

## Nanoscale Palladium Cluster Immobilized on a TiO<sub>2</sub> Surface as an Efficient Catalyst for Liquid-phase Wacker Oxidation of Higher Terminal Olefins

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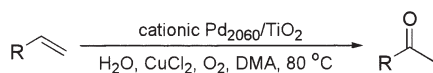
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A Pd nanocluster immobilized on a TiO<sub>2</sub> surface acted as an efficient catalyst for the liquid-phase Wacker oxidation of higher terminal olefins in the presence of water and CuCl<sub>2</sub> under an O<sub>2</sub> atmosphere.

The Wacker oxidation is a powerful method to the synthesis of methyl ketones from terminal olefins, catalyzed by an aqueous solution of Pd<sup>II</sup> salt combined with Cu<sup>II</sup> and HCl under aerobic conditions.<sup>1</sup> HCl is required to achieve a favorable reoxidation of Pd<sup>0</sup> by Cu<sup>II</sup> ions, and to prevent aggregation of transient atomic Pd<sup>0</sup> species to inactive Pd precipitates. However, an acidic chloride medium not only corrodes the reactor wall, but also leads to formation of chlorinated by-products. Hence, much effort has been devoted to the development of HCl-free Wacker systems.<sup>2-4</sup> The vapor-phase Wacker oxidation of light olefins progresses substantially by solid Pd catalysts combined with Cu ions or alternative reoxidants,<sup>3</sup> but there are few heterogeneous catalysts for the Wacker oxidation of unreactive higher terminal olefins in liquid phase. Pd complex catalysts immobilized on organic and inorganic supports have been reported for this purpose,<sup>4</sup> but some catalyst systems require an acid of CH<sub>3</sub>SO<sub>3</sub>H and exhibit poor activity, selectivity, and stability.

We have pioneered a method for the synthesis of a mono-dispersed Pd nanocluster having a mixed-valence state of Pd<sup>0</sup>, Pd<sup>I</sup>, and Pd<sup>II</sup> to afford Pd<sub>2060</sub>(NO<sub>3</sub>)<sub>360</sub>(OAc)<sub>360</sub>O<sub>80</sub> (cationic Pd<sub>2060</sub>).<sup>5</sup> The unique catalytic abilities of the cationic Pd<sub>2060</sub> nanocluster were exploited for liquid-phase acetoxylation of toluene<sup>5a</sup> and dehydrogenation of allylic alcohols<sup>5b</sup> under an O<sub>2</sub> atmosphere. The cationic Pd<sub>2060</sub> cluster could be immobilized on a TiO<sub>2</sub> surface while retaining the cluster size and surface ordering of the Pd atoms, thus providing a new type of heterogeneous catalyst.<sup>5</sup> Herein, we found the nanoscale Pd<sub>2060</sub> cluster immobilized on a TiO<sub>2</sub> surface acts as an efficient catalyst for the liquid-phase Wacker oxidation of higher terminal olefins under acid-free conditions (Scheme 1).



**Scheme 1.**

The cationic Pd<sub>2060</sub> nanocluster was prepared by treatment of Pd<sub>4</sub>phen<sub>2</sub>(CO)<sub>2</sub>(OAc)<sub>4</sub> (phen = 1,10-phenanthroline)<sup>6</sup> with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O under atmospheric O<sub>2</sub>.<sup>5a</sup> Using the neutral TiO<sub>2</sub> as a support,<sup>7</sup> the above procedure afforded an immobilized cationic Pd<sub>2060</sub> nanocluster (cationic Pd<sub>2060</sub>/TiO<sub>2</sub>) having a mean diameter and standard deviation ( $d \pm \sigma$ ) of  $38 \pm 2.1$  Å.<sup>5b</sup>

Oxidations of 1-decene were carried out using the cationic Pd<sub>2060</sub> nanocluster as summarized in Table 1.<sup>8</sup> The cationic

