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Palladium Nanoparticles Stabilized by Alkylated Polyethyleneimine as Aqueous Biphasic Catalysts for the Chemoselective Stereocontrolled Hydrogenation of Alkenes

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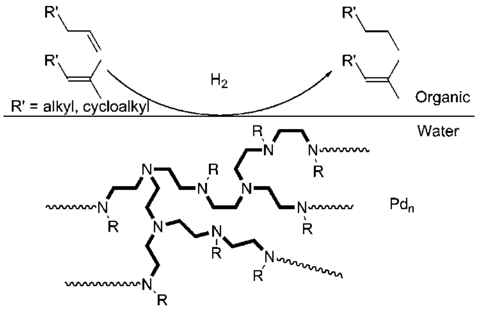
ABSTRACT



Alkylated PEI R = $C_{12}H_{25}$

Palladium nanoparticles were prepared, stabilized, and dispersed in water by alkylated branched polyethyleneimine. The palladium nanoparticles were effective aqueous biphasic catalysts for the chemoselective hydrogenation of alkenes with preferential reduction of less hindered double bonds, such as reduction of 3-methylcyclohexene in the presence of 1-methylcyclohexene and 1-octene in the presence of 2-methyl-2-heptene.

Much recent research in catalysis has been related to development of alternative reaction media in order to achieve synthetic procedures with a low environmental load.[1] Thus, instead of using classical organic solvents, efforts are being made to apply aqueous,[2] fluorous,[3] ionic liquid,[4] and supercritical fluid[5] as reaction solvents. In our opinion, the use of water as solvent and aqueous biphasic catalysis is the most potentially attractive alternative that combines a benign, inexpensive solvent (water) and easy catalyst recovery and recycle (phase separation). Unfortunately, low reaction rates because of slow mass transfer of organic substrates into the aqueous catalytic phase and the requisite synthesis of water-soluble ligands for the metallorganic catalysts have been an obstacle to more widespread application of aqueous biphasic catalysis. Mass transfer of the substrate to the aqueous phase may be facilitated by addition of amphiphiles to reduce surface tension. In this context, besides the more often used micellar and (micro)emulsion catalyst systems, the use of alkylated quaternized polyethylenimines as amphiphiles has led to their application in general acid−base and oxidation reactions.[6]

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(1) Adams, D. J.; Dyson, P. J.; Taverner, S. J. *Chemistry in Alternative Reaction Media*; Wiley: Weinheim, 2003.

(2) (a) Li, C.-J.; Chen, L. *Chem. Soc. Rev.* **2006**, *35*, 68−82. (b) Cornils, B. *J. Mol. Catal. A. Chem.* **1999**, *143*, 1−10. (c) Cornils, B. *Org. Proc. Res. Dev.* **1998**, *2*, 121−127.

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(4) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083. (b) Sheldon, R. A. *Chem. Commun.* **2001**, 2399−2407. (c) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2002.

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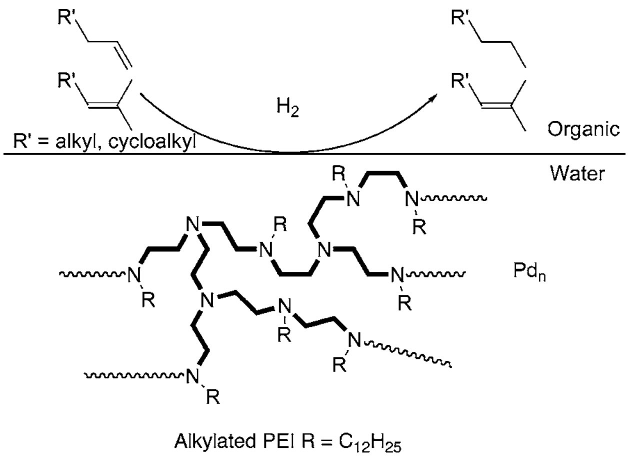
Recently, there has been an exponential growth in the use of the colloids or nanoparticles as catalysts.[7] Typically, in such applications the nanoparticles have been either dispersed in the reaction medium leading to a “semi-heterogeneous” catalyst or supported on a matrix leading to a more classic heterogeneous catalyst. Thus, aqueous biphasic catalysis that classically has dealt with intrinsically homogeneous catalysts with known molecular structure[2] can now evolve, as described herein, to aqueous biphasic catalysis with “semi-heterogeneous” nanoparticle catalysts. An important, flexible parameter that can be manipulated in the study of catalysis with nanoparticles, especially in the “semi-heterogeneous” reaction mode, is the identity of the stabilizing agent that can vary from the more established use of polymers[7c] and surfactants[7c] to the more recent use of dendrimers[8] and polyoxometalates.[9]

In this paper, we present our research on the use of a simply prepared alkylated polyethylenimine as a stabilizer for palladium nanoparticles, which upon dispersion into water allows the aqueous biphasic hydrogenation of hydrophobic alkenes. Beyond the practical and ecological advantage indigenous to this hydrogenation method, it was very surprising to observe that the hydrogenation was highly chemoselective with reaction of less sterically hindered alkenes being significantly preferred. Such considerable chemoselectivity, typically a domain of homogeneous catalysis is now demonstrated for catalysis by nanoparticles. The entire concept is pictorially summarized in Scheme 1.

