



# Environmentally-benign palladium(II)-exchanged hydroxyapatite-catalyzed allylic alkylation of allyl methyl carbonate in water

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## ABSTRACT

Palladium(II)-exchanged hydroxyapatite (PdHAP; for example, PdHAP-B has a Pd/Ca ratio = ca 1/200) was prepared by ion-exchanging with  $\text{Ca}^{2+}$  from calcined hydroxyapatite and  $\text{Pd}(\text{NO}_3)_2$  in water at 70 °C for 24 h. The ion-exchange was revealed by inductively coupled plasma analysis;  $\text{Pd}^{2+}$  was almost absent in any filtrate that included over 1.6 equimolar amounts of  $\text{Ca}^{2+}$  relative to the amount of  $\text{Pd}^{2+}$  consumed. The PdHAP (1 mol% Pd) functioned as a catalyst for the allylic alkylation of allyl methyl carbonate with active methylene compounds such as diethyl malonate, 2-ethoxycarbonylcyclopentanone, 2-ethoxycarbonylcyclohexanone, and 2,2-dimethyl-1,3-dioxane-4,6-dione at 50 °C in water under air. Over 97% of the PdHAP was recovered by centrifugation followed by decantation, and the material could be reused. The catalytic activity of PdHAP accompanied by satisfactory yields of monoallylated products was maintained in ten repetitive uses for the allylic alkylation of allyl methyl carbonate with diethyl malonate at 50 °C for 24 h in water under air. From the standpoints of yield and handling, using water as a solvent was superior to using an organic medium such as ethanol, THF or DMF. Thus, this heterogeneous PdHAP-catalyzed allylic alkylation will be one of the environmentally-benign organic syntheses.

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## 1. Introduction

Allylic substitution of allylic esters with homogeneous palladium complex catalysts, namely the nucleophilic substitution of  $\pi$ -allylpalladium complexes, is one of the most useful methodologies for the synthesis of a wide variety of natural compounds and other complex organic molecules [1,2]. From a viewpoint of sustainable chemistry, some environmentally-benign heterogeneous palladium catalysts such as amphiphilic resin-supported phosphine-coordinated palladium [3] and palladium nanoparticles [4,5] have been developed for the allylic substitution in water.

The availability of hydroxyapatites (HAP) for supporting transition metals has been demonstrated; it has been attributed to their cation-exchange ability and adsorption capability [6,7]. Some HAP-supported transition metals, such as ruthenium, palladium, copper and silver, have been applied as heterogeneous catalysts to environmentally-benign organic syntheses [8–20]. These materials have been prepared by four kinds of methods: adsorption [12,13,15], incorporation [14], ion-exchange [8–10,16–19], and nanoparticles [11,20]. Most of the heterogeneous catalytic

reactions with transition metals introduced into insoluble inorganic matrices can be categorized into oxidation reactions and Lewis acid-mediated reactions. The transition metals on inorganic matrices have seldom functioned as recyclable catalysts for organic syntheses via the formation of organometallic intermediates. In the application of HAP-supported transition metals to organic syntheses, an incorporated non-ion-exchanged PdHAP, prepared from nonstoichiometric Ca-deficient hydroxyapatite [ $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$ ] and  $\text{PdCl}_2(\text{PhCN})_2$  in acetone [14], is available as a catalyst for carbon–carbon bond-forming reactions via the formation of arenylpalladium intermediates; these reactions include Mizoroki–Heck reaction [21] and Suzuki–Miyaura coupling reaction [22]. We hoped that the coordination of phosphate moieties to palladium, generated by the ion-exchange of Ca(II) for Pd(II) in HAP matrices, might prevent the leaching of either the Pd(II) or the reduced Pd(0) into the reaction medium, and might assist the reduction of Pd(II) to Pd(0) with phosphines accompanied by the transformation of two phosphates to one phosphoric anhydride [1,2]. Thus, we planned an environmentally-benign synthetic process, namely palladium-exchanged hydroxyapatite-catalyzed allylic alkylation in water: (1) the preparation of palladium-exchanged hydroxyapatite (PdHAP) bearing monomeric Pd(II) components by an ion-exchange of Ca(II) in HAP matrices with palladium nitrate; (2) the application of the PdHAP to the allylic alkylation with carbon nucleophiles such as diethyl mal-

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onate (**2**) in water via the formation of a  $\pi$ -allylpalladium complex prepared from allyl methyl carbonate (**1**) [1–5]; and (3) the demonstration of the reusability of the PdHAP for the allylic alkylation in water.

