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Development of a convoluted polymeric nanopalladium catalyst: α-alkylation of ketones and ring-opening alkylation of cyclic 1,3-diketones with primary alcohols

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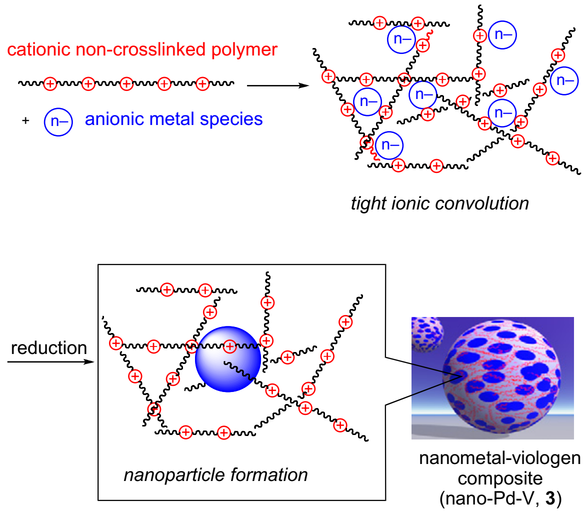
Abstract—A novel solid-phase catalyst of palladium nanoparticles, nano-Pd-V, was prepared from $PdCl_2$ with main-chain viologen polymers via complexation and reduction. This insoluble nanocatalyst nano-Pd-V efficiently promoted α-alkylation of ketones with primary alcohols in the presence of $Ba(OH)_2 \cdot H_2O$ under atmospheric conditions without organic solvents. The nano-Pd-V catalyst was reused without loss of catalytic activity. Ring-opening alkylation of cyclic 1,3-diketones with primary alcohols was also catalyzed by the nano-Pd-V catalyst.

1. Introduction

The development of solid-phase metal-nanoparticle catalysts is an important topic for organic synthesis and for chemical and pharmaceutical processes.[1] Because they can be recovered easily by simple operations thereby preventing contamination of products by toxic metals, nanoparticle catalysts are considered promising candidates for useful, safe, and reusable catalysts. Although immobilized nanoparticle catalysts have been reported, they are generally deactivated during their reuse owing to leaching of the metal species from their supports and/or aggregation of the metal-nanoparticles. Recently, we[2] and others[3] have been involved in developing improved nanoparticle catalysts to overcome these problems.

We have developed a new strategy for the preparation of highly active and reusable solid-phase metal catalysts via self-assembly of inorganic materials with non-crosslinked polymeric ligands.[4,5] Thus, complexation of inorganic materials and non-crosslinked polymeric ligands gives networked, supramolecular, and insoluble complexes in which the polymeric ligands are crosslinked by the inorganic species. Using this methodology, we prepared insoluble catalysts and applied them to heterogenous organic synthetic reactions. These catalysts showed outstanding stability and reusability in reaction media such as water, aqueous or anhydrous organic solvents.

We planned to expand this methodology to the preparation of solid-phase metal-nanoparticles via self-organization of inorganic materials and non-crosslinked polymers. Anionic inorganic materials self-assembled with non-crosslinked cationic polymers to give ionically convoluted insoluble polymeric complexes, which were converted by reduction into metal-nanoparticles having the convoluted polymers as matrices (Scheme 1). These metal-nanoparticles should be stabilized by convoluted matrix polymers to prevent from leaching, aggregation, and deactivation, so that they can become active and recyclable solid-phase catalysts. In this article, we would like to report a full detail of the development of an environmentally benign solid-phase polymeric catalyst of nanopalladium particles (nano-Pd-V) as well as its application to the α-alkylation of ketones[6] and to the ring-opening



Scheme 1. Working hypothesis for the preparation of solid-phase metal-nanoparticles via ionic convolution of non-crosslinked polymers and reductive metalparticle formation.

