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# Highly efficient Wacker oxidation catalyzed by heterogeneous Pd montmorillonite under acid-free conditions

Takato Mitsudome, Takuya Umetani, Kohsuke Mori, Tomoo Mizugaki,
Kohki Ebitani and Kiyotomi Kaneda*

*Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan*

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**Abstract**—Palladium-montmorillonite was proven to be highly efficient for the Wacker oxidation of terminal olefins to the corresponding methyl ketones. The catalyst was reusable while maintaining high activity and selectivity.

Wacker oxidation is one of the most efficient and important organic synthetic methods for converting terminal olefins to the corresponding methyl ketones and is generally catalyzed by homogeneous palladium salts combined with copper salts under aerobic conditions.[1] Addition of strong acids, for example, $HClO_4$, $H_2SO_4$, and $MeSO_3H$ is often required to achieve a favorable reoxidation of $Pd^0$, preventing aggregation of transient atomic $Pd^0$ species to inactive Pd metal.[2] However, these not only corrode the reactor wall but also lead to the low selectivity toward methyl ketone.[3] In the context, some acid-free Wacker oxidation systems have been reported.[4]

Conventional Wacker oxidation using homogeneous Pd catalysts often leads to difficulties in isolation of the products, separation of the catalysts from the reaction mixture, and recyclability of the catalysts. Therefore, much effort has been devoted to development of highly efficient Wacker oxidation by heterogeneous catalysts.[5,6] Various Pd complex catalysts immobilized on organic or inorganic supports have been reported for this purpose, but these catalyst systems often have drawbacks such as low catalytic activity, and are limited in application to a narrow range of terminal olefins.

Montmorillonites (mont) have attracted considerable interest as highly efficient heterogeneous catalysts.[7] These minerals are hydrophilic clays and can be structurally defined as layers of negatively charged two-dimensional silicate sheets separated by interlayer cationic species. Various metal cations can be successfully introduced within the interlayers via a simple ion-exchange method, providing active metal ion species having unique structures owing to the sterically restricted nano-order interlamellar regions. Recently, we have succeeded in creating within the interlayers of the mont a chain-like metal species and a monomeric aqueous metal complex, which act as unique heterogeneous catalysts for various C–C bond-forming reactions and for oxidation of olefins using molecular oxygen.[8]

We report herein that a Pd montmorillonite (Pd-mont), prepared by cation-exchange in an aqueous $Pd(CF_3COO)_2$ solution, acted as a highly efficient heterogeneous catalyst for liquid-phase Wacker oxidation of a wide range of terminal olefins to the corresponding methyl ketones under acid-free conditions. The catalytic activity of the Pd-mont for the above oxidation was superior to those of other reported Pd catalysts. Furthermore, the spent Pd-mont catalyst could be reused without an appreciable loss of catalytic activity and selectivity.

A mixture of 1.0 g of $Na^+$-mont $Na_{0.66}(OH)_4Si_{7.7}(Al_{3.34}Mg_{0.66}Fe_{0.19})O_{20}$ (Kunipia F, Kunimine Industry Co., Ltd) and aqueous hydrogen chloride (100 mL, 0.027 M) was stirred at 80 °C for 48 h to afford a

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*Keywords*: Wacker oxidation; Palladium; Heterogeneous catalyst; Montmorillonite.

* Corresponding author. Tel./fax: +81 6 6850 6260; e-mail: kaneda@cheng.es.osaka-u.ac.jp

