ChemComm

View Article Online / Journal Homepage / Table of Contents for this issue

Dynamic Article Links

Cite this: *Chem. Commun.*, 2011, **47**, 2529–2531

www.rsc.org/chemcomm

COMMUNICATION

Rhodium nanoparticle catalysts stabilized with a polymer that enhances stability without compromising activity†

Ning Yan,* Yuan Yuan and Paul J. Dyson*

Received 27th October 2010, Accepted 14th December 2010
DOI: 10.1039/c0cc04641h

Rh NPs coated with a PVP-derived polymer, that combines several distinct protective interactions, exhibit superior thermal and catalytic stability compared to analogue NPs coated with PVP.

Metal nanoparticles (NPs) are thermodynamically unstable and therefore require stabilizers in both their preparation and application. Stabilizers can be categorized according to the type of bond/interaction formed between the stabilizer and the NP surface, *viz.* steric, electrostatic and coordinative interactions.[1] Manipulating one or more of these interactions should result in the formation of more efficient stabilizers that ultimately will afford NPs with superior properties to those in current use.[2] In NP catalysis it is imperative to strike a balance between catalytic activity and stability[3] since, in many cases, the two factors are counter-productive.[4] A general strategy for the preparation of stable NPs, without significantly sacrificing their catalytic activity, was recently proposed that is based on the design of stabilizers that incorporate several weak stabilization mechanisms.[5] In principle, each individual functionality may contribute to the stability of the NPs without hindering their overall catalytic activity.

To test this hypothesis modified polyvinylpyrrolidone (PVP) systems that include functionalities which provide all the types of interactions were prepared and studied. PVP was selected as it is the most widely used polymer for stabilizing NP catalysts, combining a weakly coordinating amide functionality with steric protection.[6] The synthesis of stabilizers that are superior to PVP, *i.e.* providing NP catalysts with similar activity but higher stability, has proven to be very challenging. We postulated that the introduction of carboxylate group into PVP could further increase NP stability, by weak coordination of the carboxylate group with the metal surface, and additionally *via* electrostatic stabilization with the formation of a protective electrical double layer. Accordingly, polymers **1** and **2** (Fig. 1) were prepared and evaluated as stabilizers for Rh NPs in organic-aqueous and organic-ionic liquid (IL) biphasic hydrogenation reactions. Furthermore, the new systems were compared with NPs stabilized by PVP, the 'benchmark' stabilizer.

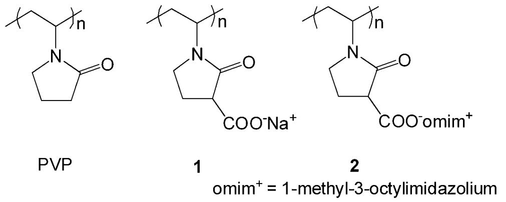

Fig. 1 Structures of the polymers used as NP stabilizers in this study.

Polymer **1** is known,[7] but as far as we are aware has not been used as a NP stabilizer. A slightly modified procedure was used to prepare **1** in this study. *N*-Vinyl-2-pyrrolidone (NVP) was reacted with lithium diisopropylamide (LDA) and then with ethyl chloroformate to afford 3,3-di(ethoxycarbonyl)-1-vinylpyrrolidin-2-one (DEVP). Free radical polymerization of DEVP yielded the corresponding polymer poly-3,3-di-(ethoxycarbonyl)-1-vinylpyrrolidin-2-one (PDEVP), which upon hydrolysis in NaOH/ethanol/H_2O mixture gave **1** as the only product. The average molecular weight (M_n) of PDEVP, based on GPC analysis, is 5.9 kDa, corresponding to *ca.* 230 repeating units per molecular chain. The structures of both PDEVP and **1** were verified by IR and NMR spectroscopy (see ESI†). TGA analysis (see ESI†, Fig. S1a) shows that the decomposition temperatures of **1** under both an inert and oxygen containing atmosphere exceed 300 °C, similar to that of PVP or alkyl modified PVPs.[8] Polymer **1** is soluble in water, slightly soluble in alcohol, and insoluble in other common solvents. The solubility of **1** can be tuned by replacement of Na^+ cation with other cations. For example, **2**, corresponding to the 1-methyl-3-octylimidazolium (omim) salt of **1**, is readily obtained by cation exchange, and exhibits good solubility in both polar organic solvents and ILs. The TGA curve for **2** indicates a two-stage weight loss process, corresponding to the decomposition of omim and polymer chain, respectively (see ESI†, Fig. S1b).