## 2. Experimental

### 2.1. General methods

Hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] (HAP) was purchased from Taihei Chemical Industrial Co. Ltd. and was used as received or after calcining with a heating rate of  $10^\circ\text{C}/\text{min}$  from room temperature to  $800^\circ\text{C}$  and then at  $800^\circ\text{C}$  for 3 h. Palladium nitrate was purchased from Furuya Metal Co. Ltd. and was used as received. Allyl methyl carbonate and allyl acetate were purchased from Tokyo Chemical Industry Co. Ltd. Ethyl cyanoacetate and malononitrile were purchased from Kanto Chemical Co. Inc. Diethyl malonate, 2-ethoxycarbonylcyclopentanone, 2-ethoxycarbonylcyclohexanone and 2,2-dimethyl-1,3-dioxane-4,6-dione were purchased from Sigma–Aldrich, Inc. The commercial compounds were purified by distillation or by column chromatography. Inductively coupled plasma (ICP) analysis was carried out on a Seiko Instruments Inc. SPS7700. The textural properties of fresh PdHAP-B and used PdHAP-B were determined by nitrogen adsorption at 77 K (BEL JAPAN, BELSORP-mini). XRD measurements were performed on a RIGAKU Electronic RINT 2100/PC X-ray diffraction spectrometer equipped with a carbon monochromator and  $\text{Cu K}\alpha$  (40 kV, 40 mA) irradiation, covering  $2\theta$  values between  $20^\circ$  and  $55^\circ$ . Samples were run as fine powders mounted on glass slides. XPS measurements were performed on a ULVAC-Phi ESCA 5800ci using monochromatic  $\text{Al K}\alpha$  (14 kV, 25 mA) irradiation. Samples were mounted on the spectrometer probe using a piece of double-sided adhesive tape. The binding energies of XPS spectra of Ca(2p) and Pd(3d) were calibrated by the observed binding energy of C(1s). Allylic alkylations were carried out on an AS ONE Co. shaking water bath SWB-17 (stroke: 30 mm, speed: 130 rpm) or on a NISSIN block shaker NX-70B (stroke: 1.5 mm). TLC analyses were carried out with silica gel plates (Merck Art.5735), and column chromatography was carried out with silica gel (Kanto Chemical Co. Inc. Cat. No. 37564). HPLC purification was carried out on a Japan Analysis Industry Co. Ltd. LC-908 (JAIGEL-2H;  $\text{CHCl}_3$ ). NMR spectra were recorded on a JEOL JMS-LA500 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer.

### 2.2. Preparation of palladium(II)-exchanged hydroxyapatite (PdHAP)

A calcium hydroxyapatite (2.0 mmol) sample of  $\text{Ca}/\text{P}=1.67$  [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] (HAP) was stirred with 150 mL of a  $6.3 \times 10^{-4}$  M aqueous  $\text{Pd}(\text{NO}_3)_2$  ( $9.5 \times 10^{-2}$  mmol) solution at  $70^\circ\text{C}$  for 24 h. The obtained slurry was filtered, washed with deionized water, and dried overnight at  $110^\circ\text{C}$  to afford a Pd(II)-exchanged hydroxyapatite (PdHAP-B, Pd content:  $0.05 \text{ mmol g}^{-1}$ ) as a brown powder. Since no Pd(II) was detected in the filtrate or in the washing water by ICP analysis, the Pd content was estimated to be the same molar amount as that of the  $\text{Pd}(\text{NO}_3)_2$  used. The specific surface of PdHAP-B area calculated according to the B.E.T. model was  $18.7 \text{ m}^2 \text{ g}^{-1}$ , and the pore volume of PdHAP-B calculated according to the Dollimore and Heal model was  $0.0462 \text{ cm}^3 \text{ g}^{-1}$ .