Pd<sub>2060</sub> nanocluster showed high catalytic activity in the presence of water and CuCl<sub>2</sub>·2H<sub>2</sub>O under O<sub>2</sub> at atmospheric pressure to afford 2-decanone selectively (entry 1). The catalytic activity of the cationic Pd<sub>2060</sub> cluster was higher than that of the Pd<sub>560</sub>(NO<sub>3</sub>)<sub>100</sub>(OAc)<sub>250</sub>O<sub>10</sub> (entry 2).<sup>5</sup> Immobilization of active metal species on a solid surface makes the workup strikingly simple.<sup>9</sup> In the present oxidation, the cationic Pd<sub>2060</sub> nanocluster immobilized on the TiO<sub>2</sub> could maintain the high catalytic activity and selectivity (entry 3). Water, O<sub>2</sub>, and CuCl<sub>2</sub>·2H<sub>2</sub>O were necessary to obtain high yields of 2-decanone.<sup>10</sup> Among the metal chlorides tested, CuCl<sub>2</sub>·2H<sub>2</sub>O was the most effective (entries 3–6). Only 3 equivalents of CuCl<sub>2</sub> to Pd were sufficient for achieving high catalytic activity. Other copper(II) compounds, such as Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, barely functioned as reoxidants (entries 7 and 8). *N,N*-Dimethylacetamide was the best solvent. Use of 1,4-dioxane, *N,N*-dimethylformamide, ethanol, and acetic acid resulted in low yields of 2-decanone (entries 9–12). A similar solvent effect has been observed in homogeneous Wacker catalyst systems.<sup>2b,11</sup> It is notable that the cationic Pd<sub>2060</sub> nanocluster catalyst enables the Wacker oxidation in liquid phase under acid-free conditions.

The cationic Pd<sub>2060</sub>/TiO<sub>2</sub> catalyst selectively oxidized terminal olefins such as 1-hexene, 1-octene, 1-decene, 1-dodecene, vinylcyclohexane, and *n*-butyl vinyl ether to give the corresponding methyl ketones and *n*-butyl acetate, respectively, in high yields (entries 13, 15–19). The oxidation of an internal olefin of *cis*-2-decene, however, resulted in low yields of 2-decanone (20%) and 3-decanone (10%). A cyclic olefin such as cyclopentene was scarcely oxidized under the present conditions. The reactivity of olefins with the cationic Pd<sub>2060</sub>/TiO<sub>2</sub> catalyst resembles that of the conventional Wacker system.<sup>1</sup>

As 1-decene was consumed, additional 1-decene was added to the reaction mixture. As shown in Figure 1, the oxidations in the second and third runs proceeded at similar reaction rates. Increasing the oxygen pressure accelerated the reaction rate; oxidation of 1-decene afforded a 99% yield of 2-decanone within 1 h under 3 atm of O<sub>2</sub>. The spent catalyst was easily separated from the reaction mixture by filtration and could be reused with retention of high activity and selectivity (entry 14). However, no oxidation occurred when the filtrate was reacted for an additional 2 h. This Wacker oxidation occurs at the interface between the Pd cluster surface and liquid phase, and the Pd nanocluster provides a unique acid-free Wacker oxidation system for higher terminal olefins.

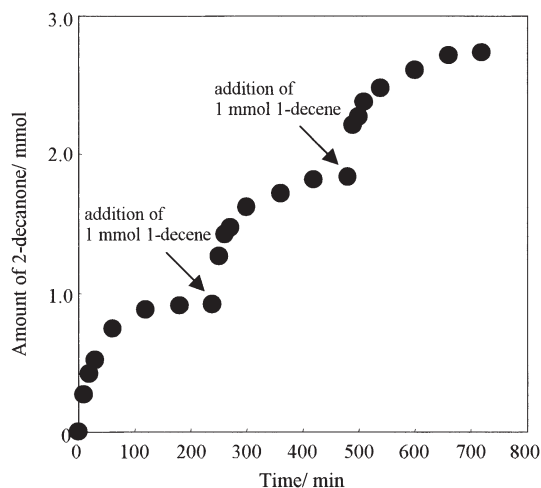
An isotopic experiment using H<sub>2</sub><sup>18</sup>O in the cationic Pd<sub>2060</sub>/TiO<sub>2</sub>-catalyzed oxidation of 1-decene led to formation of <sup>18</sup>O-labeled 2-decanone exclusively. The oxygen atom incorporated into 2-decanone stems from water. The molar ratio of O<sub>2</sub> uptake to 2-decanone was 1:2. The present oxidation occurred via the Pd<sup>II</sup>