NPs coated with **1** or PVP were prepared in water from $RhCl_3$ by reduction with $NaBH_4$ in the presence of the polymer (denoted as **1**–Rh and PVP–Rh, respectively, see ESI† for full details). For both samples the resulting NP solutions were black and transparent. Micrographs of the Rh NPs are shown in Fig. 2 (and HRTEM is provided in Fig. S2a–b in ESI†). Relatively narrow unimodal size distributions with a diameter

---

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. E-mail: ning.yan@epfl.ch, paul.dyson@epfl.ch

† Electronic supplementary information (ESI) available: Experimental details, TGA analysis, additional (HR)TEM images, XPS and IR spectra. See DOI: 10.1039/c0cc04641h

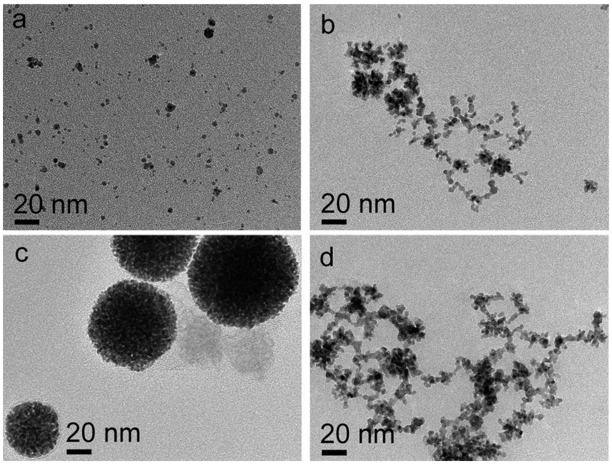

Fig. 2 TEM images of Rh NPs. (a) PVP–Rh; (b) **1**–Rh; (c) PVP–Rh after 5 batches; (d) **1**–Rh after 5 batches.

of *ca.* 4 nm were observed for both **1** and PVP protected Rh NPs. The thermal stability of the Rh NP solutions was studied by heating them at a heating rate of 1 °C min^{-1} to 200 °C and then maintaining the solutions at this temperature for 2 hours; PVP protected NPs do not generally survive at temperatures higher than 180 °C.[9] As the temperature was increased above 160 °C a black precipitate was observed for the PVP–NPs and at the end of the heating period the majority of the NPs have decomposed (Fig. 3). In contrast, for the **1**–NPs no precipitate was observed and based on TEM the size of Rh NPs remained unchanged (ESI†, Fig. S2c), indicating that the thermal stability offered by **1** is superior to that of PVP. A second method was used to prepare Rh NPs based on coating preformed (naked) Rh NPs, synthesized in glycol,[10] with PVP or **1**. This method ensures that the size and shape of Rh NPs for the two samples is the same. The same heat treatment to that described above applied to these NPs and essentially the same observations were made, *i.e.* the PVP protected Rh NPs undergo extensive precipitation whereas those stabilized by **1** remain essentially largely unchanged (ESI†, Fig. S3).