### 2.3. Typical procedure for PdHAP-catalyzed allylic alkylation

To a suspension of PdHAP-B (0.2 g, 1 mol% Pd) and triphenylphosphine (3 mg, 0.01 mmol) in water (1 mL) were added diethyl malonate (**2**, 0.32 g, 2 mmol) and allyl methyl carbonate (**1**, 0.12 g, 1 mmol). After the suspension was shaken at  $50^\circ\text{C}$  for 24 h

under air in a shaking water bath (AS ONE Co., SWB-17, stroke: 30 mm, speed: 130 rpm), the solution was separated from PdHAP-B by centrifugation followed by decantation. The separated PdHAP-B was washed with methanol ( $3 \text{ mL} \times 2$ ) and ether ( $3 \text{ mL} \times 5$ ) successively by the same operations. Over 97% of the PdHAP-B was recovered on the average and could be reused. The residue after removal of the methanol was combined with more ether (200 mL). The mixed ethereal solution was washed with water (30 mL) and brine (30 mL), and then was dried over anhydrous  $\text{MgSO}_4$ . After evaporation of ether, purification by column chromatography (silica gel, hexane/EtOAc = 25:1) and HPLC (Japan Analytical Industry Co. Ltd., LC-908, JAIGEL-2H;  $\text{CHCl}_3$ ) afforded 0.16 g (84%) of ethyl 2-ethoxycarbonyl-4-pentenoate (**3**) as a colorless oil.

Ethyl 2-ethoxycarbonyl-4-pentenoate (**3**): colorless oil;  $R_f=0.53$  (hexane:ethyl acetate = 3:1);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.28 (t,  $J=7.0$ , 6H), 2.62–2.66 (m, 2H), 3.42 (t,  $J=7.5$ , 1H), 4.15–4.24 (m, 4H), 5.06 (d,  $J=10.5$ , 1H), 5.12 (d,  $J=17.0$ , 1H), 5.78 (dd,  $J=17.0$ , 10.5, 1H); IR (neat) 3086, 3017, 2986, 2939, 1736, 1643, 1605, 1466, 1443, 1373, 1335, 1273, 1219, 1188, 1157, 1119, 1057, 1034, 926, 856, 810,  $702 \text{ cm}^{-1}$ .

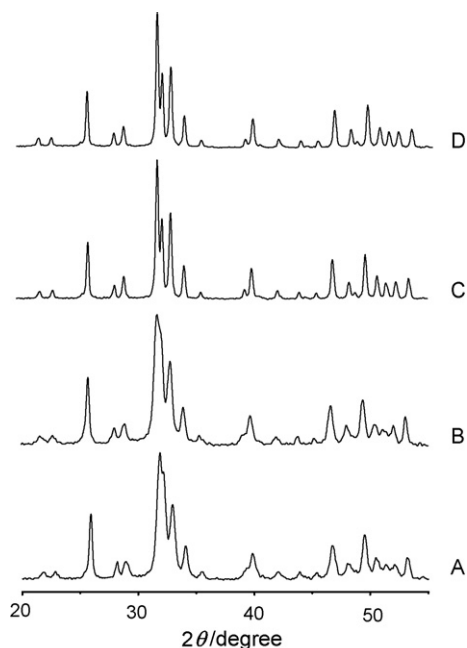
Ethyl 2-(2-propenyl)-2-ethoxycarbonyl-4-pentenoate (**4**): colorless oil;  $R_f=0.63$  (hexane:ethyl acetate = 3:1);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.25 (t,  $J=7.0$ , 6H), 2.64 (d,  $J=7.0$ , 4H), 4.18–4.22 (m, 4H), 5.09–5.14 (m, 4H), 5.62–5.70 (m, 2H); IR (neat) 3040, 3017, 2932, 2862, 1720, 1651, 1605, 1512, 1458, 1373, 1258, 1234, 1218, 1096, 1018, 903, 864,  $818 \text{ cm}^{-1}$ .