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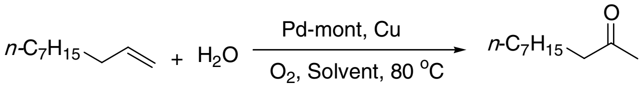
$H^+$-mont. The obtained $H^+$-mont (1.0 g) was treated with an aqueous solution of $Pd(CF_3COO)_2$ (100 mL, 1 mM) at 80 °C for 24 h. The obtained slurry was then filtered, washed with distilled water, and dried under vacuum to afford Pd-mont as a brown powder (Pd content: 0.08 mmol $g^{-1}$). The X-ray diffraction pattern verified the retention of the mont layered structure with a basal spacing of 6.1 Å, and XPS spectra (Pd $3d_{5/2}$ = 337.4 eV) revealed the oxidation state of the Pd species in the mont was divalent. IR measurement showed a $\nu$(C=O) band at around 1700 $cm^{-1}$, and the ratio of Pd/F in the Pd-mont was determined to be 1:3 by XPS. The above results as well as the curve-fitting analysis of the Fourier transform of $k^3$-weighted Pd K-edge EXAFS revealed the formation of a $[Pd^{II}(CF_3COO)]^+$ species within the interlayer of the mont.

Initially, liquid-phase Wacker oxidation of 1-decene was performed as a model reaction using the Pd-mont under several sets of conditions, as shown in Table 1. We have recently disclosed that $PdCl_2$ in combination with *N*,*N*-dimethylacetamide (DMA) solvent could offer an extremely simple and efficient catalyst system for acid-free Wacker oxidation.[9] The Pd-mont exhibited the highest catalytic activity in DMA compared with other solvents, affording 2-decanone in 85% yield with 99% selectivity without addition of acids (entry 1 vs 4–8).[10] Among Cu compounds tested, $CuCl_2$ was the most effective and only 4 equiv of $CuCl_2$ to Pd were required to achieve the high catalytic activity. Other Cu compounds, such as $Cu(OAc)_2$ and $Cu(NO_3)_2$, barely functioned as co-catalysts (entries 10 and 11).[11]

**Table 1.** Wacker oxidation of 1-decene catalyzed by Pd-mont under various conditions[a]



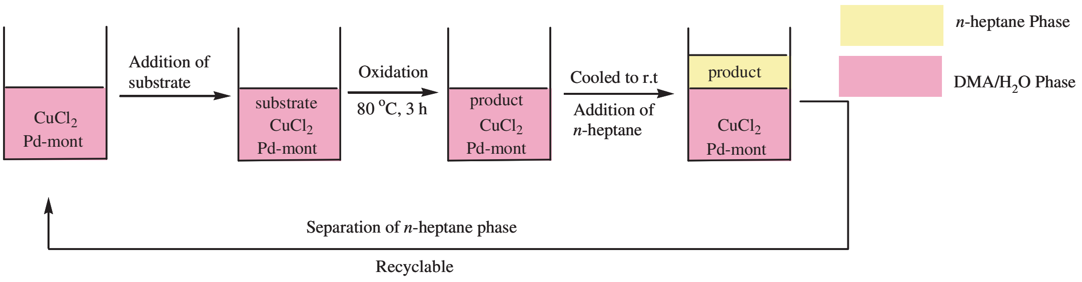
| Entry | Co-catalyst | Solvent | Conv. (%) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $CuCl_2$ | DMA | 85 | 85 |
| 2[c] | $CuCl_2$ | DMA | 85 | 84 |
| 3[d] | $CuCl_2$ | DMA | 84 | 84 |
| 4 | $CuCl_2$ | NMP[e] | 75 | 73 |
| 5 | $CuCl_2$ | DMF[f] | 17 | 17 |
| 6 | $CuCl_2$ | EtOH | 13 | 13 |
| 7 | $CuCl_2$ | $CH_3CN$ | 8 | 0 |
| 8 | $CuCl_2$ | DMSO[g] | 5 | 0 |
| 9 | $CuBr_2$ | DMA | 63 | 63 |
| 10 | $Cu(NO_3)_2$ | DMA | 8 | 0 |
| 11 | $Cu(OAc)_2$ | DMA | 5 | 0 |

[a] 1-Decene (1.0 mmol), Pd-mont (0.05 g; Pd: 0.004 mmol), Cu compound (0.016 mmol), $H_2O$ (0.5 mL), solvent (3 mL), 3 h, 80 °C, $O_2$ (1 atm).
[b] Yields were determined by GC analysis.
[c] Reuse 1.
[d] Reuse 2.
[e] *N*-Methylpyrrolidone.
[f] *N*,*N*-Dimethylformamide.
[g] Dimethyl sulfoxide.

