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Hydrotalcite-Supported Ag/Pd Bimetallic Nanoclusters Catalyzed Oxidation and One-Pot Aldol Reaction in Water

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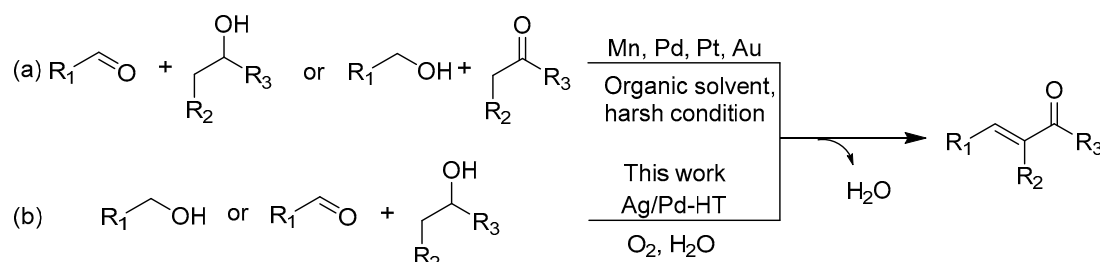
Abstract: A highly active hydrotalcite-supported Ag/Pd bimetallic nanocluster catalyst has been developed by a simple, easy and safe chemical reduction method. The catalyst was characterized by high-resolution transmission electron microscopy (HR-TEM), which revealed very small (3.2 ± 0.7 nm) nanoclusters with a narrow size distribution. The bimetallic Ag/Pd catalyst showed strong cooperation between Ag and Pd for the alcohol oxidation reaction. The developed catalyst provided an efficient and environmentally friendly method for alcohol oxidation and one-pot cross-aldol condensation in water. A broad scope of α,β -unsaturated ketones with good to excellent yields were obtained under very mild conditions. This catalytic system offers an easy preparation method with a simple recovery process, good activity and reusability of up to five cycles without significant loss in the catalytic activity.

Keywords: heterogeneous catalyst; bimetallic catalyst; hydrotalcites; alcohol oxidation; aldol reaction

1. Introduction

α,β -Unsaturated ketones are an important class of compounds which are commonly used not only as biologically active compounds but also as key intermediates for the synthesis of agrochemical, pharmaceutical, and other fine chemicals. For example, chalcone derivatives have been shown to be potent monoamine oxidase (MAO) inhibitors. The arylidene-1-indanones are considered to belong to the same chemical class as the cyclic analogues of chalcones and thus have also been found to show similar MAO inhibition properties [1]. Chalcones synthesis via Claisen Schmidt condensation is a conventional approach and the process has been promoted using various heterogeneous basic catalysts, such as alumina [2], hydrotalcite [3], zeolite [4], and hydroxyapatite [5] due to the easy separation of the catalyst from the reaction mixture during purification process. On the other hand, the synthesis of α,β -unsaturated ketones through direct oxidative coupling of primary and secondary alcohol is expected to be a more straightforward method, i.e., inexpensive and readily available alcohols and ketones can be used as starting materials and the reaction is an environmentally friendly process that combines the oxidation of alcohols to aldehydes and condensation of aldehyde with ketone producing

only H₂O or H₂ as byproducts [6–9] (Scheme 1a,b). To this date, one-pot oxidative coupling of alcohols that results in α,β -unsaturated ketones is limited due to the requirement of toxic organic solvent and high temperature.



Scheme 1. Synthesis of α,β -unsaturated ketones by oxidative coupling reaction of alcohols with aldehydes and ketones. (a) previous works for direct oxidative coupling reaction, (b) Ag/Pd-HT catalyzed oxidative coupling in water.