The structures of all products were confirmed by the comparison of spectroscopic values (IR and NMR) with those of authentic samples in the literature; ethyl 2-ethoxycarbonyl-4-pentenoate (**3**) [5,23], ethyl 2-(2-propenyl)-2-ethoxycarbonyl-4-pentenoate (**4**) [5,24], 2-ethoxycarbonyl-2-(2-propenyl)cyclopentanone (**5**) [25], 2-ethoxycarbonyl-2-(2-propenyl)cyclohexanone (**6**) [23], 2,2-dimethyl-5,5-(di-2-propenyl)-1,3-dioxane-4,6-dione (**7**) [26], ethyl 2-cyano-4-pentenoate (**8**) [24], and ethyl 2-(2-propenyl)-2-cyano-4-pentenoate (**9**) [24]. Electronic supplementary information is available: IR and NMR spectra of products.

## 3. Results and discussion

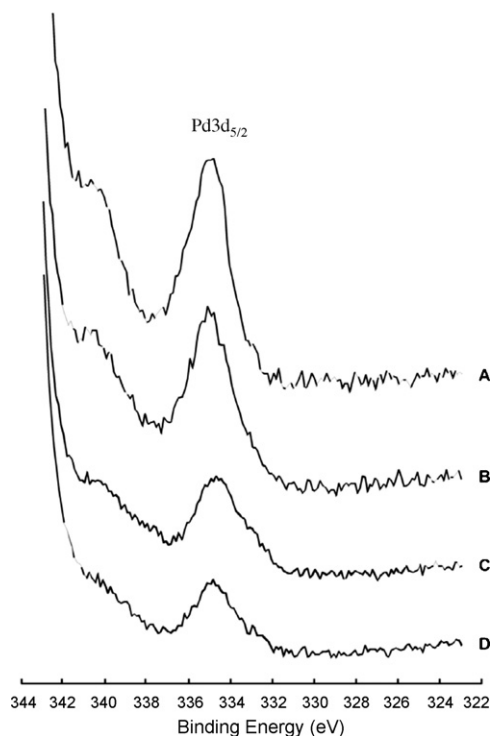
### 3.1. Palladium(II)-exchanged hydroxyapatite (PdHAP)

Palladium ion-exchange to HAP was carried out with  $\text{Pd}(\text{NO}_3)_2$  at  $70^\circ\text{C}$  in water to prepare three kinds of palladium-exchanged hydroxyapatites: namely, PdHAP-A (Pd content:  $0.02 \text{ mmol g}^{-1}$ ), PdHAP-B (Pd content:  $0.05 \text{ mmol g}^{-1}$ ) and PdHAP-C (Pd content:  $0.1 \text{ mmol g}^{-1}$ ). ICP analysis revealed that almost no  $\text{Pd}^{2+}$  was present in any filtrate that included over 1.6 equimolar amounts of  $\text{Ca}^{2+}$  relative to the amount of  $\text{Pd}^{2+}$  consumed, in contrast to the preparation of PdHAP in organic solvents [12,14]. The powder X-ray diffraction (XRD) peaks for every PdHAP were the same as those of commercial HAP or calcined HAP. The XRD spectra of PdHAP-Bs together with those of HAPs are shown in Fig. 1. Therefore, all prepared PdHAPs and used PdHAP-Bs were found to retain the structural properties of the HAP surfaces. The specific surface ( $20.3 \text{ m}^2 \text{ g}^{-1}$ ) and the pore volume ( $0.0501 \text{ cm}^3 \text{ g}^{-1}$ ) of used PdHAP-B were almost the same as those of fresh PdHAP-B ( $18.7 \text{ m}^2 \text{ g}^{-1}$ ,  $0.0462 \text{ cm}^3 \text{ g}^{-1}$ ). We investigated the variation of binding energy and intensity of Pd  $3d_{5/2}$  peaks between fresh PdHAP-B and repetitively used PdHAP-B by X-ray photoelectron spectroscopy (XPS) (Fig. 2) [27–31]. A small peak was obtained in the Pd  $3d_{5/2}$  region for each repetitively used PdHAP-B. Since the peaks for used PdHAP-Bs seem to exhibit almost the same binding energies as the peak for fresh PdHAP-B, the oxidation state of palladium nuclear in PdHAP-B can be kept as divalent between before being used for the reaction