Scheme 1. Cartoon Representation of Palladium Nanoparticles Stabilized by Alkylated Polyethylenimine and Dispersed in Water as Catalyst for Chemoselective Hydrogenation of Hydrophobic Alkenes



Palladium nanoparticles stabilized by alkylated polyethylenimine (PEI) were prepared as follows.[10] First, branched PEI ($M_w = 60\,000$ with ~25% primary and tertiary amines and ~50% secondary amines) was alkylated with 1-iodododecane, and the resulting alkylated PEI was treated with a basic resin, Amberlite IR-900, to remove HI from the polymer solution. The ^{15}N chemical shifts (23−34 ppm) and the correlations in the $^{15}N-^{1}H$ HMBC NMR spectrum, Figure 1, reveal that the alkylated PEI contains only secondary and tertiary amine moieties;[11] all of the primary amines in the original PEI were alkylated; *no* quaternary ammonium moieties were observed using this alkylation procedure. Second, K_2PdCl_4 (10 wt % of alkylated PEI) was added to an aqueous solution of alkylated PEI, and the resulting yellow solution was treated with $NaBH_4$ leading

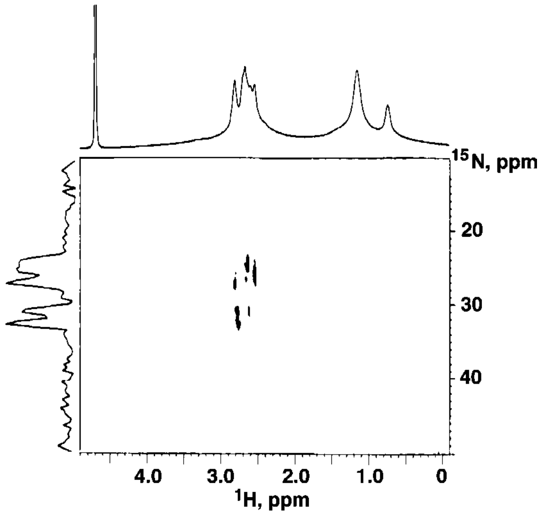


Figure 1. $^{15}N-^{1}H$ HMBC NMR spectrum of alkylated PEI.

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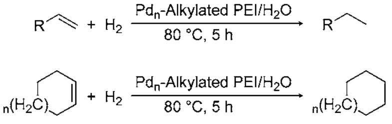
to a brown-black suspension of palladium nanoparticles in water that remained visibly unchanged for significant periods of time (7−10 days). A transmission electron micrograph of the dispersion prepared by freeze fracture of the aqueous solution confirmed the formation of palladium nanoparticles with particle sizes ranging from 2 to 4 nm (see Figure S1, Supporting Information).

Aqueous biphasic catalytic hydrogenation of sterically unhindered, hydrophobic, water-insoluble alkenes at 80 °C using the palladium nanoparticles stabilized by alkylated PEI as catalyst showed efficient hydrogenation to the corresponding alkanes, Scheme 2.[12] Thus, primary alkenes such as 1-hexene, 1-heptene, 1-octene, 1-decene, and styrene all gave high yields of the corresponding *n*-alkanes with up to 2% yield of a mixture of alkene isomers. Similarly, cyclic alkenes such as cyclohexene, cyclooctene, and cyclododecene also gave very high yields of the corresponding cycloalkanes. It should be noted that the nonamphiphilic polyethylenimine itself was also very effective for the stabilization of palladium nanoparticles, but the hydrogenation of 1-octene, under identical reaction conditions as presented in Scheme 2, proceeded poorly with only 21% 1-octene conversion at 58% selectivity to *n*-octane (the remaining products were isomers of linear octene). Importantly, using this aqueous biphasic reaction system, it was simple to recover and recycle the catalyst containing aqueous phase by decantation of the product from the aqueous phase. Thus, over five reaction cycles, using 1-octene as substrate, yields of >99% *n*-octane were obtained. A transmission electron micrograph after a catalytic reaction showed no significant change in nanoparticle size and no significant aggregation of the particles.

Scheme 2. Hydrogenation of Hydrophobic Alkenes in an Aqueous Biphasic Reaction Medium with a Pd_n-Alkylated PEI Catalyst