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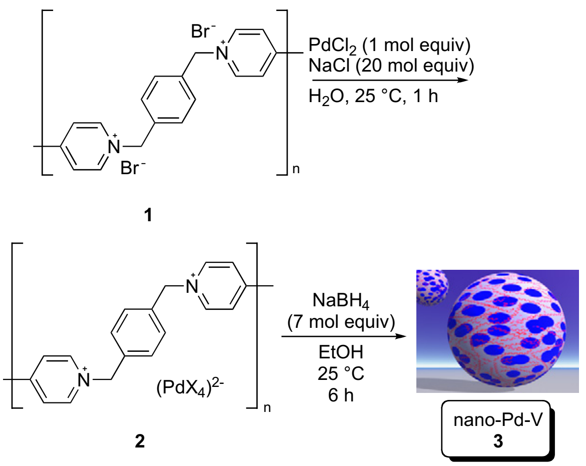
alkylation of cyclic diketones with primary alcohols. It should be emphasized that this novel catalyst was reused in the absence of organic solvents under atmospheric conditions without any loss of catalytic activity.

2. Results and discussion

2.1. Preparation of viologen-supported nanopalladium catalyst nano-Pd-V 3

The nanopalladium catalyst nano-Pd-V **3** was prepared as shown in Scheme 2. When an aqueous solution of $PdCl_2$ and 20 mol equiv of NaCl was added to an aqueous solution of the main-chain viologen polymer **1**[7] at 25 °C, the components are ionically-assembled to give the insoluble convoluted complex **2** as an orange powder. Compound **2** was reduced by $NaBH_4$ at 25 °C in EtOH to afford the black polymeric palladium nanoparticles nano-Pd-V **3**, which were insoluble in water, ethanol, ethyl acetate, dichloromethane, toluene, and hexane.

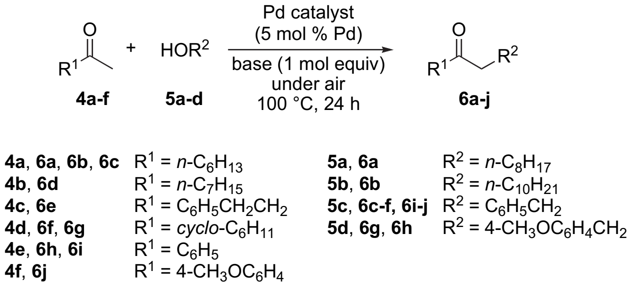


Scheme 2. Preparation of solid-phase metal-nanoparticles nano-Pd-V **3** via ionic convolution of $PdCl_2$ and non-crosslinked polymer **1**.

To elucidate the structure of **3**, several spectroscopic measurements were carried out. The morphology of **3** was evaluated by scanning electron microscopic (SEM) observation, which confirmed **3** to be a macroporous material (Fig. 1, top). The images revealed a sponge-like structure with a disordered arrangement of interconnected pores in the size range of approximately 1 μm. An energy dispersive spectrum (EDS) collected in the SEM showed the presence of palladium and bromide with a trace amount of chloride in **3** (Fig. 1, center). Transmission electron microscopy (TEM) and scanning transmission electron microscopy–energy dispersive spectroscopy (STEM/EDS) analysis proved the existence of palladium nanoparticles in **3**. TEM analysis showed that the palladium particles have a mean diameter of 2 nm with a narrow size distribution (Fig. 1, bottom).