**Table 1.** Wacker oxidation of terminal olefins catalyzed by cationic Pd nanoclusters under acid-free conditions<sup>a</sup>

Entry	Substrate	Catalyst	Additive	Solvent	Time/h	Convsn/% <sup>b</sup>	Yield/% <sup>b,c</sup>
1	1-Decene	cationic Pd <sub>2060</sub> <sup>d</sup>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA <sup>e</sup>	1	80	77
2		cationic Pd <sub>560</sub> <sup>f</sup>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	1	61	59
3		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	1	77	74
4		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	FeCl <sub>3</sub> ·6H <sub>2</sub> O	DMA	1	64	62
5		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CoCl <sub>2</sub> ·6H <sub>2</sub> O	DMA	1	56	55
6		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	MnCl <sub>2</sub> ·6H <sub>2</sub> O	DMA	1	14	12
7		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	DMA	1	<1	Trace
8		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	DMA	1	<1	Trace
9		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	1,4-Dioxane	1	23	19
10		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMF <sup>g</sup>	1	14	12
11		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	EtOH	1	10	8
12		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	AcOH	1	2	Trace
13		cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	2	91	88
14 <sup>h</sup>		reuse	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	2	91	87
15 <sup>i</sup>	1-Hexene	cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	2	96	94
16	1-Octene	cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	2	86	84
17	1-Dodecene	cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	2	85	83
18 <sup>j</sup>	Vinylcyclohexane	cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	3	92	92
19	<i>n</i> -Butyl vinyl ether	cationic Pd <sub>2060</sub> /TiO <sub>2</sub>	CuCl <sub>2</sub> ·2H <sub>2</sub> O	DMA	2	91	91

<sup>a</sup>Substrate (1 mmol), Pd (0.01 mmol), solvent (4 mL), additive (0.03 mmol), H<sub>2</sub>O (0.5 mL), 80 °C, O<sub>2</sub> atmosphere. <sup>b</sup>Determined by GC analysis using an internal standard technique. <sup>c</sup>Yield of the corresponding methyl ketones. By-products were isomerized internal olefins.

<sup>d</sup>Pd<sub>2060</sub>(NO<sub>3</sub>)<sub>360</sub>(OAc)<sub>360</sub>O<sub>80</sub>. <sup>e</sup>*N,N*-dimethylacetamide. <sup>f</sup>Pd<sub>560</sub>(NO<sub>3</sub>)<sub>100</sub>(OAc)<sub>250</sub>O<sub>10</sub> (see, ref. 5). <sup>g</sup>*N,N*-dimethylformamide. <sup>h</sup>The spent catalyst from entry 13 was used. <sup>i</sup>50 °C. <sup>j</sup>60 °C.



**Figure 1.** Time profile of the Wacker oxidation of 1-decene catalyzed by a cationic Pd nanocluster immobilized on TiO<sub>2</sub>. Reaction conditions: Pd 0.01 mmol, CuCl<sub>2</sub>·2H<sub>2</sub>O 0.03 mmol, H<sub>2</sub>O 0.5 mL, DMA 4 mL, 80 °C, O<sub>2</sub> atmosphere.

species on the Pd nanocluster surface. Use of even small amounts of CuCl<sub>2</sub> efficiently promoted the reoxidation of Pd<sup>0</sup> to Pd<sup>II</sup> species, which might be ascribed to a cooperative action of Pd<sup>II</sup>, Pd<sup>I</sup>, and Pd<sup>0</sup> species on the cluster surface.

In conclusion, a Pd nanocluster immobilized on a TiO<sub>2</sub> surface acted as a highly active and recyclable catalyst for the Wacker oxidation of higher terminal olefins without acid additives. Further studies on the scope and limitation of this Wacker oxidation are currently in progress.

