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ChemComm
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First example of high loaded polymer-stabilized nanoclusters immobilized on hydrotalcite: effects in alkyne hydrogenation

Jules C. A. A. Roelofs* and Peter H. Berben
Engelhard De Meern b.v. Strijkviertel 67, 3454 ZG De Meern, The Netherlands.
E-mail: jules.roelofs@Engelhard.com; Fax: +31 30 666 9369; Tel: +31 30 6669306

Received (in Cambridge, UK) 16th January 2004, Accepted 19th February 2004
First published as an Advance Article on the web 16th March 2004

Poly(*N*-vinyl-2-pyrrolidone)-stabilized Pd-nanoclusters, for the first time exclusively supported on the hydrotalcite lateral surface, showed a remarkable catalytic performance in the selective hydrogenation of 3-hexyn-1-ol, which can be ascribed to both the influence of the protecting polymer PVP as well as the nature of the support.

In recent years, interest in the synthesis of colloidal metal nanoclusters of controlled sizes and catalytic applications thereof has emerged.[1,2] Many preparation routes include the use of a protecting polymer, capable of coordinating to the metal atoms and thereby stabilizing the small metal clusters in solution. One of the most commonly used polymers for this purpose is poly(*N*-vinyl-2-pyrrolidone) (PVP). Recently, the use of microwave radiation has been applied to prepare colloidal metal nanoclusters of small sizes and with narrow size distributions.[3] This offers the possibility of synthesizing these nanoclusters in a facile, reproducible and fast way, without the commonly applied long synthesis times.[4] Studies on the immobilization of nanoclusters are relatively scarce and mostly limited to loadings below 1%.[5] In recent years, a growing interest has developed for the utilization of hydrotalcite compounds (HT) for various catalytic applications.[6] The structure of HT consists of positively charged layers containing Mg^{2+} and Al^{3+}, octahedrally coordinated by hydroxyl groups. These octahedra share adjacent edges to form sheets or layers. The space between the stacked cation layers is filled with charge-compensating anions, with preference for carbonate having the highest affinity.[7] Some Pd-containing HTs are known, prepared by well-established methods, *i.e.* co-precipitation[8] and impregnation,[9] usually followed by reduction at elevated temperatures. Mastalir *et al.*[10] synthesized low-loaded organophilic Pd/HT *via* an inventive ion-exchange, with interesting catalytic properties. However, this method is not applicable for HT with interlayer carbonate and is furthermore limited by the anion exchange capacity. In this communication, we demonstrate that highly loaded polymer-protected Pd-nanoclusters supported on hydrotalcite and carbon show remarkable differences in selectivity and activity in the *cis*-selective hydrogenation of 3-hexyn-1-ol towards the fragrance leaf alcohol.[11]

In a typical experiment, 6 gram (27 mmol) of PVP was dissolved in 150 gram (2.4 mol) of ethylene glycol. After obtaining a clear solution, 7.3 gram of Na_2PdCl_4 solution (10 wt% Pd) was added and this brown solution was heated in a laboratory microwave at 750 W for 90 seconds. The colour changed to black, indicative of the reduction of Pd^{2+} by ethylene glycol and the applied energy input. The hot solution was added to a 400 ml aqueous support-containing solution. The solution was stirred overnight at room temperature and after filtration dried at 110 °C under nitrogen atmosphere. The Pd content was varied up to 9 wt%, which was easily tuned by variation of the amount of support. At high loadings not all filtrates became colourless, indicative of the presence of nanoclusters in the filtrate. This implies that at these loadings not all nanoclusters were immobilized on the support. However, addition of the dried catalyst powders to known solvents for these polymer-stabilized nanoclusters like methanol, ethanol and water[4] did not result in coloured solvents. For catalytic measurements, a known amount of catalyst (typically 30 mg) was dispersed into 80 ml MeOH containing 3-hexyn-1-ol (around 1.3 g, 13 mmol). The hydrogenation reactions were performed at 29 °C and 2200 rpm using a glass reactor equipped with baffles and 0.13 atm pressure of H_2.