To establish the simple and mild one-pot oxidative coupling of alcohols, development of efficient heterogeneous catalyst for oxidation of alcohols is required. So far, several heterogeneous catalysts including Au, Ag, Pt, Pd and Ru have been developed and their utility in oxidation reactions has been extensively investigated. Among them, palladium-catalyzed oxidation reactions using molecular oxygen as a co-oxidant have long been the most versatile strategies [10–18]. For example, Uozumi et al. developed amphiphilic polystyrene-poly (ethylene glycol) (PS-PEG) resin-dispersion of Pd-nanoparticles, Kobayashi et al. developed Polymer-incarcerated carbon-stabilized Gold nanoclusters and Minati et al. developed microgel-stabilized metal nanoclusters for alcohol oxidation in water under O₂ and reflux condition [13–15]. Furthermore, Kakiuchi et al. reported layered double hydroxide (LDH) supported Pd(II)-pyridine complex catalyst for aerobic oxidation of alcohol using toluene as a solvent [10]. In addition, heterogeneous bimetallic catalysts have also been developed. Ni-Ga hydrotalcite catalyzed oxidation of alcohol by molecular oxygen has also been studied [16]. Hou et al. reported bimetallic Au/Pd-PVP catalyzed alcohol oxidation; although they clearly demonstrated that bimetallicity enhanced the catalytic activity, the reaction suffered catalyst instability [17]. Various heterogeneous oxidation catalysts have been developed as described above, however, there is still a need to study and develop new heterogeneous catalysts that will work under low temperature using molecular O₂ as oxidant and water as solvent. A heterogeneous catalyst with the ability to activate alcohols and carbonyl-containing molecules in aqueous media would not only be advantageous in terms of low cost, abundance, and environmental concerns, but would also provide an exciting opportunity for the conversion of biomass to fuels and chemicals [19–22].

Recently, we reported the development of a highly active and reusable hydrotalcite (HT)-supported Pd nanocluster catalyst and its efficient catalytic performance for the cross-coupling reaction of aryl chlorides and bromides under mild reaction conditions [23]. HT has been an attractive option as a support for dispersing noble metals due to a number of useful properties, such as its variable composition of cations, tunable acidity, basicity of the surface and high metal-adsorption abilities, which help in obtaining highly dispersed nanoparticles on this support [24,25]. Bimetallicity is a strategy for preparing an active and stable catalyst, and bimetallic alloys exhibit superior catalytic activities in various types of reactions under mild conditions [26–31]. In our continuing investigation into the synthesis of new, LDH-supported Pd and Pd-based nanocluster catalysts and testing of their catalytic activities, we prepared HT-supported Ag/Pd bimetallic nanocluster catalysts and efficiently applied them to the oxidation reaction of primary and secondary alcohols to aldehydes and ketones under mild conditions in water. Further, we found that chalcones and arylidene-1-indanones can easily be prepared by aldol condensation in one pot. Hence, in this paper, we report an efficient and environmentally friendly method for alcohol oxidation and one-pot aldol condensation in water. A broad scope of α,β -unsaturated ketones were also presented under very mild conditions.

2. Results and Discussion

2.1. Synthesis of Catalyst

Quantities of 0.025 mmol 12.5 mM aq. Pd(OAc)₂ (for monometallic Pd-HT) or AgOAc (for monometallic Ag-HT) solution or 0.0125 mmol 12.5 mM aq. Pd(OAc)₂ solution and 0.0125 mmol AgOAc (for 1:1 bimetallic Ag/Pd-HT) were mixed with 300 mg of HT and stirred at room temperature overnight. Then, the temperature was reduced to 15 °C, 2.5 mmol of 0.27 mM aqueous NaBH₄ was added and stirring was continued for 1 h. The catalyst was then centrifuged, washed several times with deionized water, dried under a vacuum and directly used for reaction.

