Heterogeneous Catalysis

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Montmorillonite-Entrapped Sub-nanoordered Pd Clusters as a Heterogeneous Catalyst for Allylic Substitution Reactions**

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Metal nanoclusters are applicable in a wide range of technologies—from electronic, optic, and magnetic devices to advanced catalytic materials.[1] Current studies on the synthesis of metal nanoclusters for catalysis are focused on controlling the size and shape, with much emphasis placed on the use of organic stabilizing ligands.[2] Sub-nanoordered clusters possess extremely large surface-to-volume ratios and large numbers of coordinatively unsaturated surface atoms. They are more likely to exhibit strong metal–support interactions (SMSI), which can lead to greatly altered catalytic performances. The preparation of supported sub-nanoordered metal clusters is challenging because of their instability against aggregation into larger nanosized clusters during removal of the ligand or under the reaction conditions.

Montmorillonites (monts) of smectite clays comprise negatively charged layers and interlayers with alternating Na^+ species. Various metal ions can be introduced into the narrow interlayers by simple ion-exchange methods.[3] We have recently succeeded in creating active metal species with diverse structures in the interlayers which show high catalytic activity for various reactions.[4]

Herein we describe the preparation of stable sub-nanoordered Pd clusters entrapped within the sterically restricted Angstrom-sized ordered interlamellar spaces of a mont. These novel Pd clusters in the montmorillonites efficiently catalyze heterogeneous allylic substitution reactions,[5] with the coordinatively unsaturated Pd atoms enabling facile formation of π-allyl palladium intermediates. In spite of the expected utility of the sub-nanoordered Pd clusters as catalysts for diverse organic syntheses,[6] there have been few studies on their precise preparation and catalytic properties.[7] To the best of our knowledge, this is the first demonstration of allylic substitution using a Pd catalyst under organic-ligand-free conditions.[8]

Treatment of Na^+-mont with an aqueous solution of $Ca(OH)_2$ yielded Ca^{2+}-mont. The degree of exchange of the sodium cations in the Ca^{2+}-mont was 99 %, as determined by inductively coupled plasma (ICP) spectroscopy. The obtained Ca^{2+}-mont was added to a solution of $[Pd(dba)_2]$ (dba = *trans,trans*-dibenzylideneacetone) in *N,N*-dimethylacetamide (DMA) at room temperature to afford a Pd^{II}-mont (Figure 1 a),[9] followed by reduction with an aqueous solution of KBH_4 in an Ar atmosphere to give Pd clusters entrapped within the mont (Pd-mont, Figure 1 b). Immobilization using $[Pd(dba)_2]$ did not occur to a significant extent when the parent Na^+-mont was used instead of the Ca^{2+}-mont.

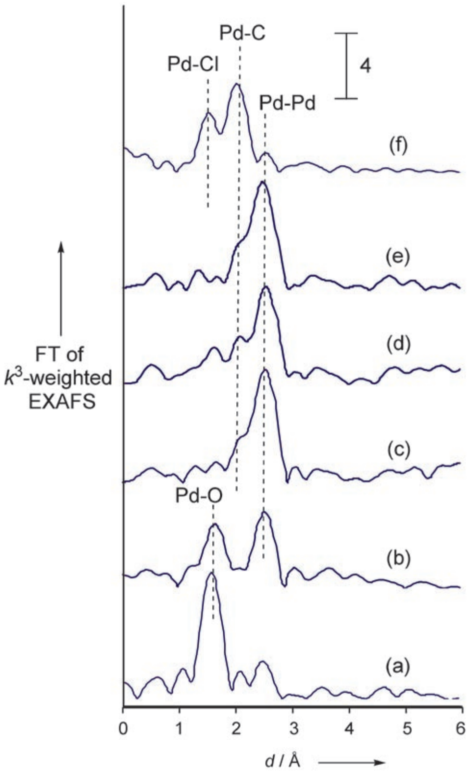

Figure 1. FT magnitude of k^3-weighted EXAFS of Pd-mont: a) without treatment by KBH_4, b) after treatment with KBH_4, c) after the third reuse, d) after treatment of (c) with **1a**, e) after subsequent treatment of (d) with **2a**, and f) $[PdCl(C_3H_5)]_2$.