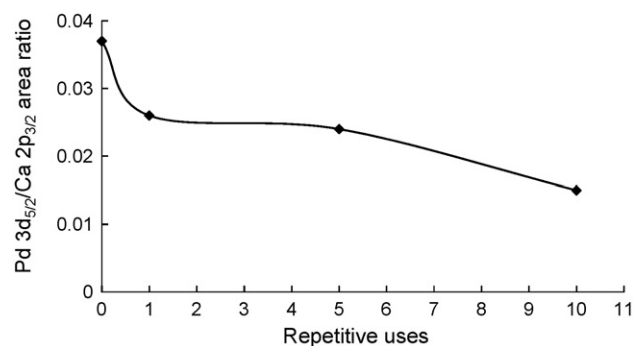


**Fig. 1.** XRD patterns of HAP and PdHAP-B. (A) HAP, (B) PdHAP-B, (C) calcined HAP, (D) calcined PdHAP-B.

(fresh PdHAP-B) and after being separated from the reaction mixture (used PdHAP-B). It can support the observation of XPS that an equimolar amount of  $\text{PPh}_3$  to  $\text{Pd}^{2+}$  is necessary for the reaction either with fresh PdHAP-B or with used PdHAP-B, because  $\text{PPh}_3$  can be useful to reduce  $\text{Pd(II)}$  to active  $\text{Pd(0)}$ . The variation of Pd contents in PdHAP-Bs after repetitive uses was estimated by calcu-



**Fig. 2.** XPS spectra in the Pd  $3d_{5/2}$  region for fresh PdHAP-B and repetitively used PdHAP-Bs. (A) Fresh PdHAP-B, (B) PdHAP-B after being used once, (C) PdHAP-B after five repetitive uses, (D) PdHAP-B after ten repetitive uses.



**Fig. 3.** The variation of Pd contents in PdHAP-Bs after repetitive uses.

lating the ratio between the intensity of Pd  $3d_{5/2}$  and Ca  $2p_{3/2}$  peaks by XPS; Pd content after being used once reduced to 70% in fresh PdHAP-B, whereas 40% of Pd remained even after ten repetitive uses (Fig. 3).

### 3.2. Catalytic activity and reusability of PdHAP for allylic alkylation in water

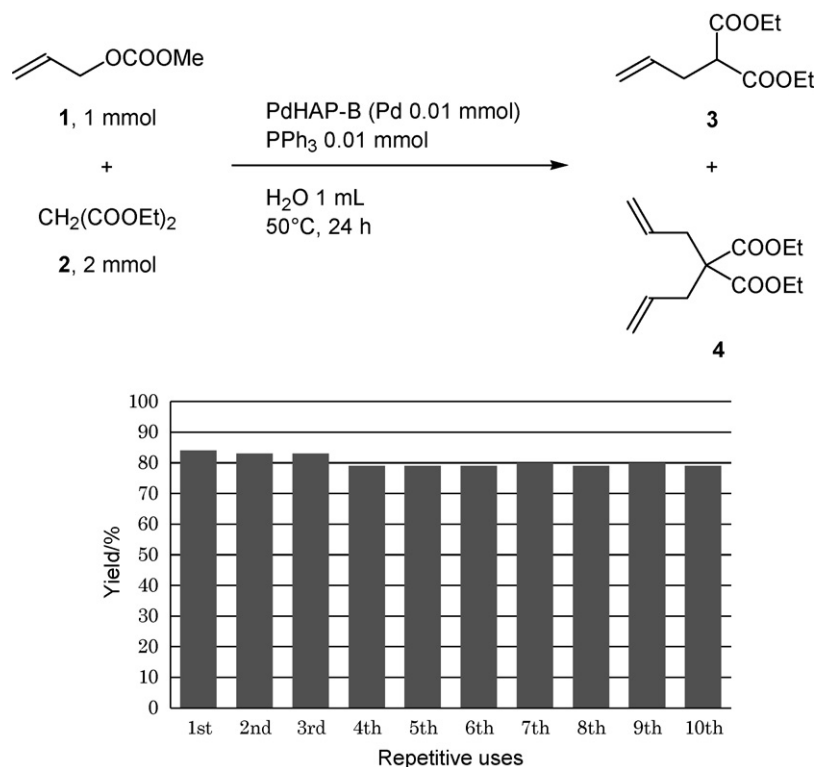
The catalytic activity and reusability of PdHAPs were investigated for the allylic alkylation of allyl methyl carbonate (**1**) with diethyl malonate (**2**), as shown in Fig. 4. Two equimolar amounts of **2** to **1** were employed for obtaining **3** preferentially in the allylic alkylation, and one or two equimolar amounts of  $\text{PPh}_3$  to  $\text{Pd(II)}$  were added for reducing  $\text{Pd(II)}$  to active  $\text{Pd(0)}$  in situ. In the allylic alkylation with low Pd-loading PdHAP-A (0.5 mol% Pd) at  $50^\circ\text{C}$  for 24 h under air, the efficiency of the solvent was estimated from the standpoints of yield, handling and environmental protection; use of water as a solvent was superior to use of an organic medium such as ethanol, THF or DMF. The yields of **3** are summarized in Table 1. Water as a solvent would function to disperse either PdHAP particles or organic substrates, and consequently the water-insoluble substrates **1** and **2** could adhere on PdHAP surfaces to facilitate the allylic alkylation. The allylic alkylation did not occur without an equimolar amount of  $\text{PPh}_3$  to palladium; the  $\text{PPh}_3$  presumably functioned as a reducing agent to prepare  $\text{Pd(0)}$  species from  $\text{Pd(II)}$  species. PdHAP-B is also effective for the allylic alkylation in the presence of an equimolar amount of  $\text{PPh}_3$  to Pd at  $50^\circ\text{C}$  for 24 h in water under air to produce monoallylated malonate **3** and diallylated malonate **4** in 84% and 4% yields respectively. The catalytic activity of PdHAP-B was maintained in ten repetitive uses under the same conditions as those of the typical procedure in water. The yields of **3** are shown in Fig. 4.