2.2. α-Alkylation of ketones with primary alcohols

To demonstrate the potency of nano-Pd-V **3** as a reusable heterogenous catalyst for organic synthesis, dehydrative α-alkylation of ketones with primary alcohols was selected because this reaction system is environmentally benign: it does not use harmful alkyl halides as electrophiles, and the resulting products are only the desired α-alkylated ketones and water.[8,9] In 2004, Kaneda et al. reported the first heterogenous α-alkylation of ketones with alcohols at 180 °C in toluene catalyzed by Ru-hydrotalcite.[9a] Recently, Cho reported Pd–C-catalyzed α-alkylation of ketones with alcohols at 100 °C in dioxane in the presence of 1-decene as an additive.[9b] Park et al. reported the first reusable catalytic system of α-alkylation of ketones with alcohols catalyzed by Pd/AlO(OH) at 80–110 °C in toluene while its recyclability was not sufficient.[9c] We decided to use this nanoparticle catalyst under atmospheric conditions without organic solvents to comply with the goals of green chemistry. As shown in Scheme 3 and Table 1, reaction of 2-octanone (**4a**) with 2 mol equiv of 1-octanol (**5a**) was performed in the presence of 5 mol % palladium of a catalyst and 1 mol equiv of barium hydroxide octahydrate at 100 °C for 24 h. The dehydrative α-alkylation was found to proceed with nano-Pd-V **3** to provide 59% yield of the desired product 7-hexadecanone (**6a**) (entry 1). In a control experiment, it was confirmed that the viologen polymer **1** used as a redox material[5b] had no catalytic activity (entry 2), and that the heterogenous catalysts Pd–C, ARP-Pd,[2] and PdAS[5c,f] promoted the reaction sluggishly (entries 3–5). It was gratifying to see that, after thorough optimization, the combination of nano-Pd-V **3**, $Ba(OH)_2\cdot H_2O$, and 7 mol equiv of water is essential to construct an efficient catalyst system with much higher activity. Thus, when a mixture of **4a**, **5a**, $Ba(OH)_2\cdot H_2O$, and 7 mol equiv of H_2O was stirred at 100 °C for 24 h in the presence of 5 mol % palladium of nano-Pd-V catalyst **3**, the α-alkylation took place under atmospheric conditions to give 83% yield of **6a** (entry 6). The precursor **2** had low catalytic activity to give **6a** in 12% yield (entry 7).



Scheme 3.

Table 1. α-Alkylation of **4a** with **5a** in the presence of catalyst and barium hydroxide[a]

Entry	Catalyst/base	Additive	Yield[b] (%) of **6a**
1	**3**/$Ba(OH)_2\cdot 8H_2O$	—	59
2	**1**/$Ba(OH)_2\cdot 8H_2O$	—	No reaction
3	Pd–C/$Ba(OH)_2\cdot 8H_2O$	—	4
4	ARP-Pd/$Ba(OH)_2\cdot 8H_2O$	—	14
5	PdAS/$Ba(OH)_2\cdot 8H_2O$	—	24
6	**3**/$Ba(OH)_2\cdot H_2O$	H_2O (7 mol equiv)	83
7	**2**/$Ba(OH)_2\cdot H_2O$	H_2O (7 mol equiv)	12

[a] All the reactions were carried out in the presence of 5 mol % palladium of the catalyst and a base (1 mol equiv) at 100 °C for 24 h under atmospheric conditions, **4**/**5**=1.0:2.0.

[b] GC yield.