Fig. 1 shows the XRD patterns for the nanoclusters supported on carbon (NC/C) and HT (NC/HT).† The (111) and (200) reflections of Pd have been indicated with arrows. The obtained pattern for HT showed the typical characteristics for this layered clay material. The position of the (003) reflection indicated that carbonate was still present in the interlayer,[7] suggesting that the nanoclusters were immobilized at the basal platelet surfaces. The catalysts prepared by Mastalir *et al.*[10] showed increased basal spacings caused by Pd particles present in the interlayer, or partly within organoclay tactoids,[12] unfavourable for catalysis. Due to the position and intensity of interfering reflections of the basic support the Pd signals were not visible in case of HT. However, the polymer-protected nanoclusters *were* present on the platelet surface of HT, as shown by TEM in Fig. 2. Uniform nanoparticles can be seen throughout the image, only present on the support material (Fig. 2A). Dark field TEM shows that these Pd nanoparticles are of high crystallinity (Fig. 2B). This indicates that the reduction of Pd^{2+} by ethylene glycol and microwave radiation was successful, even with the absence of stirring during radiation in our experimental setup. From TEM analysis of the nanoclusters of uniform size an average particle size of 4.2 ± 0.8 nm was determined. Many factors are known to influence the final nanocluster size, *i.e.* pH, choice of reducing agent, reduction time, concentrations and ratio of PVP and Pd salt.[13,14] Reported value sizes relevant to our procedure vary between 1.7 nm[3] and 5.0 nm.[13] When compared with TEM images of the colloidal solution no change in size due to the immobilization was observed. Another interesting feature is the regular distribution of the particles on the HT support, likely due to the presence of PVP, preventing agglomeration. PVP is removed only above 350 °C, according to TPR (results not shown). As compared to reported loadings of Pd particles on hydrotalcites,[8–10,12] a tenfold higher loading can be achieved with the described procedure.

The hydrogenation activities of the catalysts (including a commercial Engelhard 5% Pd/C as reference) were tested in the hydrogenation of 3-hexyn-1-ol (Scheme 1). Besides the products shown, further hydrogenation to hexanol and hexane is possible, which was also observed in our experiments (Table 1). As expected,[11] the commercial Pd/C showed a high activity, but poor selectivity. The NC/C behaved completely differently: a low activity and a preferred formation of the *cis*-isomer were observed. An almost threefold increase in activity was found with the NC/HT catalyst as compared to the NC/C without loss of selectivity

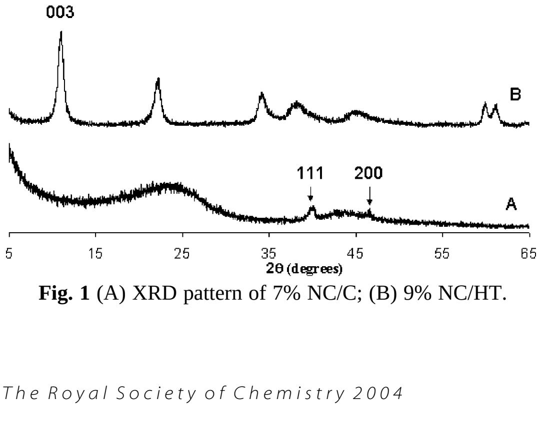


Fig. 1 (A) XRD pattern of 7% NC/C; (B) 9% NC/HT.

