Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Aerobic alcohol oxidation using a PdCl₂/*N*,*N*-dimethylacetamide catalyst system under mild conditions

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ARTICLE INFO

Article history: Received 24 May 2011 Received in revised form 8 July 2011 Accepted 15 July 2011

Keywords: Aerobic oxidation Alcohols PdCl₂ N,N-dimethylacetamide Nanoparticles

ABSTRACT

A new and simple $PdCl_2/DMA$ catalytic system for the alcohol oxidation has been developed using molecular oxygen as the sole oxidant under mild conditions. The catalytic system could be reused for three runs without significant loss of catalytic activity. A variety of active and non-active alcohols were oxidized to their corresponding carbonyl compounds in good to excellent yields. Gas-uptake kinetics for the catalytic system was also investigated. The *ca*. 1:1 molar ratio of O_2 uptake to product yield is observed, suggesting the in situ formation of H_2O_2 .

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1. Introduction

The selective oxidation of alcohols to the corresponding carbonyl compounds is an important transformation in organic synthesis [1–5]. The palladium-catalyzed oxidation of alcohols is one of the most important methods for this transformation [6-8]. In 1977, the first example of the use of molecular oxygen as the sole reoxidant of palladium-catalyzed alcohol oxidation was reported by Blackburn and Schwartz [9]. The catalytic system with a catalytic amount of PdCl₂ and NaOAc in ethylene carbonate at 38 °C and 1 atm of oxygen pressure led to the efficient oxidation of saturated secondary alcohols. But an attempt to oxidize an olefinic alcohol failed. The significant breakthrough was reported by Peterson and Larock [10]. They employed the Pd(OAc)₂/DMSO catalytic system for the oxidation of benzylic and allylic alcohols with molecular oxygen. The reactions are very slow and the yields of the products are in moderate to excellent. Nearly concurrently, Uemura et al. reported an excellent catalyst system for the aerobic oxidation of alcohols [11,12]. The catalytic system includes 5 mol% Pd(OAc)₂, 20 mol% pyridine and MS3A in toluene at 80 °C and 1 atm oxygen pressure. Primary, secondary, benzylic, and allylic alcohols are oxidized under these conditions in good to excellent yields. Pyridine as a ligand was necessary to prevent the precipitation of

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palladium metal [7]. Sheldon et al. reported the use of palladium complexes of chelating dinitrogen (bathophenanthroline disulfonate) catalyst in combination with NaOAc at 100 °C and 30 bar air pressure in water for the aerobic oxidation of alcohols [1]. Sigman et al. reported an efficient Pd(OAc)₂/triethylamine catalytic system for the aerobic alcohol oxidation, in which the active catalyst may be a Pd-complex containing a single triethylamine ligand [13]. Very recently, Muldoon et al. reported the first use of anionic N,O-ligated Pd (II) complexes for the alcohol oxidation. A number of N,Oligands delivered high TOFs for the palladium-catalyzed oxidation of aliphatic alcohols [14]. Navarro et al. reported the use of (NHC)-Pd (N-Heterocyclic Carbene)-catalyzed anaerobic secondary alcohol oxidation with short reaction time and low palladium loading [15]. It has been well-known that ligated Pd (II) complexes can undergo direct dioxygen-coupled catalytic turnover without cocatalysts for oxidation reaction. However, most common ligands degrade rapidly under oxidizing reaction conditions. The development of oxidatively stable ligands remains attractive. Waymouth et al. reported the use of oxidatively resistant ligands for the palladium-catalyzed aerobic oxidation of alcohols [16].

Herein, we report a simple and efficient PdCl₂/DMA catalytic system for the aerobic oxidation of alcohols into corresponding carbonyl compounds. This catalytic system does not need any additional cocatalysts or special ligands and could also be reused for three runs without significant loss of catalytic activity under mild aerobic conditions.





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Table 1		
Optimiza	n of the palladium-catalyzed oxidation of 2-octa	nol.ª

Entry	Solvent	Base	Palladium Complex	Conversion ^b (%)	Yield ^b (%)
1	DMF	NaOAc	PdCl ₂	52	52
2	NMP	NaOAc	PdCl ₂	88	86
3	DMA	NaOAc	PdCl ₂	98	97
4	DMSO	NaOAc	PdCl ₂	65	64
5	DEF	NaOAc	PdCl ₂	30	28
6	CH₃CN	NaOAc	PdCl ₂	43	42
7	DMA	NaOAc	$Pd(OAc)_2$	91	90
8	DMA	NaOAc	Pd(PPh ₃) ₄	75	74
9	DMA	NaOAc	PdCl ₂ (CH ₃ CN) ₂	95	92
10	DMA	NaOAc	$Pd(OCOCF_3)_2$	53	52
11	DMA	NaOAc	Pd ₂ (dba) ₃	28	27
12 ^c	DMA	NaOAc	PdCl ₂	76	75
13 ^c	DMA	NaOAc	$Pd(OAc)_2$	25	25
14 ^d	DMA	NaOAc	PdCl ₂	90	89
15	DMA	none	PdCl ₂	28	26
16	DMA	K ₂ CO ₃	PdCl ₂	75	72
17	DMA	Na ₂ CO ₃	PdCl ₂	89	85
18	DMA	Cs ₂ CO ₃	PdCl ₂	53	50
19 ^e	DMA	MS3A	PdCl ₂	77	73
20	DMA	$Zn(OAc)_2 \cdot 2H_2O$	PdCl ₂	33	31
21	DMA	NH ₄ OAc	PdCl ₂	~0	~0