The stability of PVP–Rh and **1**–Rh under catalytic conditions was also investigated with toluene hydrogenation used as a model reaction under biphasic conditions. Unfortunately, both PVP–Rh and **1**–Rh deactivated at 200 °C under catalytic condition, although **1**–Rh is highly thermally stable at this temperature. In the case of **1**–Rh, however, higher conversion of toluene was indeed observed (15% *vs.* 6%), suggesting **1**–Rh is somewhat more stable than PVP–Rh under forcing catalytic condition. At 100 °C PVP–Rh achieved a toluene conversion of 93%, slightly more active than **1**–Rh (88%), but NP precipitation is observed after reaction, which is not the case for the catalyst solution containing **1**–Rh. Evaluation of the long term catalytic stability of **1**–Rh relative to PVP–Rh was undertaken at a reaction temperature of 60 °C. Five batches were carried out, and in the first run a quantitative conversion was obtained with PVP–Rh and a conversion of 93% was reached with **1**–Rh. Upon recycling the activity of PVP–Rh decreases with a conversion of <70% after five batches whereas the conversion with **1**–Rh remains essentially constant and always exceeds 90%. The decrease in activity of PVP–Rh may be correlated to NP aggregation which is observed visually by the formation of metallic deposits and also by TEM (Fig. 2c and ESI†, Fig. S6). TEM analysis revealed that PVP–Rh forms spherical superstructures ranging from 40–100 nm. In contrast, **1**–Rh remains essentially unchanged. With phenol, a substrate that is more readily hydrogenated than toluene,[11] a similar trend was observed in recycling experiments. **1**–Rh maintained its activity over 15 batches (after which experiments were stopped) whereas PVP–Rh was completely deactivated after 12 batches (ESI†, Fig. S7). In fact, the difference in the performance between **1**–Rh and PVP–Rh is more significant when the polymer : metal is reduced. As an example, when the ratio is reduced to 2, PVP–Rh can no longer stabilize Rh NPs effectively and a conversion of only 7.6% is obtained after three batches for the hydrogenation of toluene, whereas **1**–PVP can be recycled for at least 8 times without any loss of activity (ESI†, Fig. S8). Being able to operate at low stabilizer ratios is advantageous since PVP coated NPs require a large excess relative to the metal in order to achieve efficient stabilization.

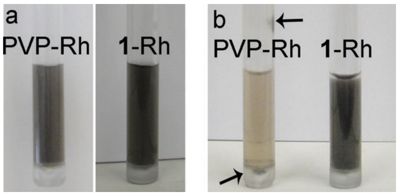

Fig. 3 Thermal stability of PVP–Rh and **1**–Rh; (a) before heating; (b) after heating at 200 °C for 2 h. Arrows indicate the formation of metallic deposits.

1–Rh was evaluated as a catalyst for the hydrogenation of other aromatic substrates under the same conditions (Table 1), demonstrating the utility of the nanocatalyst system. Even for relatively challenging substrate such as propylbenzene a conversion of 69% was achieved, representing a turnover frequency of 170 h^{-1}. This value is higher than that observed for other Rh NPs that range from 7 to 80 h^{-1},[12] although the comparison should be treated with caution due to the different conditions applied. Rh NPs protected by **2**, *i.e.* **2**–Rh, are highly soluble in ILs and these solutions were also found to be catalytically active under biphasic conditions (Table 1).

X-Ray photoelectron spectroscopy (XPS) was used to study the interactions between the surface of the Rh NPs and the polymers. XPS spectra of the C 1s and N 1s for the two samples are very similar (ESI†, Fig. S4), indicating that C and N atoms on the two polymers are not responsible for the differences in stability between the two Rh NPs. For O 1s spectra, however, considerable differences are observed. Compared to PVP that has a single peak for the amide (N–C=O) oxygen atom at 531.3 eV, the PVP–Rh NPs contain a peak at 532.0 eV, implying a reduction of electron density of the oxygen, due to the interaction between PVP and Rh NPs. This new peak is also observed in **1**–Rh NPs, which is not unexpected due to the presence of amide group. Additionally, a weak O ls signal at 535.5 eV indicates the presence of surface absorbed carboxylic acid species.[13] IR spectroscopy confirms the interaction between the carboxylic acid group in **1** with the Rh NP surface (ESI†, Fig. S5), and provides a rationale for the greater stability of **1** compared to PVP.