DOI: 10.1039/b400737a

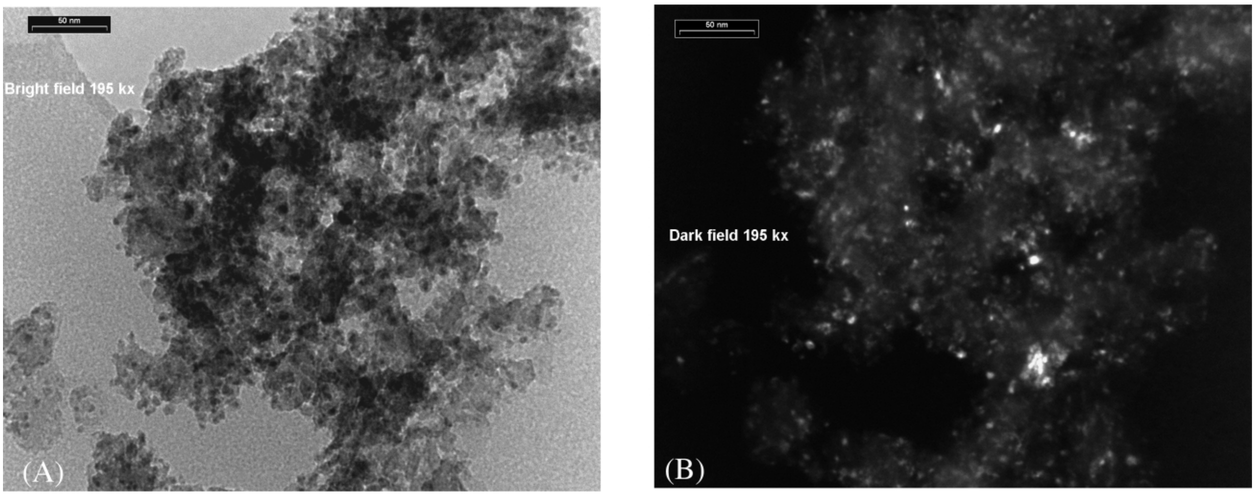
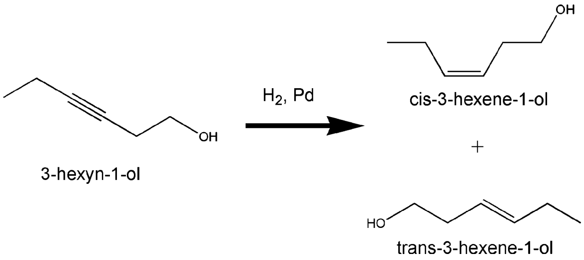


Fig. 2 (A) Bright field TEM image of NC/HT. (B) Dark field TEM image of same area, exposing crystalline Pd-nanoclusters (scalebar = 50 nm).



Scheme 1 Hydrogenation reaction of 3-hexyn-1-ol.

Table 1 Results from hydrogenation of 3-hexyn-1-ol

Catalyst	ml H_2 $Pd^{-1}min^{-1}$	Products (%)[a]
Pd/C	254	HE (80) HA (7) TR (2)
NC/C	32	CS (91) TR (4) HE (2)
NC/HT	85	CS (91) TR (4)

[a] HE = hexanol; HA = hexane; CS = *cis*-3-hexen-1-ol; TR = *trans*-3-hexen-1-ol. Selectivity was determined at > 95% 3-hexyn-1-ol conversion.

towards *cis*-3-hexen-1-ol. Likely, the basic character of the HT support has a positive influence on the activity, without the loss of the favorable effect of the PVP polymer.[11]

In conclusion, poly(*N*-vinyl-2-pyrrolidone)-stabilized Pd-nanoclusters were synthesized using microwave radiation and, for the first time, supported exclusively on the hydrotalcite lateral platelet surface. The catalytic performance in the selective hydrogenation of 3-hexyn-1-ol showed a high selectivity due to the influence of the protecting polymer PVP, and an increased activity, which can be ascribed the nature of the HT-support.

The authors wish to thank Prof. J. Geus for the TEM images and Dr H. Donkervoort for discussions in the development of this concept.

Notes and references

† The HT (Mg/Al = 2.2) was synthesized using the well-established and widely used co-precipitation procedure using Mg and Al nitrate salts, as described previously.[15] The resulting HT support had a BET surface area of 97 m^2 g^{-1} and a pore volume of 0.62 ml g^{-1} and contained no micropores (pores < 2 nm). The immobilization did not result in significant changes of these values as well as in pore structure. The NC were supported on activated carbon, after which a BET surface area of 534 m^2 g^{-1} and a pore volume of 0.26 ml g^{-1} was obtained. The *t*-plot method[16] was used to calculate the amount of mesoporous surface area on which the NC were present, which was 238 m^2 g^{-1}.

Powder X-Ray diffraction (XRD) patterns were obtained by using a Philips PW 1710 diffractometer control and a PW 1830 generator with Cu–Kα radiation (40 kV; 45 mA). Transmission Electron Microscopy (TEM) images were obtained with a Philips CM-10. Inductively Coupled Plasma (ICP) analysis was performed using a Thermal Jarrell Ash Atom scan.

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