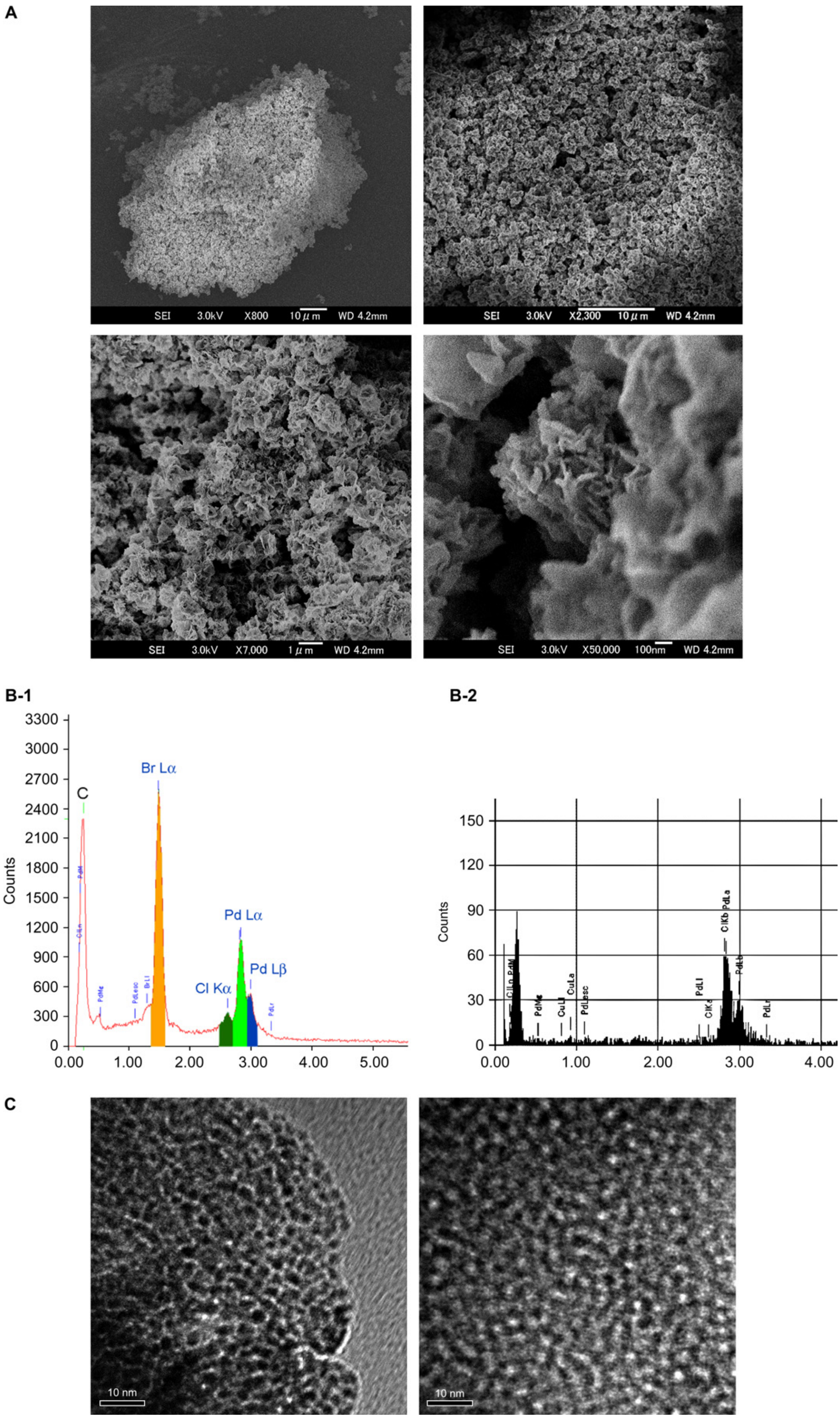


Figure 1. SEM (A), TEM (C) images, EDS (B-1) and STEM/EDS (B-2) analysis of nano-Pd-V **3** (bar length: SEM 10 μm, 10 μm, 1 μm and 100 nm, respectively; TEM 10 nm).

Table 2. α-Alkylation of ketones **4** with primary alcohols **5** promoted by nano-Pd-V **3** and $Ba(OH)_2 \cdot H_2O$[a]

Entry	Ketones **4** (R^1)	Primary alcohols **5** (R^2)	Yield[b] (%) of **6**
1	**4a** (R^1=*n*-C_6H_{13})	**5a** (R^2=*n*-C_8H_{17})	**6a**: 83[f]
2[c]	**4a**	**5a**	**6a**: 90[f]
3[d]	**4a**	**5a**	**6a**: 91[f]
4	**4a**	**5b** (R^2=*n*-$C_{10}H_{21}$)	**6b**: 84
5	**4a**	**5c** (R^2=$C_6H_5CH_2$)	**6c**: 91
6	**4b** (R^1=*n*-C_7H_{15})	**5c**	**6d**: 84
7	**4c** (R^1=$C_6H_5CH_2CH_2$)	**5c**	**6e**: 93
8	**4d** (R^1=*cyclo*-C_6H_{11})	**5c**	**6f**: 81
9	**4d**	**5d** (R^2=4-$CH_3OC_6H_4CH_2$)	**6g**: 83
10	**4e** (R^1=C_6H_5)	**5d**	**6h**: 90
11[e]	**4e**	**5c**	**6i**: 82
12	**4f** (R^1=4-$CH_3OC_6H_4$)	**5c**	**6j**: 95

[a] All the reactions were carried out in the presence of 5 mol % palladium of nano-Pd-V catalyst and 1 mol equiv of $Ba(OH)_2 \cdot H_2O$ at 100 °C for 24 h under atmospheric conditions, **4**/**5**=1.0:2.0. H_2O (7 mol equiv) was added except for entries 2 and 3.

[b] Isolated yields unless otherwise noted.