2.2. Catalytic Performance

We began our investigation by testing the catalytic activity of HT-supported Pd and Ag catalysts for the oxidation reaction of 1-indanol as a test reaction. The catalytic activities of monometallic Ag-HT, Pd-HT and bimetallic Ag/Pd-HT were tested under the reaction condition of Cs₂CO₃ as base in dioxane at 70 °C for 24 h. Ag-HT gave a moderate yield (60%) of the oxidation product and only Pd-HT gave a lower yield (38%) under the same reaction condition (Table 1, entries 1–2). However, the bimetallic catalyst of (1:1) Ag/Pd gave the best result (Table 1, entry 3), showing the promotional effect of Pd on Ag. We also compared the activity of bimetallic Ag and Pd by varying their ratios. Ag/Pd catalyst in a ratio of 3:7 gave only 28% of the desired product and 7:3 Ag/Pd gave 51% yield, which is not significantly different compared to the yields using pure Pd or pure Ag as catalyst probably due to formation of core-shell type nanoclusters or segregated Ag and Pd clusters. A significant enhancement in the catalytic activity was only observed by mixing Ag with Pd at a 1:1 ratio. We expect that the reaction on pure Ag or Pd nanoclusters are slow because of the low efficiency of substrate activation. In contrast, in the bimetallic system of 1:1 ratio, the electronic effect of Ag on Pd caused activation of the adjacent Pd atoms in the nanocluster, which efficiently activated adsorbed oxygen on its surface to facilitate the oxidation reaction of alcohol. Finally, the optimized reaction condition was the use of 3 atom% of the catalyst and Cs₂CO₃ in dioxane at 50 °C (entry 6). In addition, the reaction could be successfully carried out in H₂O with Cs₂CO₃ or NaOH as base in good yield of the product (entries 7 and 10). The reaction also occurred under air in the absence of oxygen balloon with low yield (30%, entry 8). Blank experiments were performed in the absence of catalyst and in the absence of Ag/Pd metal by using only the prepared HT. No oxidation product was observed under these reaction conditions (entries 9–10). This confirmed the role of Ag and Pd in the oxidation of benzyl alcohols and the further enhancement of activity by a bimetallic system. Next, the optimized reaction condition in dioxane was applied to the oxidation reaction of various alcohols to extend the scope of the reaction. The reaction of 4-methoxybenzyl alcohol (**2ad**) showed slight decline in yield due to the formation of benzoic acid. However, other alcohols, including secondary (**2bd**, **2ed** and **2fd**), allylic (**2dd**) and propargylic (**2cd**) alcohols gave the desired ketones and aldehydes in good to excellent yield (Scheme 2).

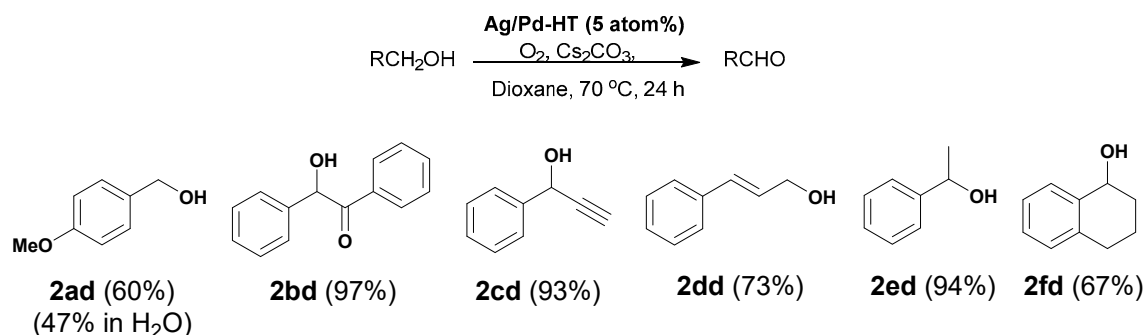
Next, we characterize this best catalytic system containing (1:1) Ag/Pd-HT by transmission electron microscope (TEM). The images of the catalyst show a uniformly dispersed Ag/Pd-NPs on the support (Figure 1a,b). Based on the histogram plot of one hundred randomly selected particles using the Gatan Digital Micrograph software, the average size of the nanoparticles was ca. 3.2 ± 0.7 nm (Figure 1c). The high-resolution TEM image further reveals the homogeneous distributions of crystalline Ag/Pd-NPs on the support material (Figure 1d).

Table 1. Catalyst screening and optimization of reaction conditions for oxidation of 1-indanol ^a.