#### References and Notes

1 An excellent review of the Wacker oxidation: J. Tsuji, *Synthesis*, **1984**, 369; J. Tsuji, "Palladium Reagents and Catalysts Innovations in

Organic Synthesis," John Wiley & Sons, New York (1998).

- Recent examples of the acid-free homogeneous catalyst system for the Wacker oxidation of higher olefins, see, Pd-Cu complexes: a) T. Hosokawa, M. Takano, and S.-I. Murahashi, *J. Am. Chem. Soc.*, **118**, 3990 (1996). PdCl<sub>2</sub>-Cu(OAc)<sub>2</sub>: b) A. B. Smith, III, Y. S. Cho, and G. K. Friestad, *Tetrahedron Lett.*, **39**, 8765 (1998). Pd-amine complexes: c) G.-J. ten Brink, I. W. C. E. Arends, G. Papadogianakis, and R. A. Sheldon, *Chem. Commun.*, **1998**, 2359. d) T. Nishimura, N. Kakiuchi, T. Onoue, K. Ohe, and S. Uemura, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1915.
- A recent review of the vapor-phase Wacker oxidation of light olefins by heterogeneous catalysts: D. E. De Vos, B. F. Sels, and P. A. Jacobs, *Adv. Catal.*, **46**, 1 (2001).
- Pd complex-immobilized catalysts for the Wacker oxidation of higher olefins in liquid phase, see, PdCl<sub>2</sub>-CuCl<sub>2</sub>/pore glass: a) J. P. Arhancet, M. E. Davis, and B. E. Hanson, *Catal. Lett.*, **11**, 129 (1991). PdCl<sub>2</sub>-CuCl<sub>2</sub>/*N*-cyanomethylated polybenzimidazole: b) H. G. Tang and D. C. Sherrington, *J. Catal.*, **142**, 540 (1993). Pd(OAc)<sub>2</sub>-molybdovanadophosphate/carbon with CH<sub>3</sub>SO<sub>3</sub>H: c) A. Kishi, T. Higashino, S. Sakaguchi, and Y. Ishii, *Tetrahedron Lett.*, **41**, 99 (2000).
- a) K. Ebitani, K.-M. Choi, T. Mizugaki, and K. Kaneda, *Langmuir*, **18**, 1849 (2002). b) K.-M. Choi, T. Akita, T. Mizugaki, K. Ebitani, and K. Kaneda, *New J. Chem.*, in press.
- I. I. Moiseev, *J. Organomet. Chem.*, **488**, 183 (1995).
- TiO<sub>2</sub> was supplied from the Catalysis Society of Japan as JRC-TIO-2 (anatase, BET surface area: 14 m<sup>2</sup>g<sup>-1</sup>), and is characterized by its low acidity and basicity compared with other TiO<sub>2</sub> reference samples.
- A typical example for the oxidation of 1-decene catalyzed by the cationic Pd<sub>2060</sub>/TiO<sub>2</sub> is as follows. Into a reaction vessel equipped with a reflux condenser and balloon were placed the cationic Pd<sub>2060</sub>/TiO<sub>2</sub> (0.0394 g, Pd: 0.01 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (0.0054 g, 0.03 mmol). After the reaction vessel was filled with O<sub>2</sub>, *N,N*-dimethylacetamide (4 mL), H<sub>2</sub>O (0.5 mL), and 1-decene (0.14 g, 1 mmol) was added. Then, the reaction mixture was vigorously stirred at 80 °C for 2 h. The catalyst was separated by filtration, and GC analysis of the filtrate showed 88% yield of 2-decanone.
- a) I. W. C. E. Arends and R. A. Sheldon, *Appl. Catal., A*, **212**, 175 (2001). b) K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, and K. Kaneda, *J. Am. Chem. Soc.*, **124**, 11572 (2002).
- Absence of O<sub>2</sub>, H<sub>2</sub>O, or CuCl<sub>2</sub>·2H<sub>2</sub>O resulted in less than a 1% yield of 2-decanone.
- W. H. Clement and C. M. Selwitz, *J. Org. Chem.*, **29**, 241 (1964).