[c] Second use of **3**.

[d] Third use of **3**.

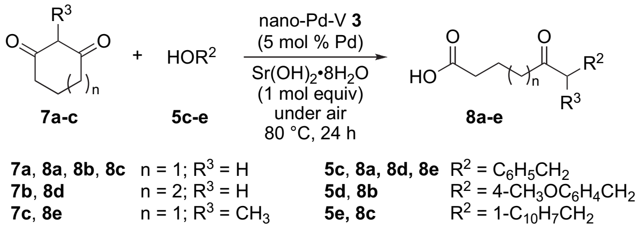
[e] The reaction was performed at 80 °C for 12 h.

[f] GC yield.

Using the catalyst system identified above, the reaction of a variety of ketones with primary alcohols was investigated as shown in Table 2. The following reactions were performed under the same conditions as that for entry 6, Table 1, and the α-alkylated products **6b–j** were isolated via purification by column chromatography. The α-alkylation of 2-octanone (**4a**) with 1-octanol (**5a**) and 1-decanol (**5b**) proceeded regioselectively to afford 7-hexadecanone (**6a**) and 7-octadecanone (**6b**) in 83% and 84% yields, respectively (entries 1 and 4). The reaction of the aliphatic ketones **4a–d** with benzyl alcohol (**5c**) gave the corresponding α-alkylated ketones **6c–f** in 81%–93% yields (entries 5–8). When **4d** and 4-methoxybenzyl alcohol (**5d**) were used, 1-cyclohexyl-3-(4-methoxyphenyl)-1-propanone (**6g**) was obtained in 83% yield (entry 9). The catalytic system was applied to the coupling of aromatic ketones with benzylic alcohols (entries 10–12). Thus, the alkylation of acetophenone (**4e**) with **5d** proceeded smoothly to give 3-(4-methoxyphenyl)-1-phenyl-1-propanone (**6h**) in 90% yield. The ketone **4e** and the solid ketone 4-methoxyacetophenone (**4f**) were alkylated with **5c** to afford 1,3-diphenyl-1-propanone (**6i**) and 1-(4-methoxyphenyl)-3-phenyl-1-propanone (**6j**) in yields of 82% (at 80 °C for 12 h) and 95%, respectively. Although α-alkylation of ketones generally suffers from poor regioselectivity, it was found that the reactions in Table 2 gave no regioisomers. Recyclability of the nano-Pd-V catalyst **3** was examined for the subsequent reaction of **4a** and **5a**. Thus, after the first reaction, which gave 83% yield of **6a** (Table 2, entry 1), the catalyst polymer was recovered by centrifugation and successively subjected to second and third series of the reactions under the same conditions to afford 90% and 91% yields of **6a** (Table 2, entries 2 and 3). No Pd leaching in the filtrate was detected by inductive coupled plasma (ICP) analysis.

2.3. Ring-opening alkylation of cyclic 1,3-diketones with primary alcohols

A useful recyclable catalyst for dehydrative α-alkylation of ketones with primary alcohols in hand, we have applied nano-Pd-V-catalyzed alkylation to the functionalization of cyclic 1,3-diketones where ring-opening alkylation forming alkylated ketocarboxylic acids was found to proceed.[10,11] Thus, the reaction of 1,3-cyclohexanedione (**7a**) with benzyl alcohol (**5c**) (5 mol equiv) with nano-Pd-V **3** (5 mol %) and strontium hydroxide octahydrate (1 mol equiv) with water (7 mol equiv) at 80 °C for 24 h followed by quenching with 1 N aqueous HCl afforded 5-oxo-7-phenylheptanoic acid (**8a**) in 80% yield (Scheme 4 and Table 3, entry 1).[12] Cyclic diketone **7a** also underwent the ring-opening alkylation with *p*-anisyl alcohol (**5d**) and 1-naphthylmethanol (**5e**) to give δ-oxocarboxylic acids **8b** and **8c** in 81% and 73% yields, respectively (entries 2 and 3). The reaction of 1,3-cycloheptanone (**7b**) with **5c** gave 6-oxo-8-phenylheptanoic acid (**8d**) in 73% yield (entry 4). 2-Methyl-1,3-cyclohexanedione (**7c**) reacted with **5c** under the similar conditions to afford 6-methyl-5-oxo-7-phenylheptanoic acid (**8a**) in 78% yield (entry 5). As far as we know, this is the first example of the catalytic ring-opening alkylation cascade system of 1,3-diketones with primary alcohols.



