Selective Semihydrogenation of Alkynes on Shape-Controlled Palladium Nanocrystals

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Abstract: A systematic study on the selective semihydrogenation of alkynes to alkenes on shape-controlled palladium (Pd) nanocrystals was performed. Pd nanocrystals with a cubic shape and thus exposed $\{100\}$ facets were synthesized in an aqueous solution through the reduction of Na₂PdCl₄ with L-ascorbic acid in the presence of bromide ions. The Pd nanocubes were tested as

Introduction

Selective semihydrogenation of alkynes to alkenes is of great importance in the production of olefins in relation to the synthesis of natural products and fine chemicals.^[1] Palladium is one of the most widely used catalysts for hydrogenation reactions,^[2] but it usually exhibits low alkene selectivity in alkyne hydrogenation owing to its high efficiency in promoting the addition of hydrogen to carbon–carbon double bonds, which leads to further reduction into alkanes. Traditionally, the use of the Lindlar catalyst, which consists of deactivated palladium supported on CaCO₃ or BaCO₃, has

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catalysts for the semihydrogenation of various alkynes such as 5-decyne, 2butyne-1,4-diol, and phenylacetylene. For all substrates, the Pd nanocubes exhibited higher alkene selectivity (>

Keywords: chemoselectivity • hydrogenation • nanocrystals • nanocubes • palladium 90%) than a commercial Pd/C catalyst (75–90%), which was attributed to a large adsorption energy of the carbon–carbon triple bond on the {100} facets of the Pd nanocubes. Our approach based on the shape control of Pd nanocrystals offers a simple and effective route to the development of a highly selective catalyst for alkyne semihydrogenation.

been the method of choice for semihydrogenation of alkynes owing to its high alkene selectivity, although Pd/C catalysts have also been employed.^[3–5] The Lindlar catalysts are usually poisoned by a lead complex, with quinoline as an additional poison, to enhance the alkene selectivity. This makes the Lindlar catalysts often suffer from the production of harmful wastes due to the incorporation of toxic additives.^[5]

The catalytic properties of metal nanocrystals can be drastically enhanced by the control of their shapes, which determine surface atomic arrangements and thus affect activity and/or selectivity toward a specific catalytic reaction.^[6] Here we demonstrate that for alkyne hydrogenation, high alkene selectivity can be achieved simply by shaping Pd nanocrystals to expose facets that favor the adsorption of alkyne. In this work, we synthesized Pd nanocrystals with a cubic shape and thus exposed {100} facets and then applied them to selective semihydrogenation of various alkynes including 5-decyne, 2-butyne-1,4-diol, and phenylacetylene. For all substrates, the Pd nanocubes exhibited higher alkene selectivity (>90%) as compared to commercial Pd/C catalyst (75–90%). Our results show great promise for the development of highly efficient and reliable catalysts for selective semihydrogenation of alkynes without employing toxic additives.

Results and Discussion

Palladium nanocubes were synthesized using a previously reported method.^[7] A typical transmission electron microscopy (TEM) image of the as-prepared Pd nanocrystals showed the formation of nanocubes as major product in addition to a small portion of nanobars that were slightly elongated along one direction (Figure 1 a). The nanocubes exhib-



Figure 1. Characterization of Pd nanocubes. a) TEM image, b) particle size distribution, and c) powder XRD pattern. d) HRTEM image of a single Pd nanocube shown in (a) and the corresponding FT pattern (inset).

it an average edge length of approximately 11 nm (Figure 1 b). The powder X-ray diffraction (XRD) pattern of the Pd nanocubes (Figure 1 c) shows that they have a face-centered cubic (fcc) structure (*Fm3m*, a=3.958 Å, JCPDS Card No. 87-0641). The six faces of a Pd nanocube are bounded by {100} facets, as revealed by high-resolution TEM (HRTEM) imaging and the array of spots with square symmetry in the corresponding Fourier-transform (FT) pattern (Figure 1 d).

