Aquacatalytic Aerobic Oxidation of Benzylic Alcohols with a Self-supported Bipyridyl–Palladium Complex

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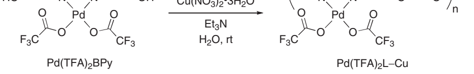
The aerobic oxidation of alcohols was promoted in water under atmospheric molecular oxygen by a readily recyclable self-supported bipyridyl–palladium polymeric complex, which was prepared via construction of a metal–organic framework (MOF) of a bipyridyl–palladium complex bearing carboxylic groups and a copper(II) linker.

Catalytic oxidation of alcohols to carbonyl compounds is one of the most fundamental and important, yet undeveloped, processes in organic chemistry.[1] Recently, catalytic aerobic oxidation of alcohols as well as organic reactions in water have attracted much attention as safe and environmentally benign processes.[2–5] Among the hitherto reported aerobic oxidation catalysts, divalent palladium complexes of hydrophilic bipyridyl-based ligands have been recognized as the most effective complex catalysts for aquacatalytic aerobic oxidation.[6] If the heterogeneous-switching of this class of palladium complexes could be achieved, the resulting catalyst system would be safe, recyclable, and environmentally benign, and would represent what may be considered an ideal oxidation catalyst. We describe herein the preparation of a novel self-supported bipyridyl–Pd^{II} complex via the self-assembly of a palladium complex of a bipyridyl ligand bearing carboxylic groups and copper nitrate (Scheme 1), and its catalytic application in the aerobic oxidation of benzylic alcohols in water.

Self-supported catalysts have recently emerged as a new type of immobilized catalyst[7] and have been utilized for various reactions such as hydrogenation, C–C coupling,[8] and oxidation.[9] One of the advantages of self-supported catalysts is their ease of preparation. Thus, homogeneous catalysts are readily converted into insoluble polymer composites via self-assembly without using any exogenous solid supports. However, to the best of our knowledge, the aqueous aerobic oxidation of alcohols with self-supported catalysts has not yet been achieved. The self-supported bipyridyl–Pd^{II} complex ($Pd(TFA)_2BPy$–Cu) was prepared by mixing $Pd(TFA)_2BPy$ containing two carboxylic groups at the 5- and 5′-positons of the bipyridyl ligand and copper nitrate in the presence of Et_3N in water at room temperature to afford an insoluble polymeric composite in 71% yield (Scheme 1).[10] SEM and TEM analyses of $Pd(TFA)_2BPy$–Cu revealed that block-like nanoclusters (ca. 25–100 nm) were assembled to form big cluster units (Figure 1). ICP analysis showed that the ratio of Pd:Cu was 1:0.91 in the self-supported complex. Combustion elemental analysis revealed that the self-supported composite is comprised of $Pd(OCOCF_3)_2[OC(O)–C_5H_3N–C_5H_3N–COO]Cu•Et_3N•0.5HNO_3$.[11]



Scheme 1. Preparation of a self-supported bipyridyl complex.

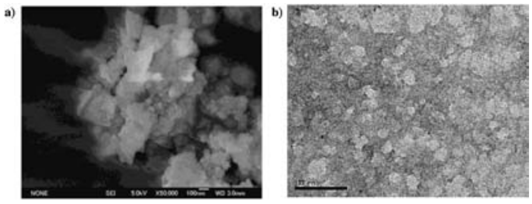
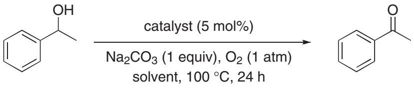


Figure 1. a) SEM and b) TEM images of $Pd(TFA)_2BPy$–Cu.

Table 1. Screening of conditions for the aerobic oxidation of 1-phenylethanol[a]

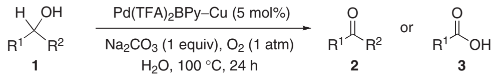


Entry	Catalyst	Solvent	Conv./%	Yield/%[b]
1	$Pd(TFA)_2BPy$–Cu	H_2O	98	82
2[c]	$Pd(TFA)_2BPy$–Cu	H_2O	100	79[d]
3	$Pd(TFA)_2BPy$–Cu	Toluene	7	0
4	$Pd(TFA)_2BPy$–Cu	DMF	54	29
5	$Pd(TFA)_2BPy$–Cu	DMSO	67	53
6	$Pd(OAc)_2BPy$–Cu	H_2O	85	57
7	$PdCl_2BPy$–Cu	H_2O	47	21
8	$Pd(TFA)_2BPy$	H_2O	64	34
9	$Pd(TFA)_2BPy$–Zn	H_2O	92	70

[a] Conditions: 1-phenylethanol (0.25 mmol), catalyst (5 mol %), Na_2CO_3 (0.25 mmol), solvent (2 mL), 100 °C, under 1 atm of O_2. [b] GC yields. [c] 1-Phenylethanol (1 g, 8.2 mmol), catalyst (5 mol %), Na_2CO_3 (8.2 mmol), and H_2O (65 mL) were used. [d] Isolated yield.