Scheme 4.

Table 3. The ring-opening alkylation of cyclic diketones **7** with primary alcohols **5** with catalytic nano-Pd-V **3** and $Sr(OH)_2 \cdot 8H_2O$[a]

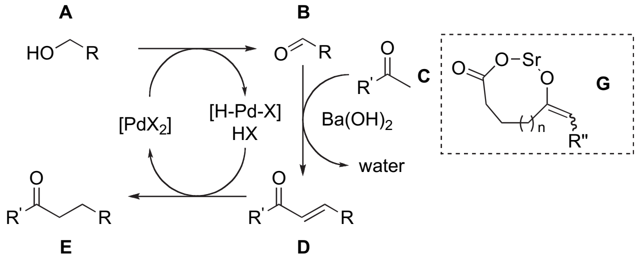
Entry	Diketones **7** (R^1)	Primary alcohols **5** (R^2)	Yield[b] (%) of **8**
1	**7a** (*n*=1; R^3=H)	**5c** (R^2=$C_6H_5CH_2$)	**8a**: 80
2	**7a**	**5d** (R^2=4-$CH_3OC_6H_4CH_2$)	**8b**: 81
3	**7a**	**5e** (R^2=1-$C_{10}H_7CH_2$)	**8c**: 73
4	**7b** (*n*=2; R^3=H)	**5a**	**8d**: 73
5	**7c** (*n*=1; R^3=CH_3)	**5a**	**8e**: 78

[a] All the reactions were carried out in the presence of 5 mol % palladium of nano-Pd-V catalyst, 1 mol equiv of $Sr(OH)_2 \cdot 8H_2O$ and 7 mol equiv of H_2O at 80 °C for 24 h under atmospheric conditions, **7**/**5**=1.0:5.0.

[b] Isolated yields.

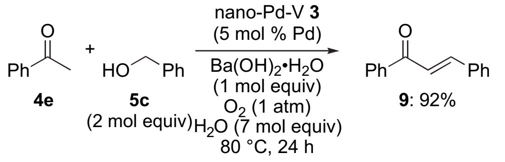
2.4. Reaction pathway

Although the reaction pathway for these reactions has not been proved, one plausible working model would be as shown in Scheme 5. Thus, for the α-alkylation of ketones with alcohols, an alcohol **A** is oxidized by PdX_2 to give an aldehyde **B**, which undergoes dehydrative aldol condensation (Claisen–Schmidt reaction) with a ketone **C** in the presence of $Ba(OH)_2$ to afford an α,β-unsaturated ketone **D**. The ketone **D** was reduced via hydropalladation with HPdX and protodepalladation with HX to give a desired saturated ketone **E** with reproduction of PdX_2. The ring-opening alkylation should proceed through the condensation of **B** with enolate **G** generated in situ via alkaline hydrolysis of cyclic diketone **7**. To support our working hypothesis, the reaction of **4e** with **5c** (2 mol equiv) in the presence of **3** (5 mol % Pd) was carried out under 1 atm O_2 atmospheric conditions to give the α,β-unsaturated ketone **9** in 92% yield (Eq. 1).

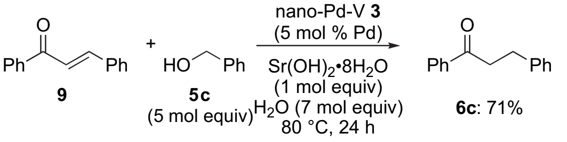


Scheme 5. Working models of α-alkylation of ketones with alcohols.

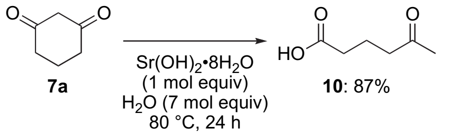
The reaction of the unsaturated ketone **9** with **5c** and **3** was performed to give the saturated ketone **6c** in 71% yield (Eq. 2). Diketone **7a** was treated with $Sr(OH)_2$ without the Pd catalyst nano-Pd-V **3** to give 5-oxo-hexanoic acid **10** in 87% isolated yield after acidic post-treatment (Eq. 3),[13] indicating generation of Sr-enolate **G** in situ under the alkaline conditions.