Entry	Catalyst (Atom%)	Solvent	Base	Temperature (°C)	Yield (%) ^b
1	Ag-HT (5)	dioxane	Cs ₂ CO ₃	70	60
2	Pd-HT (5)	dioxane	Cs ₂ CO ₃	70	38
3	Ag/Pd-HT(1:1) (5)	dioxane	Cs ₂ CO ₃	70	93
4	Ag/Pd-HT(3:7) (5)	dioxane	Cs ₂ CO ₃	70	28
5	Ag/Pd-HT(7:3) (5)	dioxane	Cs ₂ CO ₃	70	51
6	Ag/Pd-HT(1:1) (3)	dioxane	Cs ₂ CO ₃	50	92
7	Ag/Pd-HT(1:1) (3)	H ₂ O	Cs ₂ CO ₃	50	87
8 ^c	Ag/Pd-HT(1:1) (3)	H ₂ O	Cs ₂ CO ₃	50	30
9	HT	H ₂ O	Cs ₂ CO ₃	50–70	—
10	No catalyst	H ₂ O	Cs ₂ CO ₃	50–70	—
11	Ag/Pd-HT(1:1) (3)	H ₂ O	NaOH	50	90

^a Reaction conditions: 0.1 mmol of 1-indanol, 150 mol% of base, O₂ balloon, 1 mL of solvent. ^b Isolated yields.

^c reaction under air.



Scheme 2. (1:1)Ag/Pd-HT catalyzed oxidation of alcohols. Reaction condition: 0.1 mmol alcohols, 150 mol% Cs₂CO₃, (1:1) Ag/Pd-HT, O₂ balloon, Dioxane (1 mL).

After successful results of the oxidation reaction by (1:1) Ag/Pd catalyst, one-pot aldol reaction of 1-indanol with various primary aldehydes were carried out in water. We were delighted to achieve this one-pot reaction even in water to get chalcones in satisfactory yields by stepwise addition of alcohol and aldehyde (Scheme 3a, method A). A wide range of substrates was used for the arylidene-1-indanones, including 1-indanol and various primary aldehydes, revealing that the reaction proceeded successfully even in the heterogeneous system. The reactions of various benzaldehydes **2** bearing electron-donating (Scheme 3a, entries **2b–2e**) and electron-withdrawing (entries **2f–2i**) substituents also proceeded smoothly to afford desired unsaturated enones **3b–3i** in good to excellent yields. Similar results were obtained with the reactions of sterically hindered aldehydes (**2j**). Heterocycle-substituted aldehydes, including 2-furfural (**2k**) and 2-pyridinecarboxaldehyde (**2l**), also gave good results. Alternately, we also investigated whether the oxidative coupling of primary alcohol with ketone proceeded well. The stepwise addition of primary alcohol and ketone gave an excellent yield of the aldol product (Scheme 3b, method B). Next, we attempted one-step oxidative coupling reaction of primary- and

secondary alcohols by adding both alcohols simultaneously, which also gave a good result (Scheme 3c, method C).