After ca. 50% conversion, the Pd-mont was filtered off at 80 °C; subsequent treatment of the filtrate under similar reaction conditions did not afford any products, and ICP analysis of the filtrate confirmed that the Pd content was below the detection limit (<1 ppb). An obvious advantage of this catalytic system is the facile separation of the oxidized products from the reaction mixture.[12] Upon completion of oxidation, *n*-heptane is added to the reaction mixture and the *n*-heptane phase containing the oxidized products is removed from the reaction mixture. Further oxidation after addition of successive portions of olefin to the reaction mixture allows recycling of the Pd-mont and $CuCl_2$ in the residual DMA solution under identical reaction conditions (Scheme 1). For example, the second and third oxidation cycles of 1-decene proceeded at rates similar to that of the original reaction, affording 2-decanone in yields of more than 84% (entries 1–3).

It is noteworthy that the turnover number (TON) based on Pd reached 2400; this value is considerably greater than those reported for other Pd catalyst systems under acid-free conditions (Table 2).

The scope of this Pd-mont catalyst in Wacker oxidation of various alkenes is demonstrated in Table 3. Wacker oxidation of a wide range of terminal olefins proceeded efficiently, and the corresponding ketones were obtained in high yields in all cases. For example, the oxidation of long-chain olefins such as 1-hexadecene and 1-eicosene occurred efficiently to give 85% and 81% yields of the ketones, respectively (entries 7 and 8). Olefins possessing functionalized groups were also converted smoothly to the corresponding ketones selectively, with suppression of hydration and alcohol oxidation (entries 9–11).[14] In scale-up conditions, 1-decene (20 mmol; 2.8 g) was successfully converted to 2-decanone (88% isolated yield; 2.7 g) (entry 5). Furthermore, it was revealed that, in the case of 1-hexene, the TON reached 6000 (entry 2).



**Scheme 1.** Recycling of catalytic composition by phase-separation technique.

**Table 2.** The catalytic activity of Pd-mont compared with other reported catalysts in Wacker oxidation of 1-decene

| Entry | Catalyst system | Time (h) | TON | Yield (%)[a] | Ref. |
|---|---|---|---|---|---|
| 1[b] | Pd-mont/$CuCl_2$ | 48 | 2400 | 92 | This work |
| 2 | PBI-supported Pd catalyst[c]/$CuCl_2$ | 11 | 93 | 100 | 5e |
| 3 | $Pd_{2060}$ cluster–$TiO_2$/$CuCl_2$ | 2 | 88 | 88 | 5b |
| 4 | $PdCl_2$/$Cu(OAc)_2$ | 72 | 9 | 87 | 4c |
| 5 | $PdCl_2$/$CuCl_2$ | 24 | 7 | 73 | 1c |
| 6 | $PdCl_2$ + CTAB[d]/$CuCl_2$ | 48 | 18 | 73 | 13 |

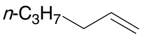
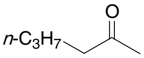
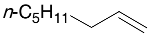
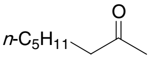
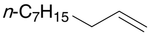
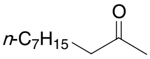
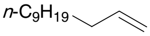
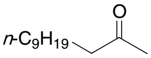
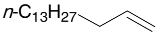
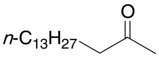
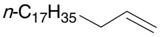
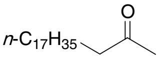
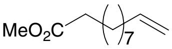
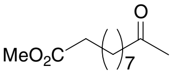
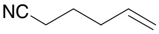
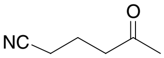
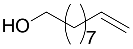
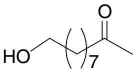
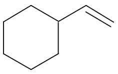
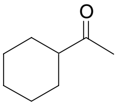
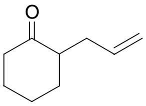
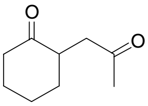
[a] Yield were based on alkene.