(1)



(2)



(3)

3. Conclusion

In conclusion, we have developed a novel polymeric catalyst nano-Pd-V **3** of palladium nanoparticles with viologen polymers via the ionic self-organization process. The α-alkylation of a variety of ketones with primary alcohols using the catalyst **3** afforded the desired products in high yields. This catalyst was applied to reactions under atmospheric conditions without organic solvents. The catalyst **3** could be reused without loss of its catalytic activity. Nano-Pd-V promoted the ring-opening alkylation of cyclic 1,3-diketones with primary alcohols to give oxo-alkanoic acids.

4. Experimental

4.1. General

The reaction of ketones or 1,3-diketones with alcohols as well as the preparation of nano-Pd-V **3** were performed in a glass tube under atmospheric conditions. Water was deionized with a Millipore system as a Milli-Q grade. NMR spectra were recorded on a JEOL JNM-AL500 spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C). MAS ^{13}C NMR spectra were recorded on a JEOL JNM-ECA920 spectrometer (232 MHz for ^{13}C). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C. Chemical shifts were reported in δ (ppm) referenced to an internal tetramethylsilane standard for ^1H NMR. Chemical shifts of ^{13}C NMR were given relative to $CDCl_3$ as an internal standard (δ 77.0 ppm). The GC–MS was measured with an Agilent 6890 GC/5973 N MS detector. ATR-FTIR spectra were measured with an FTIR-460 Plus spectrometer (JASCO). SEM images were given by using a scanning electron microscope (JEOL JSM-6700F). TEM images were obtained by using a transmission electron microscope (JEOL JEM-2100F) operated at 200 kV. Polymer **1** was prepared in accordance with the reported procedure.[7] Ketones **4**, alcohols **5**, and 1,3-diketones **7** were purchased from Aldrich, Tokyo Kasei (TCI) or Wako Co., Ltd.

CAS registry numbers: **1**: 32168-10-8; **4a**: 111-13-7; **4b**: 821-55-6; **4c**: 2550-26-7; **4d**: 823-76-7; **4e**: 98-86-2; **4f**: 100-06-1; **5a**: 111-87-5; **5b**: 112-30-1; **5c**: 100-51-6; **5d**: 105-13-5; **6a**: 45206-91-5; **6b**: 18277-00-4; **6c**: 56741-23-2; **6d**: 56705-47-6; **6e**: 5396-91-8; **6f**: 43125-06-0; **6h**: 1669-49-4; **6i**: 1083-30-3; **6j**: 5739-38-8; **7a**: 504-02-9; **7b**: 1194-18-9; **7c**: 1193-55-1; **8a**: 32764-94-6; **8b**: 49617-90-5; **8c**: 109089-80-7; **8d**: 53668-48-7; **8e**: 855899-12-6.

4.2. Preparation of 2

To a solution of **1** (1.68 g; 4.0 mmol) in water (100 mL) was added a solution[†] of $PdCl_2$ (709 mg; 4.0 mmol) and NaCl (4.68 g) in water (100 mL) at 25 °C, giving orange precipitates. The mixture was stirred at the same temperature for 1 h. Purification by filtration (pore size: 1 μm), washing with water, and drying at 5 Pa for 12 h afforded the insoluble product **2** (1.77 g) as an orange powder. CP-MAS ^{13}C NMR (232 MHz; solid) δ 148.9, 146.8, 135.0, 131.1, 128.0, 64.4; IR (ATR) ν 3471, 3117, 3055, 2920, 2851, 1636, 1611, 1436, 1421, 809, 768 cm^{-1}; Anal. Calcd for $(C_{18}H_{16}Br_2Cl_2N_2Pd\cdot 3H_2O)_n$: C 33.18%, H 3.40%, N 4.30%. Found: C 31.91%, H 2.66%, N 4.33%.