Table 1 Catalytic performance of **1**–Rh and **2**–Rh NPs in arene hydrogenation

Substrate	Stab.	Solvent	Con. (%)	Sel. (%)	
Phenol	**1**	Water	100	Cyclohexanol 99.8	Cyclohexanone 0.1
Anisole	**1**	Water	100	—	
Styrene	**1**	Water	100	Ethylbenzene 44.2	Ethylcyclohexane 55.7
Ethyl-benzene	**1**	Water	99	Ethylcyclohexane	
n-Propyl-benzene	**1**	Water	69	Propylcyclohexane	
Toluene	**2**	[bmim][BF_4]	95	Methylcyclohexane	
Toluene	**2**	[C_2OHmim][BF_4]	97	Methylcyclohexane	

Reaction conditions: reactant (0.5 mmol), 1×10^{-3} mmol of Rh NPs (Rh : stabilizer = 1 : 20) in 1 ml water or IL, H_2 (20 atm), 60 °C, 2 h.

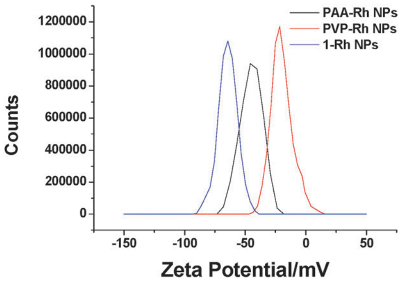

Fig. 4 Zeta potential of PVP–Rh, **1**–Rh and PAA–Rh NPs at pH = 7.

Electrostatic stabilization[14] was assessed by zeta potential measurements (Fig. 4), and as expected, the Rh NPs stabilized by PVP have a low overall charge, indicated by a zeta potential of −20 mV. The negative charge might originate from absorbed anions such as chloride from the NP precursor ($RhCl_3$) or electron donation from PVP, as demonstrated in the case of a Au NP–PVP system.[15] Compared to PVP–Rh, a highly negative value (−64 mV) is observed for **1**–Rh, indicative of an electrical double-layer around the NPs, and resulting in a Columbic repulsion between them. In general, NPs with zeta potentials higher than ±60 mV are regarded as being highly stable,[16] and NPs stabilized by carboxylate-containing polymers tend to have zeta potentials ranging from −40 to −60 mV.[17] For comparison, polyacrylic acid (PAA) coated Rh NPs were prepared in water by $NaBH_4$ reduction (PAA–Rh) and their zeta potential was found to be −49 mV, in agreement with the literature values.[16] The reason for the more negative zeta potential of **1**–Rh compared to PAA–Rh is not clear, but is likely to be due to combined electron donation from both the amide and the carboxylate group.

In summary, we have shown that Rh NPs coated by **1** exhibit superior thermal and catalytic stability to PVP coated NPs. The enhanced stability may be attributed to the presence of the carboxylate group that may provide weakly coordinate to the NP surface and an electrical double-layer that helps prevent aggregation. Combined these additional interactions result in NPs that can be recycled and reused without loss of activity.

N. Yan thanks the EU for Marie Curie International Incoming Fellowship (Number: 252125-TCPBRCBDP). Prof. J. A. Hubbell and Dr A. Vandervlies are acknowledged for assistance in zeta potential measurement. Prof. H. A. Klok and Sanhao Ji are thanked for carrying out the GPC analysis. Dr V. Laporte and S. Katsyuba are thanked for helpful discussions on the XPS data and IR spectra, respectively.