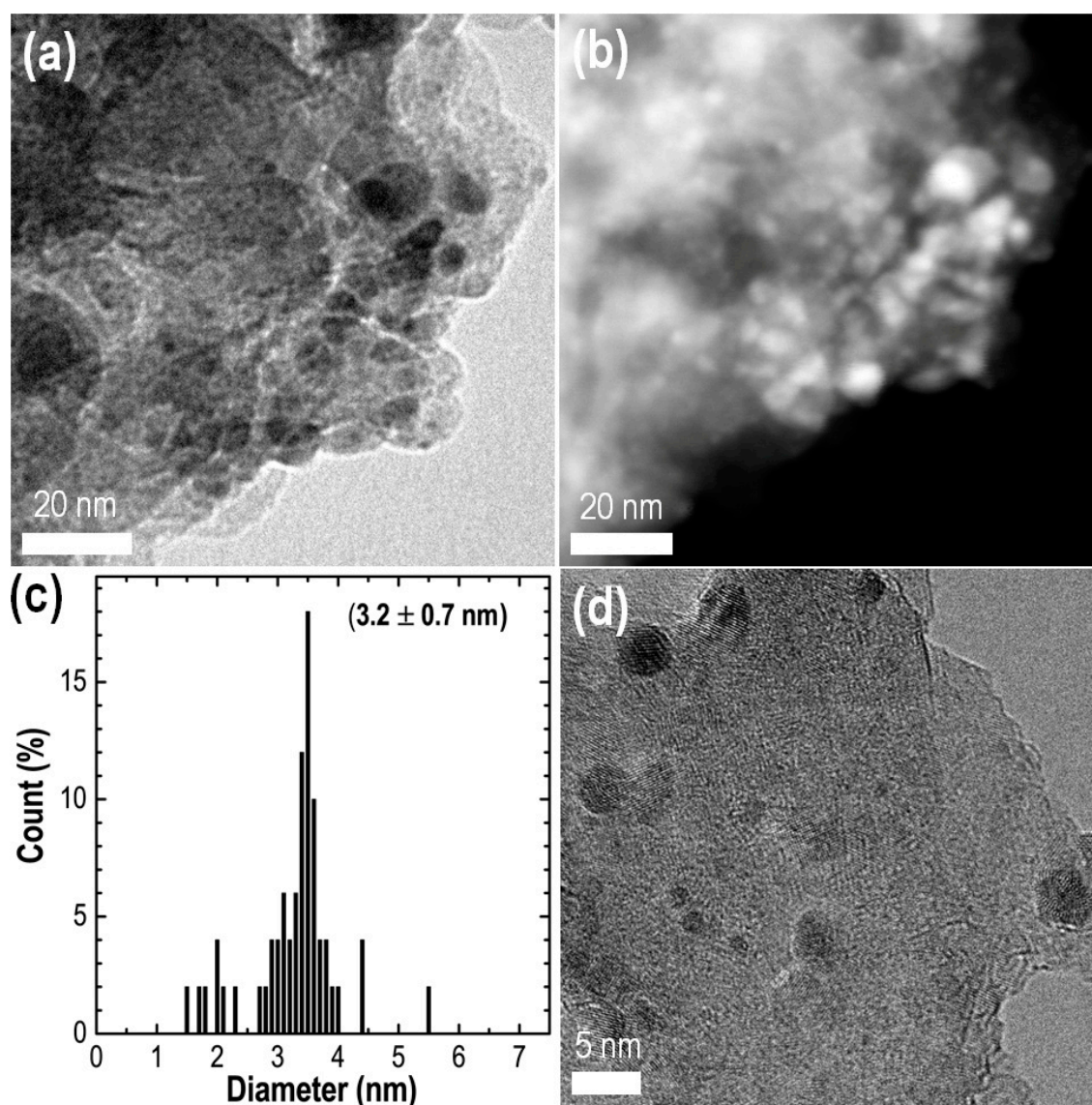