[b] Substrate (2.0 mmol), Pd-mont (0.01 g; Pd: 0.0008 mmol), $CuCl_2$ (0.0032 mmol), $H_2O$ (0.5 mL), DMA (3 mL), 48 h, 80 °C, $O_2$ (1 atm).

[c] PBI = polybenzimidazole.

[d] CTAB = cetyltrimethylammonium bromide.

**Table 3.** Wacker oxidation of various olefins catalyzed by Pd-mont[a]

| Entry | Substrate | Time (h) | Conv. (%) | Product | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 |  | 3 | 82 |  | 81 |
| 2[c] | | | 95 | | 95 |
| 3 |  | 3 | 82 |  | 82 |
| 4 |  | 3 | 85 |  | 85 |
| 5[d] | | 3 | 89 | | 89 (88) |
| 6 |  | 3 | 91 |  | 91 |
| 7 |  | 3 | 88 |  | 85 |
| 8[e] |  | 3 | 82 |  | 81 (79) |
| 9[f] |  | 4 | 90 |  | 89 (86) |
| 10[f] |  | 15 | 75 |  | 73 (70) |
| 11[f] |  | 4 | 92 |  | 91 (88) |
| 12[f] |  | 3 | 86 |  | 82 (80) |
| 13[f] |  | 12 | 90 |  | 86 (83) |

[a] Substrate (1.0 mmol), Pd-mont (0.05 g, Pd: 0.004 mmol), $CuCl_2$ (0.016 mmol), $H_2O$ (0.5 mL), DMA (3 mL), 3 h, 80 °C, $O_2$ (1 atm).

[b] Yields were determined by GC analysis. Values in parenthesis are isolated yields.

[c] Substrate (5.0 mmol), Pd-mont (0.01 g; Pd: 0.0008 mmol), $CuCl_2$ (0.0032 mmol), 48 h.

[d] Substrate (20 mmol), Pd-mont (1.0 g; Pd: 0.08 mmol), $CuCl_2$, (0.4 mmol), $H_2O$ (10 mL), DMA (60 mL).

[e] DMA (5 mL).

[f] Substrate (0.5 mmol).

In conclusion, we have developed a highly active heterogeneous Pd catalyst for liquid-phase Wacker oxidation without the external addition of strong acids. The Pd-mont catalyst was shown to have high catalytic activity for conversion of various terminal olefins. Moreover, this catalyst was reusable while maintaining the high activity and selectivity.

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10. *A typical example for Wacker oxidation using Pd-mont*: Into a reaction vessel equipped with a reflux condenser and a rubber balloon were placed the Pd-mont (0.05 g, Pd: 0.004 mmol), $CuCl_2$ (0.016 mmol), 1-decene (0.140 g; 1.0 mmol), DMA (3 mL), and $H_2O$ (0.5 mL). The mixture was vigorously stirred at 80 °C under an atmospheric $O_2$ pressure for 3 h. After the reaction, the catalyst was separated by filtration, and 15 mL water was added to the filtrate. The product was extracted using diethylether (2 × 15 mL). The diethylether layer containing the product was dried over $MgSO_4$, then filtered, and concentrated under reduced pressure. The resultant crude mixture was purified by column chromatography (silica gel), using an 1:4 EtOAc/hexane mixture as eluent, to give pure 2-decanone (0.13 g, 85%).
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12. *Recycling and reuse of the Pd-mont and $CuCl_2$*: After completion of the reaction, the reaction mixture was cooled to room temperature, and washed with *n*-heptane (2 × 5 mL). The *n*-heptane phase was decanted, and another portion of 1-decene (1 mmol) was successively added into the residual DMA phase containing Pd-mont and $CuCl_2$, followed by stirring under identical reaction conditions.
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14. The oxidation of cyclohexene did not proceed efficiently, and trace amounts of cyclohexanone were obtained.