4.3. Preparation of nano-Pd-V 3

A solution of $NaBH_4$ (450 mg) in EtOH (75 mL) was slowly added dropwise over 10 min to a suspension of **2** (900 mg) in EtOH (75 mL) at 25 °C, and the suspension was stirred for 6 h. Purification by filtration (pore size: 1 mm), washing with water, and drying at 5 Pa for 12 h gave nano-Pd-V **3** (630 mg) as a dark brown powder. The post-treatments (filtration, washing, storing) were performed under atmospheric conditions. The weight percent of Pd in **3** was estimated to be 18% by elemental analysis. CP-MAS ^{13}C NMR (232 MHz; solid) δ 130.9, 128.8, 63.9, 56.8, 52.8, 42.1, 31.5, 15.5; IR (ATR) ν 3471, 3117, 3054, 2920, 2851, 1636, 1436, 1236, 1090, 891 cm^{-1}; Anal. Calcd for $(C_{18}H_{16}Br_2N_2Pd\cdot 3H_2O)_n$: C 37.24%, H 3.82%, N 4.82%. Found: C 37.51%, H 3.72%, N 5.08%.

[†] The solution was prepared by mixing $PdCl_2$ and NaCl in water at 80 °C.

4.4. General procedure for α-alkylation of the ketones 4 with the primary alcohols 5 in the presence of nano-Pd-V 3 and $Ba(OH)_2 \cdot H_2O$

To a mixture of nano-Pd-V **3** (10 mg) and $Ba(OH)_2 \cdot H_2O$ (63 mg) was added water (42 mL), and the suspension was mixed by a vortex mixer for 1 min at 25 °C. Compounds **4** (0.334 mmol) and **5** (0.668 mmol) were added to the reaction mixture, which was stirred at 100 °C for 24 h. For the reactions shown in Table 2, entries 4–12, the mixture was purified by column chromatography (eluant: EtOAc/hexane) to give **6**. For the reactions shown in Table 2, entries 1–3, EtOAc (8 mL) was added to the reaction mixture, which was then centrifuged at 4000 rpm for 5 min. EtOAc layer was decanted and analyzed by GC to determine the GC yield of **6a**. To the residue was added water (8 mL), followed by centrifugation at 4000 rpm for 5 min and decantation of the aqueous layer to give a black powder that was dried at 5 Pa for 12 h and used for the next reaction as a reusable catalyst.

4.4.1. 1-Cyclohexyl-3-(4-methoxyphenyl)propan-1-one (6g). ^1H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J=8.5 Hz, 2H), 6.81 (d, J=8.5 Hz, 2H), 3.78 (s, 3H), 2.82 (t, J=7.6 Hz, 2H), 2.71 (t, J=7.6 Hz, 2H), 2.27–2.33 (m, 1H), 1.58–1.81 (m, 5H), 1.16–1.34 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.3, 157.9, 133.5, 129.2, 113.8, 55.2, 51.0, 42.8, 28.8, 28.4, 25.8, 25.6; IR (ATR) ν 2926, 2853, 1704, 1611, 1512, 1466, 1448, 1230, 1239, 1177, 1090, 1035, 890, 827, 630 cm^{-1}; MS(EI(+)) 246 (M^+), 163 121 (a base peak); HRMS (ESI(+)) calcd for $C_{16}H_{22}O_2Na$ ($M+Na^+$) 269.1518, found 269.1526.

4.5. General procedure for ring-opening alkylation of the cyclic diketones 7 with the primary alcohols 5 in the presence of nano-Pd-V 3 and $Sr(OH)_2 \cdot 8H_2O$

To a mixture of nano-Pd-V **3** (10 mg) and $Sr(OH)_2 \cdot 8H_2O$ (89 mg) was added water (42 μL), and the resulting suspension was mixed by a vortex mixer for 1 min at 25 °C. Compounds **7** (0.334 mmol) and **5** (0.668 mmol) were added to the suspension and the mixture was stirred at 80 °C for 24 h. After being cooled, 1 M aqueous HCl (3 mL) and EtOAc (5 mL) were added to the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The organic layer combined was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (eluant: EtOAc/hexane) to give **8**.

Acknowledgements

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References and notes

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