrices of support materials represents especially promising directions for preventing aggregation.⁶ Moreover, it can also provide the kinetic control of the catalytic reaction, plus simple isolation from the reaction solution and efficient reusability.7

Herein, we report one step synthesis of a new type of supported rhodium(0) nanoparticles, hereafter referred to as Rh@PAB, without requiring any pre-treatment such as impregnation, ion-exchange or solid grinding for grafting of metal nanoparticles to the support. Rh@PAB were prepared reproducibly in a single step hydrazine borane (N₂H₄BH₃) reduction of the chloro-(1,5-cyclooctadiene)rhodium(1) precursor ([Rh(μ -Cl)(1,5-cod)]₂) and characterized by multipronged analyses.⁸ The catalytic performance of Rh@PAB was investigated in the hydrolytic

dehydrogenation of ammonia-borane (H₃NBH₃), which has recently been considered as a suitable hydrogen storage material because of its low molecular weight (30.9 g mol⁻¹) and high hydrogen content (19.6 wt%), that is greater than the 2015 target of the U.S. Department of Energy (9 wt% hydrogen for a material to be practically applicable).⁹

When a 0.15 mol% solution of [Rh(µ-Cl)(1,5-cod)]₂ in THF was treated with a concentrated solution of hydrazine borane $([H_4N_2BH_3] = 5.0 \text{ M})$ at 25 °C, a vigorous bubble formation was observed, presumably due to H₂ evolution from the dehydrocoupling/dehydrogenation of hydrazine borane.¹⁰ During the course of reaction, a brown solid precipitate was also formed. which was isolated at the end of the reaction by the evaporation of solvent and found to be insoluble not only in water but also in the most common organic solvents.¹¹ It is noteworthy that recent studies¹⁰ have also reported the formation of insoluble, poorly defined polymeric materials, along with H₂ from the thermolysis of hydrazine borane. The ¹H NMR spectrum of the aliquot taken at the end of the reaction shows only the formation of cyclooctane (1.3 ppm) from the hydrogenation of a cyclooctadiene ligand, whereas the ${}^{11}B{}^{1}H{}$ spectrum of the same sample shows no signal indicating that boron containing a THF-soluble product is not formed. The compositional investigation of the insoluble product in terms of inductively coupled plasma optical emission spectroscopy (ICP-OES) and elemental analyses (EA) shows the existence of an equimolar amount of boron and nitrogen plus a very small amount of rhodium metal (1.5 wt%). The solid state ¹¹B{¹H}-NMR spectrum (Fig. S1, ESI[†]) of the same material shows two signals at 0.7 and -11.7 ppm assignable to singly dehydrogenated boranes^{12,13} and high molecular weight amorphous polyaminoboranes $[BNRH_x]_v$ formed from the dehydrogenation of analogous amine-borane derivatives.¹⁴ The analyses done by matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectroscopy (Fig. S2, ESI[†]) and powder X-ray diffraction (P-XRD) for our insoluble product provide compelling evince for the formation of amorphous polymeric material with a molecular weight of > 5000. In addition, the attenuated total reflectance infrared (ATR-IR) spectrum (Fig. S3, ESI⁺), collected from the same sample, shows the characteristic bands between 3325-3083 cm⁻¹ for N-H, at 2494 cm⁻¹ for B-H¹³ and between 1588-821 cm⁻¹ for B-N stretching and bending modes.15 The oxidation state of rhodium in Rh@PAB was investigated by using X-ray photoelectron spectroscopy (XPS)

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Fig. 1 (a)–(c) SEM images of Rh@PAB at different magnifications and (d) SEM/EDS spectrum of Rh@PAB.