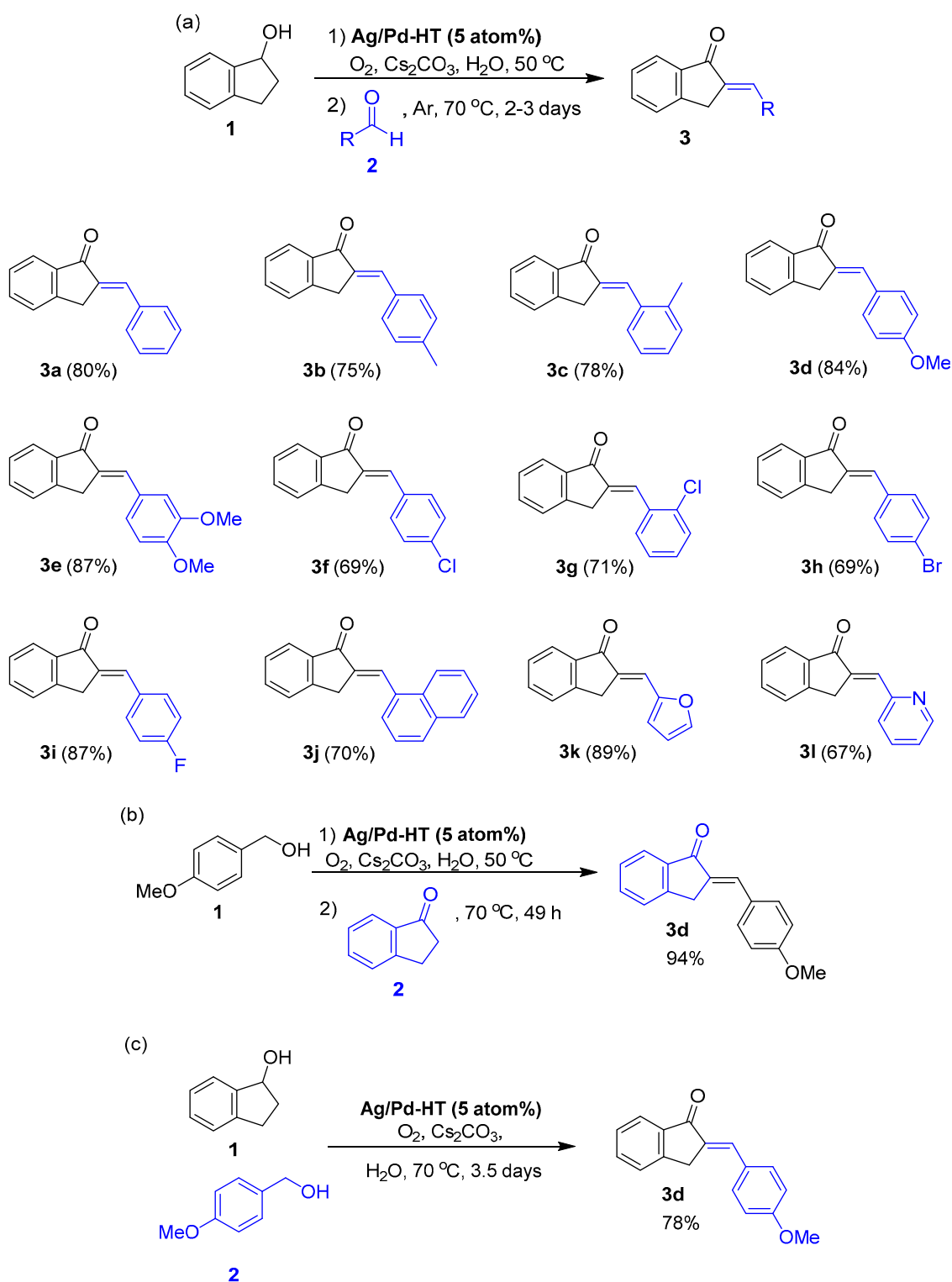


