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Recyclable Polyurea-Microencapsulated Pd(0) Nanoparticles: An Efficient Catalyst for Hydrogenolysis of Epoxides

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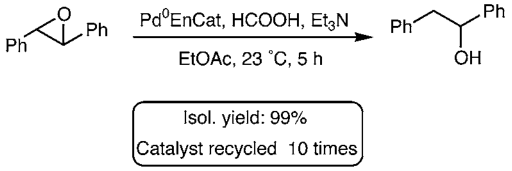
ABSTRACT



Pd nanoparticles (∼2 nm in size) microencapsulated in polyurea is an efficient and recyclable catalyst for reductive ring-opening hydrogenolysis of epoxides, using either HCOOH/Et_3N or H_2 as a hydrogen donor.

The reductive ring-opening of epoxides to the corresponding alcohols has emerged as a powerful transformation in organic synthesis owing to the rapid development of practical and efficient methods for the epoxidation of olefins.[1] Stoichiometric metal hydride or dissolving metals are frequently employed for this reductive cleavage reaction.[2] The need for a practical, economical, and environmentally benign version of this transformation has generated considerable interest in heterogeneous catalytic systems. Catalysts based on Ni, Pd, and Pt have been used, and further efforts are directed toward improving the chemoselectivity and regioselectivity of this ring-opening reaction.[3] For example, the use of the Pd/C-ethylenediamine complex under conventional hydrogenation conditions has improved the chemoselectivity by preventing further hydrogenolysis of the alcoholic C−O bond, although solvolysis with methanol is problematic, particularly with benzylic epoxides.[4] It was also observed that transfer hydrogenation with Pd/C/HCOOH/EtN_3 often exhibits better chemoselectivity than conventional hydrogenation involving Pd/C/H_2.[5] This could be explained by our recent mechanistic study, which showed that the hydrogen directly delivered from the Pd formate species has a much stronger hydridic nature compared to that from Pd hydride species, which makes it less reactive for hydrogenolysis of alcoholic C−O bonds.[6] To translate this laboratory method into a cost-effective large-scale operation it is essential to develop a recyclable catalyst for hydrogenolysis of epoxides under transfer hydrogenation conditions.

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Recently we described a robust and recyclable polyurea-encapsulated palladium catalyst [Pd^0EnCat] that was shown to be a highly efficient transfer hydrogenation catalyst for chemoselective reduction of a wide range of aryl ketones to benzyl alcohols.[7] [Pd^0EnCat] was prepared by reduction of the polyurea-coordinated $Pd(OAc)_2$ with HCOOH. Reduction with H_2 in place of HCOOH, however, did not produce an active catalyst. Here we disclose the characterization and comparison of the microencapsulated palladium particles prepared under the two different reducing conditions (H_2 or HCOOH). Further application of this catalytic system in the reductive ring-opening of benzylic epoxides via transfer hydrogenation was investigated. Hydrogenolysis of terminal epoxides with conventional hydrogenation conditions was also examined.

The most frequently used methodology for the synthesis of metallic nanoparticles involves the reduction of the precursors of metal salts or complexes stabilized in homogeneous form. It has been reported that the atomic structure of Pd particles in terms of morphology is dominated by the reduction speed.[8] Our rationale for using HCOOH was based on the expectation that the polyurea-coordinated $Pd(OAc)_2$ [PdEnCat] would undergo anionic ligand exchange with formate resulting in efficient local reduction to deposit fine nanoparticles in the support material with less agglomeration. To test this hypothesis, two samples prepared from [PdEnCat] by reduction with H_2 and HCOOH respectively were examined with use of a JEOL JEM-2010 electron microscope operating at 200 keV. The resolution of the microscope is approximately 0.19 nm, allowing direct imaging of the arrangement of heavy atoms in crystalline particles even when the particle size is very small. In the sample prepared by reduction with H_2, the majority of the particles are larger than 5 nm in size. These particles are single domain and well ordered (Figure 1a).