(Fig. S4, ESI[†]). The XPS survey scan spectrum shows the signals of N 1s at 398.2 and B 1s at 190.1 eV for boron nitride (B=N).¹⁶ The high resolution Rh 3d XPS spectrum of Rh@BNp shows two prominent signals at 307 and 311 eV that can readily be assigned to Rh $3d_{5/2}$ and Rh $3d_{3/2}$, respectively.¹⁷ The size, morphology and regional composition of Rh@PAB were investigated by scanning electron microscopy (SEM), SEM modulated by energy dispersive X-ray spectroscopy (SEM/EDS), transmission electron microscopy (HRTEM), high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and STEM modulated by local energy-dispersive X-ray micro-analysis (STEM/EDX). Fig. 1a–c show the SEM images of Rh@PAB with a rhodium loading of 1.5 wt% in different magnifications, clearly indicating that there is no bulk rhodium formed in observable size on the surface of the resulting polymeric

material. However the SEM-EDX spectrum in Fig. 1d confirmed the existence of rhodium in the analyzed region as judged by $L_{\alpha 1}$, $L_{\beta 1}$, $L_{b 1}$, $L_{b 2}$ lines of rhodium in the range of 2.3–3.0 keV.¹⁸

Indeed, low resolution TEM images of Rh@PAB given in Fig. 2a and b show the presence of well dispersed rhodium nanoparticles in the range of 1.2-4.9 nm with a mean diameter of 2.7 ± 0.6 nm (Fig. 2c). In addition, the high resolution-TEM images shown in Fig. 2d-f reveal the highly crystalline feature of these rhodium nanoparticles with a crystalline spacing of 0.23 nm, which can be assigned to Rh(111) face.¹⁹ In addition, the dispersion of rhodium nanoparticles was also investigated by STEM modulated EDX (Fig. S5, ESI⁺), which shows the good dispersion of rhodium nanoparticles across the framework of the support. These results are solid evidence for the fact that polymeric material acts only as a support for guest rhodium nanoparticles and not as a surfactant that can stabilize supported free rhodium nanoparticles by capping them as known in the case of PVP stabilized metal nanoparticles.²⁰ The porosity and the surface area of Rh@PAB were also investigated under mild pretreatment conditions by nitrogen adsorption-desorption analyses. Fig. 3 shows a representative nitrogen adsorptiondesorption isotherm and corresponding pore size distribution of Rh@PAB. The shape of the isotherm follows type III, which is indicative of multilayer formation at the interface with high coverage and characteristics for certain kinds of polymeric materials.²¹ The BET (Brunauer-Emmett-Teller) surface area and single point total pore volume are 44 m² g⁻¹ and 0.21 cm³ g⁻¹, which are considerably large values, as the rhodium nanoparticles were included in the calculations. The average BJH (Barret-Joyner-Halenda) pore diameter calculated from the desorption branch of the isotherm is determined to be 2.5 nm.

The catalytic performance of Rh@PAB was tested in the hydrolytic dehydrogenation of ammonia-borane (Scheme 1).²² We found that Rh@PAB provide high activity even at high substrate/catalyst ratios and low temperatures (see Fig. S6, ESI†).



Fig. 2 (a) and (b) Low resolution TEM images of Rh@PAB, scale bars correspond to 100 and 20 nm, respectively; (c) size histogram of rhodium nanoparticles constructed from counting >100 particles given in (b); (d)–(f) High resolution TEM images of Rh@PAB in which scale bars are equal to 10, 5, and 2 nm, respectively.





Fig. 3 N₂ adsorption/desorption isotherms of Rh@PAB. The inset shows the corresponding pore size distribution.