The investigation into the participation of Pd species leaching from PdHAP was carried out during the repetitive uses shown in Fig. 4; to the suspension of fresh PdHAP-B or used PdHAP-B (used once or five times) in water (1 mL) was added  $\text{PPh}_3$  (0.01 mmol). After the suspension was shaken at  $50^\circ\text{C}$  for 24 h under air in a shaking water bath, the water solution was separated from PdHAP-B by centrifugation followed by decantation. The allylic alkylation of **1** with **2** was carried out using each water solution including another aliquot of  $\text{PPh}_3$  (0.01 mmol) at  $50^\circ\text{C}$  for 24 h to produce **3** in a 37%

**Table 1**  
Efficiency of solvent in PdHAP-catalyzed allylic alkylation of **1** with **2**.

Solvent	$\text{H}_2\text{O}$	EtOH	THF	DMF
Yield/%	74	51	25	75

Isolated yields of **3** were averaged for three runs. Reaction conditions: PdHAP-A (0.2 g, 0.5 mol% Pd),  $\text{PPh}_3$  (3 mg, 0.01 mmol), allyl methyl carbonate (**1**, 0.12 g, 1 mmol), diethyl malonate (**2**, 0.32 g, 2 mmol), solvent (1 mL),  $50^\circ\text{C}$ , 24 h under air in a shaking water bath (AS ONE Co., SWB-17, stroke: 30 mm, speed: 130 rpm).