With the self-supported bipyridyl–Pd^{II} polymeric complex in hand, we began to explore the optimal conditions for the aerobic oxidation of 1-phenylethanol in water (Table 1). $Pd(TFA)_2$-BPy–Cu catalyzed the aerobic oxidation of 1-phenylethanol in the presence of Na_2CO_3 in H_2O at 100 °C for 24 h to afford acetophenone in 82% yield (Entry 1).[12] A gram scale oxidation of 1-phenylethanol also gave acetophenone in 79% isolated yield (Entry 2). The catalyst was much less effective in organic solvents (Entries 3–5).[13] When the counter ion was replaced with acetate and chloride,[10] the catalytic activity decreased significantly.[14] It was expected that a cationic Pd^{II}–BPy complex would be generated as the active species by dissociation of the relatively stable trifluoroacetate anion from palladium in a polar solvent. A control experiment with the parent palladium complex $Pd(TFA)_2BPy$ gave acetophenone in low yield under otherwise similar conditions (Entry 8).[6] A similar self-supported

Table 2. Substrate scope for the aerobic oxidation[a]



Entry	R^1	R^2	Conv./%	Product	Yield/%
1	C_6H_5	CH_3	98	**2**	82[b]
2	4-$CH_3C_6H_4$	CH_3	85	**2**	83[b]
3	4-$CH_3OC_6H_4$	CH_3	95	**2**	80[b]
4	2-Naphthyl	CH_3	100	**2**	81[b]
5	C_6H_5	C_2H_5	91	**2**	73[b]
6	C_6H_5	c-C_3H_5	100	**2**	89[b]
7	C_6H_5	C_6H_5	95	**2**	95[b]
8	C_6H_5	H	100	**3**	94[c]
9	4-$CH_3C_6H_4$	H	100	**3**	92[c]
10	4-$CH_3OC_6H_4$	H	100	**3**	78[c]
11	4-ClC_6H_4	H	100	**3**	79[c]
12	4-$CF_3C_6H_4$	H	100	**3**	71[c]
13	2-Naphthyl	H	100	**2**	82[c]

[a]Conditions: substrate (0.25 mmol), Pd(TFA)$_2$BPy–Cu (5 mol %), Na_2CO_3 (0.25 mmol), H_2O (2 mL), 100 °C, under 1 atm of O_2. [b]GC yields. [c]NMR yields.

complex Pd(TFA)$_2$BPy–Zn, prepared by self-assembly of Pd(TFA)$_2$BPy and Zn(NO$_3$)$_2$ instead of Cu(NO$_3$)$_2$, also showed good catalytic activity (Entry 9). These results clearly indicate that the self-supporting structure formed via the ionic assembly of Pd(TFA)$_2$BPy with Cu^{II} or Zn^{II} is essential in bringing about high activity toward aquacatalytic aerobic alcohol oxidations.

Having determined the optimal reaction conditions, we investigated the aerobic oxidation of various alcohols with Pd(TFA)$_2$BPy–Cu in H_2O (Table 2). Various benzylic alcohols were smoothly oxidized under the conditions to afford the corresponding ketones or carboxylic acids in 71–95% yield (Entries 1–12). When 2-naphthylmethanol was used, 2-naphthaldehyde was obtained in 82% yield (Entry 13).

The recyclability of Pd(TFA)$_2$BPy–Cu was examined for the oxidation of 1-phenylethanol. Thus, after the first reaction, which gave 82% yield of acetophenone, the catalyst was recovered by centrifugation, and successively subjected to a 2nd, 3rd, 4th, and 5th reaction under the same conditions to afford acetophenone in 80, 72, 83, and 72% yield, respectively.[15] ICP analysis of the aqueous solutions after the first reaction showed no significant leaching of metal contents (the leached amounts of Pd and Cu were 0.17 and 0.08% of the initial amounts, respectively). This result clearly demonstrates the practical recyclability of this catalyst.

In conclusion, we have developed a novel self-supported catalyst Pd(TFA)$_2$BPy–Cu via the self-assembly of a palladium complex supported by a bipyridyl ligand containing carboxylic groups with copper nitrate, which catalyzed the aerobic oxidation of benzylic alcohols in water under 1 atm of O_2 to give the corresponding carbonyl compounds with high recyclability. Development of self-supported aerobic oxidation catalysts exhibiting more broad substrate tolerance is currently under investigation in our lab and will be reported in due course.

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