Figure 1. (a) TEM image, (b) STEM image (dark field), (c) histogram plot of particle size distribution and (d) HR-TEM image of (1:1) Ag/Pd-HT.



Scheme 3. Preparation of arylidene-1-indanone derivatives by one-pot oxidation and aldol reaction using (a) method A. Reaction condition: **1** (0.1 mmol), Cs_2CO_3 (150 mol%), O_2 balloon, Ag/Pd-HT, H_2O (1 mL), $50\text{ }^\circ C$, 24 h, then **2** (0.3 mmol), $70\text{ }^\circ C$, Ar balloon); (b) method B. Reaction condition: **1** (0.3 mmol), Cs_2CO_3 (150 mol%), O_2 balloon, Ag/Pd-HT, H_2O (1 mL), $50\text{ }^\circ C$, 24 h, then **2** (0.1 mmol), $70\text{ }^\circ C$, and (c) method C. Reaction condition: **1** (0.1 mmol), **2** (0.3 mmol), Cs_2CO_3 (150 mol%), O_2 balloon, Ag/Pd-HT, H_2O (1 mL), $70\text{ }^\circ C$.

To investigate the stability and reusability of the prepared catalyst, the catalyst was recovered by a simple centrifuging method and washed with acetone at least 3 times. Finally, the catalyst was washed one more time with water, dried under a vacuum at 80 °C and used for the next cycle. Similar catalytic activity was observed even after the 5th cycle, giving good yield of the products (Figure 2a, Tables S3 and S4). In addition, a heterogeneity test was carried out by performing the one-pot oxidative coupling reaction under similar conditions in dioxane/water (1:3) at 70 °C, with single-step addition of 1-indanol and 4-methoxybenzaldehyde. The time profile of the reaction was shown in Figure 2b, Tables S1 and S2. At about 3 h, the catalyst was removed by centrifugation and filtration, and the filtrate was left to react for an additional 4 h. The ratio of product 3 to reactant 1 remained the same even after 7 h, confirming no further conversion of the reactants (Figure 2b blue dotted line, Table S1 and Figure S1). However, in the other reaction with catalyst, the ratio of 3 to 1 increased and gave 86% yield of product 3 in 24 h. This suggests that a completely heterogeneous mechanism proceeded on the Ag/Pd nanocluster surface, however, it does not completely exclude the possibility of leaching and reclusterization of metal species after the catalytic cycle.

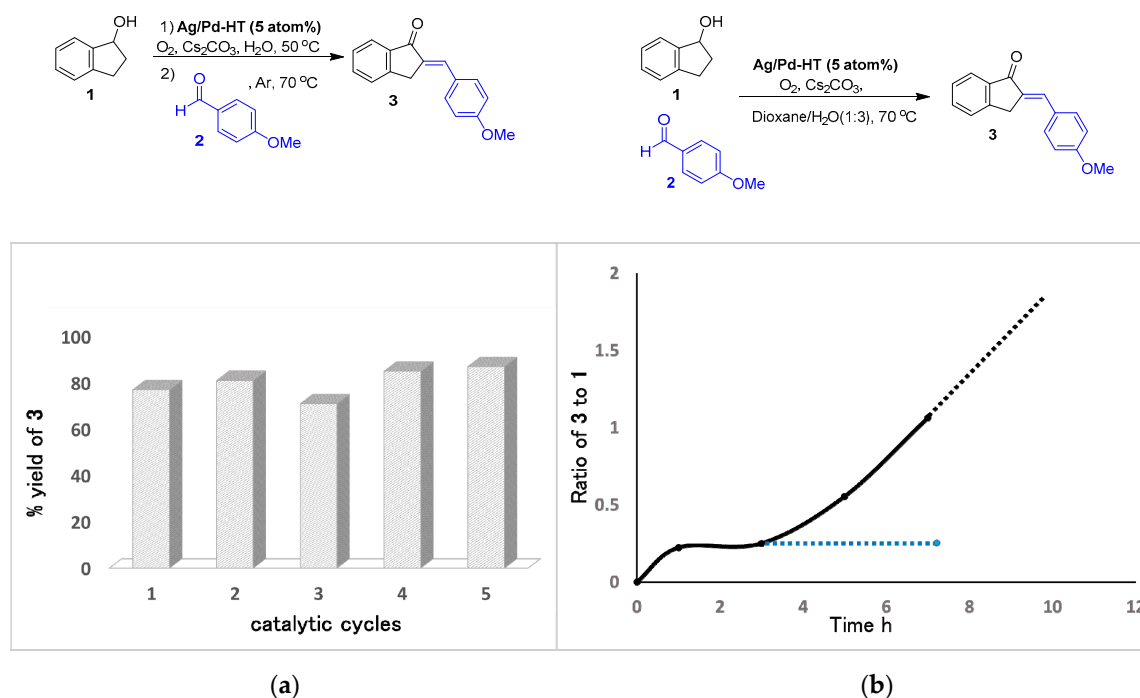


Figure 2. (a) Reusability test of (1:1) Ag/Pd-HT in oxidative coupling of 1-indanol with 4-methoxybenzaldehyde and (b) time-course study and hot filtration test for the (1:1) Ag/Pd-HT catalyzed oxidation of 1-indanol.