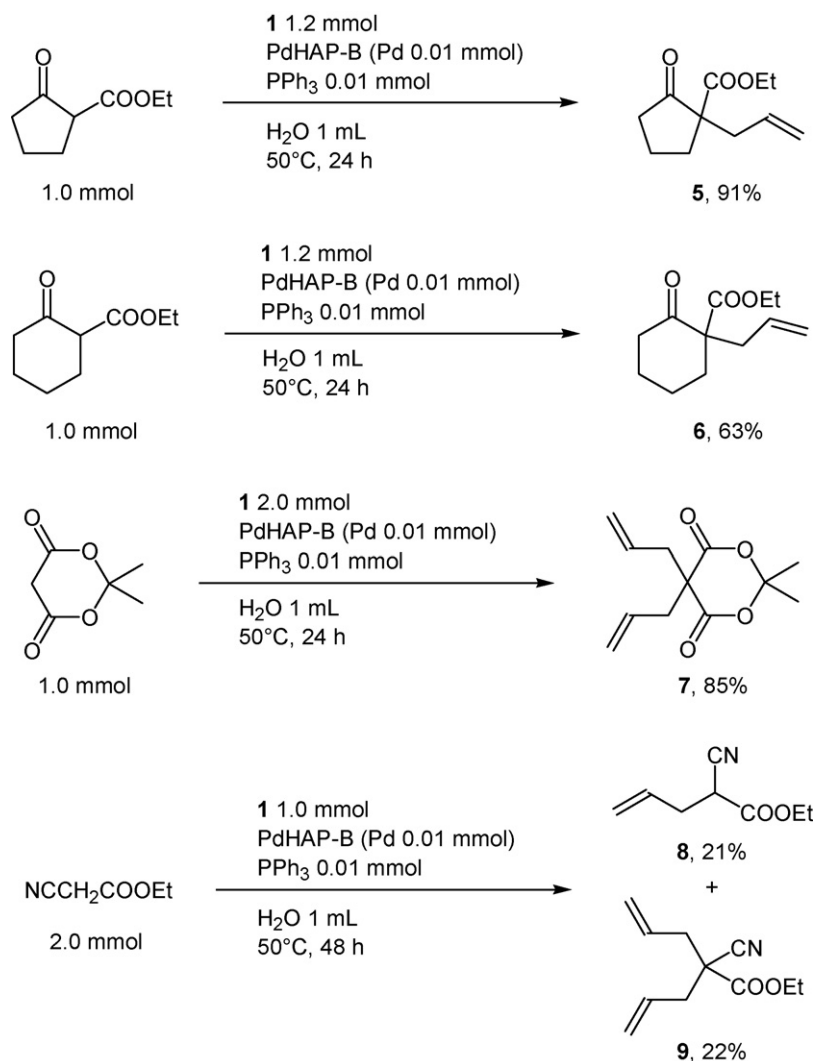
**Fig. 4.** PdHAP-catalyzed allylic alkylation of allyl methyl carbonate (**1**) with diethyl malonate (**2**) and reusability of PdHAP-B in the allylic alkylation. Isolated yields of **3** were averaged for three runs. Reaction conditions: PdHAP-B (0.2 g, 1 mol% Pd),  $\text{PPh}_3$  (3 mg, 0.01 mmol), allyl methyl carbonate (**1**, 0.12 g, 1 mmol), diethyl malonate (**2**, 0.32 g, 2 mmol),  $\text{H}_2\text{O}$  (1 mL), 50°C, 24 h under air in a shaking water bath (AS ONE Co., SWB-17, stroke: 30 mm, speed: 130 rpm). Over 97% of the PdHAP-B was recovered on the average by centrifugation followed by decantation accompanied by washing with methanol (3 mL  $\times$  2) and ether (3 mL  $\times$  5) successively by the same operations, and the material could be reused.

yield (fresh PdHAP-B), a 13% yield (PdHAP-B after being used once), or a trace (PdHAP-B after being used five times) respectively. These results suggest that the leaching Pd causes the allylic alkylation at the initial stages in the repetitive use, whereas the leaching at the late stages in the repetitive use does not occur or does not have so much effect on the allylic alkylation. The results also suggest that palladium on the hydroxyapatite matrix functions as a catalyst for the allylic alkylation.