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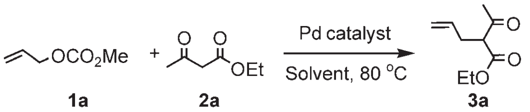
The catalytic ability of the Pd-mont was explored in the allylic substitution reaction of allyl methyl carbonate (**1a**) with ethyl acetoacetate (**2a**) in various solvents (Table 1). Water and ethanol were efficient solvents and afforded high yields of 2-acetyl-4-pentenoic acid ethyl ester (**3a**, entries 1 and 2). Moderate yields of **3a** were obtained in DMF and THF, while the use of nonpolar solvents such as *n*-heptane and toluene resulted in low yields.[10] The interlayer space of the Pd-mont expanded when it was soaked in H_2O and EtOH, which allowed easy access of the substrates to the Pd species within the mont.[11]

Table 1: Allylic substitution reaction of **1a** with **2a** using various Pd catalysts in different solvents.[a]



Entry	Catalyst	Solvent	Yield [%][b]
1	Pd-mont	H_2O	91
2	Pd-mont	EtOH	93
3[c]	Pd-mont	EtOH	93
4[d]	Pd-mont	EtOH	50
5[e]	Pd-mont	EtOH	98
6[f]	Pd-mont	EtOH	99
7[g]	Pd-mont	EtOH	98
8	Pd/Al_2O_3[h]	H_2O	14
9	Pd/SiO_2[h]	H_2O	trace
10	Pd/C[h]	H_2O	no reaction
11	Pd/TiO_2[h]	H_2O	no reaction

[a] Reaction conditions: Pd catalyst (Pd: 5.8×10^{-4} mmol), solvent (1 mL), allyl methyl carbonate (0.3 mmol), ethyl acetoacetate (3.6 mmol), Ar, 9 h. [b] Yields of products were determined by GC based on the amount of allyl methyl carbonate. [c] Reaction in air. [d] With 2 equiv of PPh_3. [e] Reuse 1. [f] Reuse 2. [g] Reuse 3. [h] 0.5 wt% Pd; purchased from N. E. Chemcat.

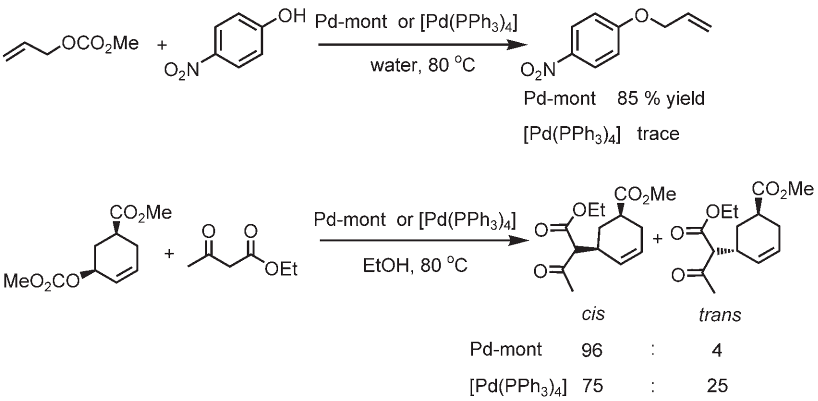
Notably, this allylation proceeded smoothly even under air (entry 3). In many conventional Pd catalyst systems, phosphine ligands are used under oxygen-free conditions to promote allylation;[5,8] however, the addition of PPh_3 to the reaction mixture containing the Pd-mont depressed allylation, and resulted in a 50% yield of **3a** (entry 4). The use of commercial Pd/Al_2O_3 resulted in an extremely low yield, and other typical solid Pd catalysts such as Pd/SiO_2, Pd/C, and Pd/TiO_2 barely functioned under the conditions used (entries 8–11).

The range of substrates suitable for the Pd-mont-catalyzed allylic substitution reaction was examined.[10] The reaction of **1a** with a variety of nucleophiles occurred efficiently to afford the corresponding allylic-substituted compounds in high yields. The reactions of allylic acetates in the presence of Na_3PO_4 as a base also gave high yields of the substituted products. Interestingly, an excellent yield of an allylphenol was obtained in the reaction of **1a** with 4-nitrophenol (Scheme 1). Substitution reactions with phenols having electron-withdrawing groups do not generally proceed readily using homogeneous Pd systems;[12] indeed, the use of $[Pd(PPh_3)_4]$ in the above reaction resulted in the production of only a trace amount of allylphenol, even after 48 h, under similar reaction conditions.