3. Materials and Methods

All the chemicals and solvents were commercially available and used without further purification. Palladium acetate (Pd(OAc)₂), silver acetate (AgOAc), (sodium tetraborohydride (NaBH₄) from Wako chemicals, Osaka, Japan) and synthesized hydrotalcite (HT) were used as precursors for the preparation of palladium nanoclusters. Magnesium nitrate (Mg(NO₃)₂·6H₂O), aluminium nitrate (Al(NO₃)₃·9H₂O, Wako, Osaka, Japan), NaOH (Sigma-Aldrich, Tokyo, Japan), and Na₂CO₃ (Kanto chemicals, Tokyo, Japan) were used for the preparation of HT. The alcohol, aldehyde and ketone substrates were obtained from TCI and Wako, and the bases and solvents were from Sigma-Aldrich and Kanto chemicals. Deionized water was used in all experiments. Analytical thin layer chromatography (TLC, Darmstadt, Germany) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography was performed on Kanto Chemical 60 N (0.04–0.05 mm) mesh silica gel.

NMR spectra were recorded on a Bruker AVANCE III 500 (500 MHz) and JEOL JNM-AL400 (400 MHz). Infrared (IR) spectra were recorded on a JASCO FT/IR-4200 spectrometer using KBr plate. The high resolution TEM (HR-TEM) images of fresh hydrotalcite-supported Ag/Pd nanoclusters (NCs) were recorded with a JEOL transmission electron microscope, Model JEM 2100F, at an accelerating voltage of 200 kV, operating in the STEM mode.

3.1. General Procedure for Oxidation

The oxidation reactions were carried out in an organic synthesizer. A test tube (13 mm) was taken and alcohols (0.1 mmol), base (150 mol%) and Ag/Pd catalysts 3–5 atom% were placed in it. The oxygen gas was supplied from the balloon. 1 mL solvent (dioxane/H₂O) was added and stirred at 1200 rpm at 50 °C for the desired time until the reaction completed as monitored by TLC. After 24 h, the reaction was cooled and quenched by 1 M HCl, and the mixture was extracted with EtOAc. The organic layer was evaporated and dried; and the yields were reported as NMR or isolated yield after purification by silica gel column chromatography (eluted with EtOAc/hexane).

3.2. General Procedure for Oxidation and One-pot Aldol Reaction in Water

3.2.1. Method A

The one-pot aldol reactions were carried out by adding aldehydes **2a-2l** (0.3 mmol) after 24 h when the oxidation reaction was completed. The oxygen balloon was exchanged with an argon balloon and the reaction mixture was further stirred at 1200 rpm at 70 °C until the reaction was completed as monitored by TLC. When the reaction was completed, it was cooled and quenched by 1 M HCl, and extracted with EtOAc. The organic layer was evaporated, dried and purified by silica gel column chromatography (eluted with EtOAc/hexane).

3.2.2. Method B

Primary alcohol (4-methoxybenzylalcohol) (0.3 mmol), Cs₂CO₃ (0.15 mmol) and Ag/Pd catalysts 5 atom% were placed in a test tube. The oxygen gas was supplied from the balloon. A total of 1 mL solvent (H₂O) was added and stirred at 1200 rpm at 50 °C for 24 h, as monitored by TLC. After completion, 0.1 mmol indanone was added, the oxygen balloon was exchanged with an argon balloon, and the reaction mixture was further stirred at 1200 rpm at 70 °C for the desired time until the reaction completed.

3.2.3. Method C

Quantities of 1-Indanol (0.1 mmol), 4-methoxybenzylalcohol (0.3 mmol), Cs₂CO₃ (0.15 mmol) and Ag/Pd catalysts 5 atom% were placed in a test tube. The oxygen gas was supplied from the balloon. A total of 1 mL solvent (H₂O) was added and the mixture was stirred at 1200 rpm at 50 °C for the desired time until the reaction was completed as monitored by TLC.

4. Conclusions

In conclusion, we have developed an active catalyst on HT support by a simple co-reduction method of Ag and Pd precursor. The resulting catalyst is effective for the oxidation of alcohols in aqueous/organic media. We successfully developed an efficient and environmentally friendly method for alcohol oxidation and one-pot aldol condensation in water to prepare various arylidene-1-indanones. The method has potential for application to the conversion of biomass to fuels and chemicals. The catalyst is reusable for up to five cycles with consistent catalytic activity.

Supplementary Materials: The details of the reusability test and characterization of the products (NMR and IR) are available in the supplementary information online at <http://www.mdpi.com/2073-4344/10/10/1120/s1>.

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