PdHAP-A and PdHAP-C are also effective in four repetitive uses for the allylic alkylation in the presence of an equimolar amount of  $\text{PPh}_3$  to Pd at 50°C for 24 h in water under air; the isolated yields of **3**, averaged for three runs, in the reaction with PdHAP-A (Pd 0.5 mol%) were 74% (1st), 57% (2nd), 43% (3rd) and 76% (4th, 48 h), and the isolated yields of **3**, averaged for three runs, in the reaction with PdHAP-C (Pd 2 mol%) were 78% (1st), 79% (2nd), 79% (3rd) and 81% (4th). PdHAP-A supporting a lower amount of Pd was found to bring about a lowering of activity in repetitive use, for which elongation of the reaction time compensated to make the yield better in the 4th use. The PdHAP (Pd content:  $0.05 \text{ mmol g}^{-1}$ ) prepared from uncalcined HAP exhibited the same catalytic activity as that of the PdHAP-B prepared from calcined HAP in four repetitive uses under the same conditions as those of the typical procedure; the isolated yields of **3**, averaged for three runs, were 83% (1st), 79% (2nd), 78% (3rd) and 77% (4th). Ethanol as a solvent was not of practical use in the allylic alkylation, because the low yields varied widely from 24% to 73% yields even with PdHAP-C (2 mol% Pd). Non-ion-exchanged PdHAP (Pd content:  $0.02 \text{ mmol g}^{-1}$ ), prepared from  $\text{PdCl}_2(\text{PhCN})_2$  and HAP in acetone at room temperature [14], caused rapid inactivation by the repetitive use; the isolated yields of **3**, averaged for three runs in the allylic alkylation with 1 mol% of the non-ion-exchanged PdHAP, were 19% (1st), 51% (2nd), 34% (3rd),

21% (4th), 3% (5th) and 3% (6th). From the results described above, we can conclude that some palladium ions in all ion-exchanged PdHAPs, generated by the ion-exchange of Ca(II) for Pd(II), coordinate strongly to phosphate moieties to prevent the leaching from HAP matrices into reaction media, in contrast to the non-ion-exchanged PdHAP prepared from  $\text{PdCl}_2(\text{PhCN})_2$  and HAP in acetone. In particular, PdHAP-B and PdHAP-C would keep a certain amount of catalytic active Pd species for the allylic alkylation, even if the leaching of some Pd species from the ion-exchanged PdHAPs had occurred at the initial stages.

The results of PdHAP-catalyzed allylic alkylation of **1** with other carbon nucleophiles are shown in Scheme 1. 2-Ethoxycarbonylcyclopentanone or 2-ethoxycarbonylcyclohexanone reacted with **1** to give the corresponding allylated product **5** or **6** in 91% or 63% yield respectively. The reaction of 2,2-dimethyl-1,3-dioxane-4,6-dione (1 mmol) with **1** (2 mmol) selectively afforded diallylated product **7** in 85% yield. Even if a half equimolar amount of **1** to 2,2-dimethyl-1,3-dioxane-4,6-dione was used, only **7** was produced in a 74% yield (50°C, 24 h). Ethyl cyanoacetate was not such a good nucleophile in the allylic alkylation in water to prepare a mixture of monoallylated **8** and diallylated **9**. Malononitrile did not cause the allylic alkylation in water at all. Allyl acetate instead of allyl methyl carbonate (**1**) did not serve very well for the allylic alkylation; the reaction of allyl acetate (1.0 mmol) and **2** (2.0 mmol) was carried out with PdHAP-C (Pd 0.02 mmol),  $\text{PPh}_3$  (0.02 mmol) and  $\text{K}_2\text{CO}_3$  (1.1 mmol) in  $\text{H}_2\text{O}$  (1 mL) at 50°C for 72 h to produce **3** (25%) and **4** (6%). The differences of yield or reactivity between **1** and allyl acetate would be dependent on the ease of the formation of  $\pi$ -allylpalladium complexes from those allyl esters.



**Scheme 1.** PdHAP-catalyzed allylic alkylation of allyl methyl carbonate (**1**) with other carbon nucleophiles.

#### 4. Conclusions

One of the ultimate goals of environmentally-benign organic syntheses is the development of repetitively-usable heterogeneous catalysts that can be applied to C–C bond-forming reactions in water. Here, we developed an environmentally-benign C–C bond-forming heterogeneous catalytic process via the formation of organometallic intermediates in water: Pd(II) introduced by the ion-exchange of Ca(II) into an insoluble inorganic matrix HAP was found to function as a reusable catalyst for the allylic alkylation via the formation of  $\pi$ -allylpalladium complex at 50°C in water under air. The reusability would be maintained by the coordination of phosphate moieties to palladium. The relatively high reactivity value of the allylic alkylation in water suggests an affinity of the HAP surfaces either for **1** or for carbon nucleophiles such as **2**.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.08.010.

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