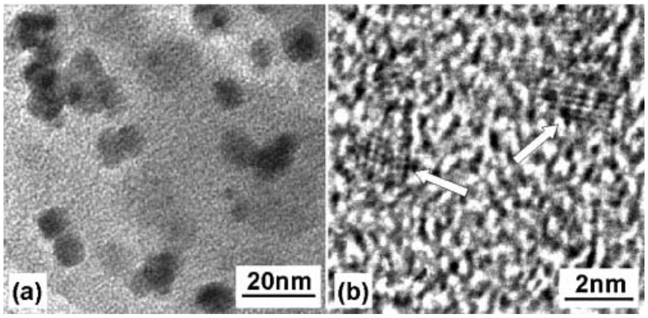


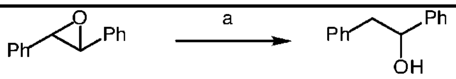
Figure 1. (a) Pd(0) particles prepared by reduction of [PdEnCat] with H_2. (b) Pd(0) particles [Pd^0EnCat] prepared by reduction of [PdEnCat] with HCOOH.

The structure of the sample prepared by reduction with HCOOH was drastically different (Figure 1b). HRTEM images revealed that most of the particles are very small with a diameter of 2 nm or less. The particle indicated by the right arrow shows 1D fringes with a d spacing of about 0.20 nm. Since the common structure of Pd metal is cubic close packed with the unit cell parameter $a = 0.388$ nm, this d spacing corresponds to the (200) crystal planes. The particle on the left side indicated by another arrow shows a 2D lattice image. Despite the small particle size (less than 2 nm), defects can still be observed. The relatively highly ordered area in the left half of the particle can be regarded as an image viewed down the [011] zone axis of the Pd unit cell.

This difference in atomic structure could contribute to the superior properties of the newly developed catalyst [Pd^0EnCat] in reduction of aryl ketones. To expand the applications of this catalyst, reductive ring-opening of epoxides by hydrogenolysis was investigated. With use of *trans*-stilbene oxide as a substrate, the hydrogenolysis reaction with 4 equiv of Et_3N and HCOOH in EtOAc at 23 °C reached completion after 5 h to give the corresponding alcohol in 99% isolated yield. It is worth noting that further hydrogenolysis of the alcoholic C−O bond was not observed at a detectable level even with prolonged reaction time, illustrating a clear advantage over Pd/C in terms of chemoselectivity.

The efficiency and stability of this catalyst was examined with *trans*-stilbene oxide as a substrate. It was pleasing to find that the microcapsules could be recovered by simple filtration and reused without loss of activity. Also of importance is that the level of palladium in the reaction mixture after filtration was lower than the detection threshold of 5 ppm by inductively coupled plasma analysis (ICP). The hydrogenolysis reaction reaches completion giving excellent isolated yields through 10 successive recycle runs (Table 1).[9]

Table 1. Recycling Experiments[a]



run	1	2	3	4	5	6	7	8	9	10
yield(%)	99	98	97	98	96	97	98	97	97	97

[a] Reagents and conditions: [Pd^0EnCat] (5 mol %), HCOOH (4 equiv), Et_3N (4 equiv), EtOAc, 23 °C, 5 h.

A variety of other benzylic epoxides were then subjected to the same hydrogenolysis conditions and good yields of the homobenzylic alcohol were consistently obtained (Table 2). It is known that the regioselectivity of epoxide opening by metal hydride depends sensitively on the epoxide structure. For example, the reduction of *cis*-β-methylstyrene oxide with $LiAlH_4$ proceeds with opposite regioselectivity

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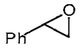
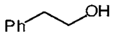
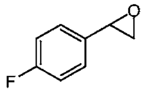
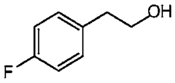
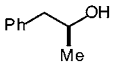
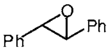
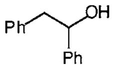
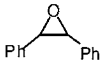
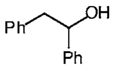
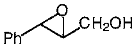
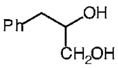
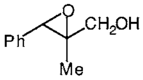
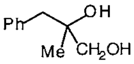
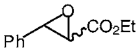
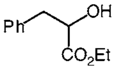
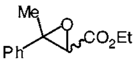
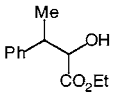
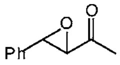
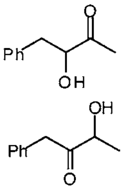
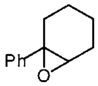
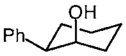
[9] Since no obvious drop of reactivity was observed, the upper limit of the recyclablity remains to be tested. TEM examinations of the samples after 1 cycle and 10 cycles observed no significant change in the particle size or distribution.