To confirm whether the substitution reaction occurs on the Pd nanoclusters within the mont layer, the Pd-mont was removed by hot filtration after 40% conversion of **1a** at 80 °C. Further treatment of the hot filtrate under the same reaction conditions did not give any products. Moreover, ICP analysis of the filtrate confirmed that the Pd content was below the detection limit (< 0.04 ppm). It is clear that the allylic substitution reaction proceeds on the Pd clusters within the interlayer of the mont.

After the allylic substitution reaction, the Pd-mont was readily separated from the reaction mixture by simple filtration and could be reused without any loss of activity. A yield of over 98% of **3a** was obtained in the reaction of **1a** with **2a** after each of three recycling steps (Table 1, entries 5–7).

Notably, TEM images of the Pd-mont after the third reuse did not show any recognizable Pd aggregates (detection limit ca. 1 nm). The atomic-scale structure of the Pd species of the used Pd-mont was analyzed by Pd K-edge extended X-ray absorption fine spectroscopy (EXAFS). The Pd species exist as sub-nanosized clusters, which prevent the agglomeration of Pd nanoparticles even after the third recycling experiment. The sub-nanoordered Pd clusters were estimated to contain approximately ten Pd atoms, and their size remained unchanged after the third reuse (Figure 1 c).[13] These phenomena are in agreement with the retention of the catalytic activity in the recycled Pd-mont. Treatment of the recycled Pd-mont with **1a** resulted in the intensity of the FT peak corresponding to the Pd-Pd shell decreasing,[14] while a new peak attributable to a Pd-C shell appeared at around 2.0 Å (Figure 1 d). The interatomic distance of the Pd-C shell was consistent with that of the reference compound $[PdCl(C_3H_5)]_2$ (Figure 1 f), thus confirming the formation of π-allylpalladium species within the mont. Furthermore, treatment of the above sample with **2a** led to the disappearance of the peak assigned to the Pd-C shell and the appearance of the allylation product, and the resulting spectrum (Figure 1 e) resembled



Scheme 1.

that of the recycled Pd-mont (Figure 1c). The above results strongly support allylation taking place on coordinately unsaturated Pd atoms in the sub-nanoordered Pd clusters.

The use of the Pd-mont in the allylation of *cis*-3-acetoxy-5-carbomethoxycyclohex-1-ene with **2a** was found to provide superior selectivity towards the corresponding *cis* product compared with [Pd(PPh$_3$)$_4$][5a] (Scheme 1). The steric steering occurred during the nucleophilic attack of **2a** on the surface π-allyl intermediate, which is strongly shielded from *endo* attack.

In conclusion, sub-nanoordered Pd clusters were synthesized within the interlayer of the montmorillonite. The Pd-mont acted as a highly efficient heterogeneous catalyst for allylic substitution reactions under organic-ligands-free conditions. Moreover, this Pd-mont has the advantage of being: 1) stable in air, 2) highly active even under aqueous conditions, and 3) reusable without any loss of activity or selectivity. The sterically hindered interlayer space of the mont plays an important role in stabilizing the highly coordinatively unsaturated Pd clusters, which suppresses agglomeration into large inactive Pd particles.

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[10] See the Supporting Information for details.

[11] The interlayer space of the Pd-mont expanded from 5.3 to 9.6 Å when soaked in H_2O.

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[13] Treatment of the Pd^{II}-mont with KBH$_4$ did not give Pd^0 species quantitatively, and some parts of the monomeric divalent species remained (Figure 1b). After the first use of the Pd-mont in the allylation, the residual Pd^{II} species could be converted into the Pd^0 species and the estimated size of the Pd clusters grew from 0.57 to 0.82 nm. Allylation did not occur when the Pd^{II}-mont was used without treatment by KBH$_4$ (Figure 1a), and Pd clusters could not be obtained.

[14] The decreased Pd-Pd shell intensity is attributable to an increase in the disordered phase difference of the XAFS wave as a result of the formation of the π-allyl complex.