$$H_3NBH_3 + 2 H_2O \xrightarrow{catalyst} NH_4^+ + BO_2^- + 3 H_2$$

Scheme 1 The catalytic dehydrogenation of ammonia-borane (NH₃BH₃) in water.²²

In the hydrolysis of 200 mM H₃NBH₃ catalyzed by Rh@PAB ([Rh] = 0.1 mM), our rhodium nanoparticles provide a TOF value of 130 mol H₂/mol Rh min in air at 25 \pm 0.1 °C, which is notably higher than that of the current best supported metal catalyst (Pt/ γ -Al₂O₃ with TOF = 74 mol H₂/mol Pt min).²³ The reusability of Rh@PAB was also tested in the hydrolytic dehydrogenation of ammonia-borane and it was found that it retains > 50% of the initial activity even at the fifth run with the complete hydrogen generation. The decrease in the activity in the fifth run can be attributed to the decrease in the number of active surface atoms due to their clumping as evidenced by TEM (Fig. S7, ESI[†]) plus a slight Rh leaching (only 3% of total Rh) from Rh@PAB to reaction solution, which was detected by ICP-OES analysis of the filtrate harvested from the fifth run.

In summary, we have demonstrated one-step synthesis of polymer supported rhodium(0) nanoparticles in organic medium by the reduction of a rhodium(I) precursor with hydrazine borane. To the best of our knowledge, this is the only example for the preparation of supported metal nanoparticles in a one-step reaction in solution without requiring any additional process (impregnation, ion-exchange, grafting, solid grinding etc.). The preliminary results for the characterization of Rh@PAB show the formation of well dispersed rhodium(0) nanoparticles within the framework of a polymeric support comprised of $[BNRH_x]_v$ units. The catalytic application of these novel materials was investigated in the hydrolytic dehydrogenation of ammonia-borane, where they provide record activity among all the supported metal catalysts reported up to date for the same reaction. Moreover, they were found to be highly durable which makes them reusable. Unsolved problems remain in the complete identification of insoluble solid material formed from the dehydrocoupling of hydrazine borane and the use of other metal precatalysts in this method. The work is ongoing to explore the formation mechanism of Rh@PAB during the dehydrogenation of hydrazine borane in detail and expand the same methodology for the synthesis of other metal nanoparticle catalysts.