R	yield
C_4H_9	>99
C_5H_{11}	98.2
C_6H_{13}	>99
C_8H_{17}	98.8
Ph	>99

n	yield
1	>99
3	>99
7	>99

Interestingly, however, the hydrogenation of 2-methyl-1-heptene under conditions described in Scheme 1, yielded only 57.4 mol % 2-methylheptane although the conversion was >98%; the remaining product was the 2-methyl-2-heptene isomer. Furthermore, 2-methyl-2-heptene did not react at all as was observed also in a separate experiment. These results indicated that sterically hindered alkenes did not undergo hydrogenation; this was verified by competition reactions between 1-octene/2-methyl-2-heptene and 3-methylcyclohexene/1-methylcyclohexene as shown in Figure 2. Both hydrogenation reactions showed entirely chemoselective hydrogenation of the less hindered alkenes, 1-octene and 3-methylcyclohexene. Furthermore, the kinetic profiles show in absolute terms that the more hindered, though reactive, 3-methylcyclohexene is reduced more slowly than 1-octene. Additional manifestation of the chemoselectivity observed can be noted in the competitive hydrogenation of 1-methylcyclohexene and 1-phenylcyclohexene. Since the planar phenyl moiety is sterically less demanding than the spherical methyl moiety, 1-phenylcylohexene is selectively reduced. There are three additional points worth mentioning. First, there is no apparent selectivity in the hydrogenation of *cis*- and *trans*-alkenes. Thus, hydrogenation of a 1:1 mixture of *cis*- and *trans*-stilbene resulted in the formation of bibenzyl with reduction of both substrates at the same rate and completion of the hydrogenation within 2 h. Second, the aqueous biphasic hydrogenation was faster than a monophasic reaction attained by using a 1:1 water/methanol solvent, though the *chemoselective nature of the hydrogenation reactions was fully retained*. Third, the classic Pd/C catalyst (substrates, 0.5 mmol each; 5% Pd/C, 0.02 g; MeOH, 1 mL; H_2, 2 bar; 80 °C, 6 h) showed no evidence of chemoselectivity in the reduction of the pairs of alkenes shown in Figure 2. These experiments would appear to indicate that the source of the chemoselectivity in these palladium nanoparticle−alkylated PEI catalytic systems is a different accessibility of hindered versus nonhindered alkenes to the palladium surface due to the structure of

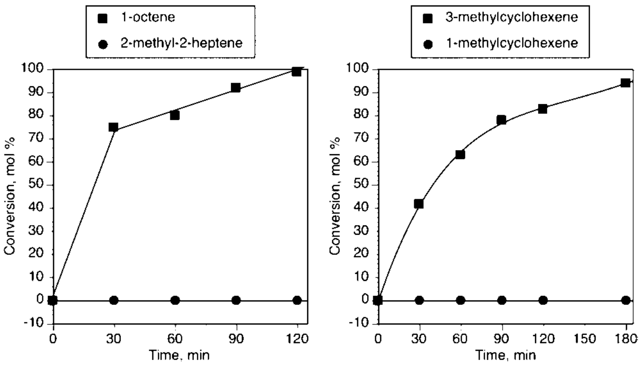


Figure 2. Reaction profiles for competitive hydrogenation of alkenes with different steric demand.

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(10) **Synthesis of the Alkylated PEI.** Polyethelenimine 60,000 (4 g) was dissolved in 200 mL of dry ethanol. 1-Iodododecane (3.33 mL, 13.5 mmol) was added, and the mixture was refluxed for 15 h. The reaction mixture was cooled, 10 g of the Amberlite IR-900 was added, and the suspension obtained was stirred for 3 h and then filtered. The filtrate was concentrated under reduced pressure and dried under high vacuum for 24 h yielding a yellow glassy compound that was used without any further purification: ^1H NMR (D_2O) δ 0.84 (br s), 1.25 (br s), 2.76 (br m) ppm; ^{15}N NMR (D_2O) δ 25.35, 27.17, 31.03, 32.66 ppm; IR (film cast from THF) ν 3408, 2954, 2923, 2852, 1552, 1466, 1376, 1361, 1304, 1101, 802, 721 cm^{-1}. **Synthesis of Palladium Nanoparticles Stabilized by Alkylated PEI.** K_2PdCl_4 (0.031 g, 0.09 mmol) and alkylated PEI (0.32 g) were dissolved in 10 mL of double-distilled water. To this vigorously stirred mixture was added $NaBH_4$ (0.1 mmol in 1 mL of water), and the mixture immediately turned brown-black.

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(12) **Typical Catalytic Hydrogenation.** A 15 mL Ace Glass pressure tube was loaded with 1 mL of the Pd_n-alkylated PEI dispersion (0.0082 mmol of Pd) and 1 mmol of alkene and then pressurized to 2 bar with hydrogen. The pressure tube was placed in an oil bath thermostated at 80 °C to initiate the reaction. Aliquots of the organic phase were analyzed by gas chromatography using a 5% phenylmethylsilicone capillary column.

alkylated PEI rather than mass transfer effects. Future research will be devoted to better understanding the source of the chemoselectivity.

Commonly, chemoselectivity is the purview of homogeneous catalysis and is realized by control of the ligand environment around the active metal center as is the case for alkene hydrogenation using the Wilkinson catalyst $RhCl(PPh_3)_3$.[13] Here, we have observed that a “semi-heterogeneous” metal cluster without a designed or defined ligand environment also displayed very significant chemoselectivity in a rather elementary hydrogenation of simple hydrophobic alkenes.[14] The aqueous biphasic reaction medium also allows for the ecologically preferred use of water as solvent coupled with effective catalyst recovery and recycle.

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Supporting Information Available: Transmission electron micrograph of the Pd nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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