We first investigated the catalytic properties of the Pd nanocubes toward the hydrogenation of 5-decyne (Scheme 1 a) and compared them with those of a commercial Pd/C catalyst (10 wt. % of ca. 3 nm Pd nanoparticles on activated carbon support, Figure 2). The hydrogenation reactions of 5-decyne were conducted at room temperature under 1 atm hydrogen pressure with initial sample concentrations of about 0.20 m in ethanol and 1.0 mol% of the Pd nanocubes or commercial Pd/C catalyst. The reactant and product distribution was evaluated by gas chromatography (GC) analysis. When the reaction was catalyzed by the Pd nanocubes, high selectivity (95%) toward cis-5-decene was observed at about 98% conversion of 5-decyne (Table 1). After full conversion of 5-decyne, 5-decene was readily overhydrogenated to decane (Figure 3a), which indicates that the {100} facets on the Pd nanocubes also catalyzed the hydrogenation of 5-decene effectively. It is worth noting that the semihydrogenation and the overhydrogenation stages are well separated, as shown in Figure 3a. In the case of the commercial Pd/C catalyst, however, semihydrogenation was accompanied by significant overhydrogenation, even at low conversion of 5-decyne (Figure 3b), resulting in the formation of a 75:20 mixture of 5decene/decane at about 95% conversion of 5-decyne (Table 1). This observation clearly demonstrates the higher alkene selectivity of the Pd nanocubes for the semihydrogenation of 5-decyne as compared to the commercial Pd/C catalyst.

We also carried out hydrogenation of 2-butyne-1,4-diol and phenylacetylene (Scheme 1,b and c). At full conversion, the Pd nanocubes exhibited high alkene selectivities of 98 and 91% for the semihydrogenation of 2-butyne-1,4-diol and phenylacetylene, respectively (Table 1 and Figure 3,c and e). On the contrary, the commercial Pd/C catalyst resulted in the formation of an 88:11 mixture of 2-

butene-1,4-diol/butane-1,4-diol at a full conversion of 2butyne-1,4-diol and an 80:19 mixture of styrene/ethylbenzene at 99% conversion of phenylacetylene (Table 1 and Figure 3,d and f). These results suggest that the Pd nanocubes could be applied as a highly selective catalyst for the semihydrogenation of various alkynes.



Scheme 1. Reaction pathways for the hydrogenation of a) 5-decyne, b) 2butyne-1,4-diol, and c) phenylacetylene.

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Figure 2. a) TEM image of the commercial Pd/C catalyst used. b) HRTEM image of a single Pd nanocrystal shown in (a). The inset shows the corresponding FT pattern.

Table 1. Product distribution in the hydrogenation of alkynes.^[a]

Substrate	Catalyst	Product distribution [%] ^[b]	
		cis-Alkene ^[c]	Alkane
5-decyne	Pd nanocubes	95	3
	Pd/C	75	20
2 huture 1.4 diel	Pd nanocubes	98	2
2-001yne-1,4-0101	Pd/C 88	88	11
nhanulaaatulana	Pd nanocubes	91	9
phenylacetylene	Pd/C	80	19

[a] Reaction conditions: Substrate (0.20 M) in ethanol and 1.0 mol % of catalyst at room temperature and 1 bar hydrogen pressure. [b] All the products were identified by comparison with authentic samples using GC analysis. [c] Formation of *trans*-alkene was not detected by GC analysis.

We then investigated the effect of the catalyst concentration on the product distribution in the hydrogenation of 5decyne. Higher alkene selectivities were still observed in the reactions in which Pd nanocubes were used at concentrations ranging from 0.5 to 2.0 mol%; by contrast, reactions with the Pd/C catalyst showed lower alkene selectivity in the same range of concentrations (Figure 4). The result illustrate that higher alkene selectivity of the Pd nanocubes in the semihydrogenation of alkynes originated from their shape rather than catalyst concentration; thus, the chemoselective reduction of alkynes by shape-controlled Pd nanocrystals is a feasible process.

Representative TEM images of the Pd nanocubes obtained after the hydrogenation of 5-decyne confirmed their morphological stability (Figure 5), thus strongly suggesting that the nanocrystal shape was indeed responsible for the observed catalytic behavior. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis revealed that Pd apparently did not leach from the Pd nanocubes into the solution during the reaction. The as-synthesized Pd nanocubes may contain residual bromide ions adsorbed on their surface. The X-ray photoelectron spectroscopy (XPS) analysis of the Pd nanocubes revealed the presence of Br signals even after extensive washing of the nanocubes with ethanol and water (Figure 6), which implies that it is very difficult to completely remove bromide ions from the nanocube surface. We therefore examined whether bromide ions adsorbed on the surface of Pd nanoparticles affect their catalytic behavior. To this end, the hydrogenation of 5-decyne was carried out with a Pd/C catalyst that had been pre-treated with KBr. We did not observe any noticeable change in the catalytic behavior of the Pd/C catalyst before and after the treatment with bromide ions (Figure 7). Our results suggest that bromide ions adsorbed on the surface of Pd nanoparticles do not have a significant effect on the behavior of the catalyst in alkyne hydrogenation.