Notes and references

- 1 J. Shwarz, C. Contescu and K. Putyera, Encyclopedia of Nanoscience and Nanotechnology, Marcel-Dekker, New York, 2nd edn, 2004.
- 2 D. Astruc, Nanoparticles and Catalysis, Wiley-VCH, Weinheim, 2008, vol. 1.
- 3 A. Roucoux, J. Schulz and H. Patin, Chem. Rev., 2002, 102,
- 4 M. Zahmakıran and S. Özkar, Nanoscale, 2011, 3, 3462.
- 5 S. Özkar and R. G. Finke, J. Am. Chem. Soc., 2002, 124, 5796. 6 M. Zahmakıran, Y. Tonbul and S. Özkar, J. Am. Chem. Soc., 2010, 132, 6541; M. Zahmakıran, Y. Tonbul and S. Özkar, Chem. Commun., 2010, 46, 4788; M. Zahmakıran, S. Akbayrak, T. Kodaira and S. Özkar, Dalton Trans., 2010, 39, 7521; M. Zahmakıran, S. Özkar, T. Shiomi and T. Kodaira, Mater. Lett., 2009, 63, 400; M. Zahmakıran and S. Özkar, Mater. Lett., 2009, 63, 1033; M. Zahmakıran and S. Özkar, J. Mater. Chem., 2009, 19, 7112.
- 7 R. J. White, R. Luque, V. L. Budarin, J. H. Clark and D. Macquarrie, Chem. Soc. Rev., 2009, 38, 481.
- See ESI[†] for experimental details.
- A. Staubitz, A. P. M. Robertson and I. Manners, Chem. Rev., 2010. 110. 4079.
- T. Hügle, M. F. Kühnel and D. Lentz, J. Am. Chem. Soc., 2009. 131, 7444; V. S. Nguyen, S. Swinnen, J. Leszcynski and M. T. Nguyen, Phys. Chem. Chem. Phys., 2011, 13, 6649.
- 11 Rhodium nanoparticles were formed from the hydrazine-borane reduction of the Rh(1) precatalyst $[Rh(\mu-Cl)(COD)]_2$. The resulting support free rhodium(0) nanoparticles were presumably stabilized by weakly coordinating chloride anions at the initial stage of the reaction; C. A. Jaska and I. Manners, J. Am. Chem. Soc., 2004, 126, 9776; S. Özkar and R. G. Finke, J. Am. Chem. Soc., 2002, 124. 5796.
- 12 R. Komm, R. A. Geanangel and R. Liepins, Inorg. Chem., 1983, 22, 1684; R. J. Keaton, J. M. Blacquiere and R. T. Baker, J. Am. Chem. Soc., 2007, 129, 184; R. P. Shrestha, H. V. K. Diyabalanage, T. A. Semelsberger, K. C. Ott and A. K. Burrell, Int. J. Hydrogen Energy, 2009, 34, 2616.
- 13 A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. S. Gunne and I. Manners, J. Am. Chem. Soc., 2010, 132, 13332.
- 14 R. A. Geanangel and J. W. Rabalais, Inorg. Chim. Acta, 1985, 97, 59; D. P. Kim, K. T. Moon, J. G. Kho, J. Economy, C. Gervais and F. Babonneau, Polym. Adv. Technol., 1999, 10, 702; H. A. McGeei, Jr. and C. T. Kwon, Inorg. Chem., 1970, 9, 2458.
- 15 J. S. Perdigon-Melon, A. Aurox, D. Cornu, P. Miele, B. Toury and B. Bonnetot, J. Organomet. Chem., 2002, 657, 98.
- 16 K. Hamrin, G. Johansson, U. Gelius, C. Nordling and K. Siegbahn, Phys. Scr., 1970, 1, 277; D. N. Hendrickson, J. M. Hollander and W. L. Jolly, Inorg. Chem., 1970, 9, 612; S. Kohiki, T. Ohmura and K. Kusao, J. Electron Spectrosc. Relat. Phenom., 1983, 31, 85.
- V. Mevellec, A. Nowicki, A. Roucoux, C. Dujardin, P. Granger, 17 E. Payen and K. Philippot, New J. Chem., 2006, 30, 1214.
- 18 I. P. Jones, Chemical Microanalysis Using Electron Beams, The Institute of Materials, London, 1992.
- 19 S. M. Humphrey, M. E. Grass, S. E. Habas, K. Niesz, G. A. Somorjai and T. D. Tilley, Nano Lett., 2007, 7, 785.
- 20 L. S. Ott and R. G. Finke, Coord. Chem. Rev., 2007, 251, 1075.
- 21 S. J. Gregg and K. S. W. Sing, Adsorption, Surface Area and Porosity, Academic Press, Waltham, USA, 2nd edn, 1991.
- 22 M. Chandra and Q. Xu, J. Power Sources, 2006, 156, 190; M. Chandra and Q. Xu, J. Power Sources, 2006, 159, 855; Y. Yamada, K. Yano, Q. Xu and S. Fukuzumi, J. Phys. Chem. C, 2010, 114, 16456; J.-M. Yan, X.-B. Zhang, T. Akita, M. Haruta and Q. Xu, J. Am. Chem. Soc., 2010, 132, 5326; J.-M. Yan, X.-B. Zhang, S. Han, H. Shioyama and Q. Xu, Inorg. Chem., 2009, 48, 7389; H.-L. Jiang and Q. Xu, Catal. Today, 2011, 170, 56; M. Zahmakıran and S. Özkar, Appl. Catal., B, 2009, 89, 104; F. Durap, M. Zahmakıran and S. Özkar, Int. J. Hydrogen Energy, 2009, 34, 7223; F. Durap, M. Zahmakıran and S. Özkar, Appl. Catal., A, 2009, 369, 53; M. Zahmakıran, T. Ayvalı, S. Akbayrak, S. Çalışkan, D. Çelik and S. Özkar, Catal. Today, 2011. 170. 76.
- 23 M. Chandra and Q. Xu, J. Power Sources, 2007, 168, 135.