Notes and references

1 A. Roucoux, J. Schulz and H. Patin, *Chem. Rev.*, 2002, **102**, 3757.
2 For examples see: (*a*) C. Chiappe, D. Pieraccini, D. Zhao, Z. Fei and P. J. Dyson, *Adv. Synth. Catal.*, 2006, **348**, 68; (*b*) I. Favier, M. Gómez, G. Muller, D. Picurelli, A. Nowicki, A. Roucoux and J. Bou, *J. Appl. Polym. Sci.*, 2007, **105**, 2772; (*c*) D. D. Ankola, K. Ravi, F. Chiellini and R. Solaro, *Macromolecules*, 2009, **42**, 7388; (*d*) G. V. Ramesh, S. Porel and T. P. Radhakrishnan, *Chem. Soc. Rev.*, 2009, **38**, 2646; (*e*) J. Dupont and J. D. Scholten, *Chem. Soc. Rev.*, 2010, **39**, 1780.
3 D. Zhao, M. Wu, Y. Kou and E. Min, *Catal. Today*, 2002, **74**, 157.
4 (*a*) Y. Li and M. A. El-Sayed, *J. Phys. Chem. B*, 2001, **105**, 8938; (*b*) A. Roucoux, J. Schulz and H. Patin, *Adv. Synth. Catal.*, 2003, **345**, 222; (*c*) C. A. Stowell and B. A. Korgel, *Nano Lett.*, 2005, **5**, 1203.
5 N. Yan, X.-C. Xiao and Y. Kou, *Coord. Chem. Rev.*, 2010, **254**, 1179.
6 D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852.
7 M. Bencini, E. Ranucci, P. Ferruti, C. Oldani, E. Licandro and S. Maiorana, *Macromolecules*, 2005, **38**, 8211.
8 (*a*) N. Yan, J. Zhang, Y. Tong, S. Yao, C. Xiao, Z. Li and Y. Kou, *Chem. Commun.*, 2009, **29**, 4423; (*b*) N. Yan, J. Zhang, Y. Yuan, G. Chen, P. J. Dyson, Z. Li and Y. Kou, *Chem. Commun.*, 2010, **46**, 1631.
9 C. Zhao, W. Gan, X. Fan, Z. Cai, P. J. Dyson and Y. Kou, *J. Catal.*, 2008, **254**, 244.
10 Y. Wang, J. Ren, K. Deng, L. Gui and Y. Tang, *Chem. Mater.*, 2000, **12**, 1622.
11 S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, John Wiley & Sons, 2001, p. 427.
12 (*a*) J. Schulz, A. Roucoux and H. Patin, *Chem.–Eur. J.*, 2000, **6**, 618; (*b*) A. Roucoux, J. Schulz and H. Patin, *Adv. Synth. Catal.*, 2003, **345**, 222; (*c*) P. Migowski and J. Dupont, *Chem.–Eur. J.*, 2006, **13**, 32; (*d*) C. Zhao, H. Wang, N. Yan, C. Xiao, X. Mu, P. J. Dyson and Y. Kou, *J. Catal.*, 2007, **250**, 33; (*e*) B. Léger, A. Denicourt-Nowicki, A. Roucoux and H. Olivier-Bourbigou, *Adv. Synth. Catal.*, 2008, **350**, 153; (*f*) B. Léger, A. Denicourt-Nowicki, H. Olivier-Bourbigou and A. Roucoux, *Inorg. Chem.*, 2008, **47**, 9090.
13 K. W. Wulser and M. A. Langell, *Catal. Lett.*, 1992, **15**, 39.
14 R. G. Finke, in *Metal Nanoparticles: Synthesis, Characterization and Applications*, ed. D. L. Feldheim and C. A. Foss, Jr., Marcel Dekker, New York, 2002, ch. 2, p. 17–54.
15 H. Tsunoyama, N. Ichikuni, H. Sakurai and T. Tsukuda, *J. Am. Chem. Soc.*, 2009, **131**, 7086.
16 "Zeta Potential of Colloids in Water and Waste Water", ASTM Standard D 4187, American Society for Testing and Materials, 1985.
17 For examples see: (*a*) S. Chen and K. Kimura, *Langmuir*, 1999, **15**, 1075; (*b*) K. Yoosaf, B. I. Ipe, C. H. Suresh and K. G. Thomas, *J. Phys. Chem. C*, 2007, **111**, 12839; (*c*) J. Hang, L. Shi, X. Feng and L. Xiao, *Powder Technol.*, 2009, **192**, 166; (*d*) K. Mori, A. Kumami, M. Tomonari and H. Yamashita, *J. Phys. Chem. C*, 2009, **113**, 16850.