We propose that the higher alkene selectivity of the Pd nanocubes may arise from a large difference in the adsorption energies of alkynes and alkenes on their surface. In hydrogenation, the adsorption strengths of substrates on a given metal surface are known to increase in the order of alkane < alkene < alkyne.^[8] To investigate the surface structure-sensitive adsorption of alkynes and alkenes, we performed density functional theory (DFT) calculations taking acetylene and ethylene as model molecules. Figure 8 illustrates the lowest energy states for the adsorption of acetylene and ethylene (-2.61 eV) is much larger than that of ethylene (-0.96 eV; see Table 2). Furthermore, the differ-

Table 2. Adsorption energies of acetylene and ethylene on Pd(100) and Pd(111) surfaces.

	D 1 4	Adsorption energy [eV]	
Substrate	Pd surface		
Asstulans	(100)	-2.61	
Acetylene	(111)	-2.01	
Etherless	(100)	-0.96	
Ethylene	(111)	-0.88	

ence in binding energies between acetylene and ethylene was larger on Pd(100) ($\Delta E = 1.65 \text{ eV}$) than on Pd(111) ($\Delta E = 1.13 \text{ eV}$), thus suggesting that Pd(100) is better suited for the selective binding of acetylene than Pd(111). The Pd nanocubes would favor the adsorption of alkynes owing to the predominant exposure of {100} facets on their surfaces. During the semihydrogenation, unreacted alkynes could readily substitute freshly formed alkenes on the {100} facets of the Pd nanocubes and thus impede the overhydrogenation into alkanes, which apparently contributes to the high alkene selectivity. Once alkynes have been consumed, alkenes could be adsorbed on the {100} facets of the Pd nano-



Figure 3. Hydrogenation of various alkynes on a, c, e) Pd nanocubes and b, d, f) commercial Pd/C catalyst. Substrates: a, b) 5-decyne; c, d) 2-butyne-1,4-diol; and e, f) phenyl acetylene.

cubes and then be hydrogenated to alkanes, as demonstrated in Figure 3. Meanwhile, small Pd nanoparticles on the Pd/C catalyst have a truncated octahedral shape, whose surface is bound by a mix of {100} and {111} facets (Figure 2b). This shape also contains a large fraction of edge atoms, which serve as active sites not only for the semihydrogenation but also for the overhydrogenation due to increased adsorption strength of alkenes^[9] and thus lower the overall alkene selectivity.

We have also carried out hydrogenation of several internal and terminal alkynes using the Pd nanocubes as catalysts. As summarized in Table 3, hydrogenation reactions using the Pd nanocubes exhibited extremely high *cis*-alkene selectivities regardless of the location of the triple bond in alkynes. In all the cases examined in the reduction of internal alkynes with the Pd nanocubes, no trace of *trans*-alkene as product was detected (Table 3, entries 3–6). Moreover, overhydrogenation to alkane could be suppressed almost completely by lowering the reaction temperature to 0°C (Table 3, entry 6). For comparison, reduction of 5-decyne to 5decene was carried out employing 1.0 mol% Lindlar catalyst. After a reaction time of 18 h, a mixture of products was obtained consisting of 93.2% cisdecene and 4.9% trans-decene (Table 3, entry 7). The Lindlar catalyst is known to be very efficient for the semihydrogenation of alkynes to cis-alkenes, but reactions with this catalysts often suffer from Z/E isomerization, low reactivity, and poor reproducibility.^[11] On the contrary, the reactions with Pd nanocubes consistently showed higher reactivity and much more enhanced cis-alkene selectivity than those with the Lindlar catalyst. Furthermore, Pd nanocubes could be easily recovered by filtration, which offers a very convenient way to recycle the catalyst.

Conclusions

In summary, we have studied the hydrogenation of alkynes on shape-controlled Pd nanocrystals enclosed by {100} facets. The Pd nanocubes exhibited higher alkene selectivity in

the semihydrogenation of various alkynes including 5decyne, 2-butyne-1,4-diol, and phenylacetylene than a commercial Pd/C catalyst owing to the predominant exposure of

Table 3. Selective hydrogenation of alkynes using Pd nanocubes.^[a]

Alkane
8.6
12.7
7.3
6.6
7.8
0.2
0.0

[a] Reaction conditions: Substrate (0.20 M) and 1.0 mol % of catalyst in ethanol were stirred at room temperature under 1 atm hydrogen pressure. [b] The reaction was carried out at 0°C. [c] Lindlar catalyst (1 mol %, Acros) was used instead of Pd nanocubes.



Figure 4. Hydrogenation of 5-decyne on a) 0.5 mol% Pd nanocubes, b) 1.5 mol% Pd nanocubes, c) 2.0 mol% Pd nanocubes, d) 0.5 mol% Pd/C, e) 1.5 mol% Pd/C, and f) 2.0 mol% Pd/C.