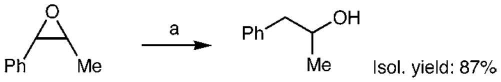
Table 2. [Pd^{0}EnCat]-Catalyzed Hydrogenolysis of Benzylic Epoxides

entry	substrate	product	time (h)	yield (%) isol.
1			4	84
2			24	82
3			3	90
4			5	99
5			5	93
6			5	95
7			3	93
8			13	92
9			24	94
10		 6 : 1	6	87
11			7	84

[a] Reagents and conditions: [Pd^{0}EnCat] (5 mol %), HCOOH (4 equiv), Et_3N (4 equiv), EtOAc, 23 °C.

to give the benzylic alcohol.[10] With [Pd^{0}EnCat] the epoxides were opened uniformly at the benzylic carbon, including *cis*-methylstyrene oxide (Scheme 1). The retention of stereochemistry was also established by using enantiomerically pure *trans*-methylstyrene oxide as shown in Table 2.

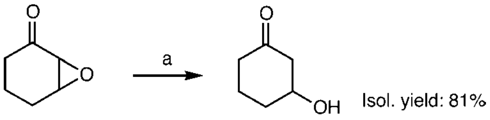
Scheme 1



[a] Reagents and conditions: [Pd^{0}EnCat] (5 mol %), HCOOH (4 equiv), Et_3N (4 equiv), EtOAc, 23 °C, 3 h.

The substrate generality of this protocol was also tested with an α,β-epoxyketone. The reductive ring-opening reaction was successfully accomplished under identical conditions producing the corresponding alcohol, which possesses an important β-hydroxy carbonyl functionality (Scheme 2).

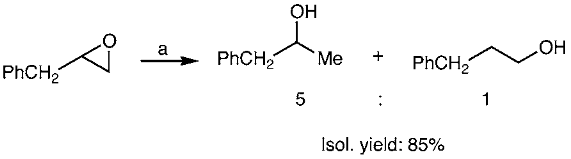
Scheme 2



[a] Reagents and conditions: [Pd^{0}EnCat] (5 mol %), HCOOH (4 equiv), Et_3N (4 equiv), EtOAc, 23 °C, 26 h.

The regioselective reduction of terminal epoxides is a particularly attractive synthetic route to substituted alcohols due to the recent advances in the area of catalytic epoxidation of terminal olefins.[11] To further expand the scope of this catalytic system, we turned our attention to epoxyalkane substrates. The hydrogenolysis of 3-phenylepoxypropane was very slow under transfer hydrogenation conditions. However, a very encouraging result was obtained by using the same catalyst (preformed by the reduction with HCOOH) under conventional hydrogenation conditions [Pd^{0}EnCat]/H_2/methanol, suggesting that the application of this catalytic system may be extended to a wider range of epoxides (Scheme 3).

Scheme 3



[a] Reagents and conditions: [Pd^{0}EnCat] (5 mol %), H_2 (40 atm), methanol, 23 °C, 19 h.

In conclusion, [Pd^{0}EnCat] prepared from the reduction of $Pd(OAc)_2$ microencapsulated in polyurea [PdEnCat] was characterized and found to consist mainly of Pd(0) nanoparticles around 2 nm in size. Under transfer hydrogenation conditions, [Pd^{0}EnCat] has been demonstrated to be an efficient and recyclable catalyst for reductive ring-opening reaction of benzylic epoxides. Further exploration of this catalyst with conventional hydrogenation conditions will be examined to extend the substrate scope of the reaction.

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Supporting Information Available: Experimental details and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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