{100} facets on their surface. The Pd nanocubes also had a *cis*-selectivity superior to that of the traditional Lindlar catalyst in the reduction of internal alkynes. Our results demonstrate that shape control of Pd nanocrystals provides a simple and efficient way for generating highly selective catalysts for alkyne semihydrogenation. The shape-controlled Pd nanocrystals reported herein could serve as attractive candidates for the fundamental study of shape effects of nanocrystals on various Pd-based catalytic reactions.

Experimental Section

Materials

Lindlar catalyst (5 wt% palladium on calcium carbonate; poisoned with lead) was purchased from Acros Organics (CAS no. 7440-05-3) and Pd/C (Palladium, 10 wt% on activated carbon, Degussa type) was purchased

from Aldrich (Catalog no. 330108). All other commercial materials were purchased from Aldrich Chemical Co. or Tokyo Chemical Industry Co. and were used without further purification.

Synthesis of Pd Nanocubes

In a typical procedure, an aqueous solution containing poly(vinylpyrrolidone) (PVP, MW=55000, 11 mL, 105 mg), L-ascorbic acid (60 mg), KBr (200 mg), and Na₂PdCl₄ (57 mg) was heated at 80 °C in air under magnetic stirring for 3 h and then cooled to room temperature.

Alkyne Hydrogenation

Pd catalyst and degassed ethanol (2.0 mL) were added to a 5 mL roundbottom flask, and the mixture was sonicated in an ultrasonic bath for 10 min. After sonication, substrate (0.40 mmol) was added to the flask and the mixture was stirred at room temperature under a hydrogen balloon. The course of the reaction was periodically followed by analyzing aliquots (10 μ L) by gas chromatography (GC) on a Hewlett Packard 5890 instrument.

Characterization

TEM studies were done with a LIBRA 120 (Carl Zeiss) microscope operated at 120 kV by drop casting a dispersion of nanoparticles on a carbon-coated copper grid. HRTEM analyses were performed using a JEOL 2100F instrument operated at 200 kV accelerating voltage. Powder XRD measurements were conducted using an M18XHF-SRA (Mac Science) diffractometer equipped with а CuK α radiation source ($\lambda =$ 1.5406 Å) at 40 kV and 300 mA (12 kW). GC analyses were performed with a HP-6980 gas chromatograph using a HP-5 capillary column (30 m×

0.25 mm; coating thickness 0.25 µm).

DFT calculations

First-principles calculations were performed to estimate the adsorption energies of acetylene and ethylene on the Pd surface using the Vienna Ab Initio Simulation Package (VASP).^[12] In the calculations, the molecules are adsorbed on a Pd slab, which has a periodic 2×2 unit cell with 4 and 5 layers for (100) and (111) surfaces, respectively. A vacuum layer of 12 A was used to separate the metal slabs. Then, the adsorption energy of the molecules was calculated by the following equation;

$$\Delta E_{\rm ads} = E_{\rm adsorbed \ system} - (E_{\rm clean \ metal \ slab} + E_{\rm gas})$$

Ultra-soft pseudopotentials^[13] were employed within a cut-off energy of 500 eV. Exchange correlation potential used in this calculation was Perdew Wang (PW-91),^[14] and the electron density was converged within a tolerance of 1×10^{-5} eV. The Monkhorst–Pack scheme was used to generate a k-point grid in the Brillouin zone, and the $7 \times 7 \times 1$ k-point grid was adapted for both Pd(111) and Pd(100) slabs.

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Figure 5. TEM images of Pd nanocubes obtained after the hydrogenation of 5-decyne.



Figure 6. Br 3d XPS core level spectrum taken of the Pd nanocubes after extensive washing with ethanol and water. In the spectrum, the Br $3d_{5/2}$ and Br $3d_{3/2}$ binding energies were 67.6 and 68.5 eV, respectively, which are close to the literature values for Br^{-[9]}

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Figure 7. Hydrogenation of 5-decyne on 2.0 mol% Pd/C catalyst pretreated with bromide ions. The pre-treatment was conducted by heating 11 mL of an aqueous mixture containing the commercial Pd/C catalyst (200 mg) and KBr (200 mg) at 80 °C for 3 h.



Figure 8. Illustrations of the lowest energy adsorption modes of acetylene and ethylene on Pd(100) and Pd(111): a) acetylene on a 4-fold hollow site of Pd(100); b) ethylene on a 2-fold aligned bridge site of Pd(100); c) acetylene on a 3-fold hcp site of Pd(111); and d) ethylene on a 2-fold aligned bridge site of Pd(111).

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