^a Reaction conditions: 2.0 mmol of 2-octanol, 0.1 mmol of palladium complex, 0.2 mmol of base, 4 mL of solvent, 80 °C, 0.1 MPa O₂, 2 h. DMF (N,N-dime-thylformamide), DEF (N,N-diethylformamide), NMP (N-methylpyrrolidone).

^b Conversion and yield are determined by GC analysis using an internal standard.
^c Reaction performed at 60 °C.

^d Reaction performed at 60 °C for 4 h.

^e 200 mg MS3A was used.

2. Results and discussion

2.1. Optimization of the palladium-catalyzed oxidation of 2-octanol

Initially, 2-octanol was used as a test substrate and allowed to react with a catalytic amount of palladium and NaOAc in the presence of oxygen at 80 °C for 2 h. The reaction yields were determined by GC analysis using an internal standard. The effect of solvents was first examined. As shown in Table 1, DMA as a solvent could obtain a good catalytic activity, compared to the coordinating ability of other solvents such as DMF, NMP and DMSO (Table 1, entries 1–4). The use of DEF or CH₃CN instead of DMA led to a lower activity (Table 1, entries 5, 6). Another benefit of employing DMA as an alternative solvent is the facile separation of the product. After reaction, the product is very easy to extract with diethyl ether.

Several frequently used palladium complexes were screened to examined their catalytic activities for the oxidation of 2-octanol in DMA. Among the screened palladium complexes, Pd₂(dba)₃ gave only a yield of 27% (Table 1, entry 11). Other palladium complexes including Pd(OAc)₂, Pd(PPh₃)₄, PdCl₂(CH₃CN)₂ and Pd(OCOCF₃)₂ could give good to excellent conversions and yields (Table 1, entries 7–10), and PdCl₂ was found to be the best catalyst for the reaction with 98% conversion and 97% yield (Table 1, entry 3). The best results mentioned above were obtained at 80 °C. By reducing the reaction temperature and increasing the reaction time, high conversion and yield were also obtained (Table 1, entries 12–14).

It was reported that a base played an important role in the alcohol oxidation, because the reaction often involved abstraction of a proton from an alcohol coordinated to the metal center [17]. A series of frequently used inorganic bases were examined. It was found that only a 26% yield of 2-octanone was obtained in the absence of base (Table 1, entry 15), indicating that a base is essential for the PdCl₂-catalyzed oxidation of alcohols. NaOAc was found to be the best base for the oxidation of alcohols (Table 1, entry 3). Other bases including K₂CO₃ and Na₂CO₃ gave good conversions (Table 1, entries 16, 17). Moderate conversion was obtained when

 Cs_2CO_3 was used, which might be due to the poor solubility of Cs_2CO_3 in the solvent (Table 1, entry 18). MS3A, a Brønsted base, could also give good conversion (Table 1, entry 19). $Zn(OAc)_2 \cdot 2H_2O$ and NH₄OAc gave low and trace conversions, respectively (Table 1, entries 20, 21). These results are in agreement with the notion that sodium acetate and alkali salts of carboxylic acids improve the reoxidation of Pd (0), thereby hindering the formation of palladium black [18–21].

A clear effect of the concentration of NaOAc on the reaction conversion and selectivity was observed in the PdCl₂-catalyzed oxidation of 2-octanol (Fig. 1). Fig. 1 showed that the reaction conversion increased with increasing the amount of NaOAc when below 0.05 M of NaOAc was used. The conversion became constant over 0.05 M of NaOAc, but the selectivity decreased a little. These results indicated that a certain amount of NaOAc is very important for a good reaction conversion and selectivity.

2.2. Oxidation of alcohols catalyzed by Pd (II)

The catalytic system was then applied to the oxidation of various benzylic, allylic, and aliphatic alcohols as summarized in Table 2. It is clear that all aliphatic secondary alcohols have been selectively oxidized to the corresponding ketones in high yields (Table 2, entries 1-4). 4-(4-Propylcyclohexyl)cyclohexanol could also be oxidized smoothly in this catalytic system (Table 2, entry 5). An industrially important intermediate compound of 4-(4propylcyclohexyl) cyclohexanone was obtained in 81% yield. It was evident that the electronic effect is important in the oxidation. The electron-rich benzylic alcohols could be oxidized smoothly to give the desired products in high yields (Table 2, entries 7, 8 and entries 12-14). On the other hand, the benzyl alcohols with electron-withdrawing groups gave lower yields (Table 2, entries 9, 10 and entries 15, 16). Increasing the reaction time did not improve the yield (Table 2, entry 17). Interestingly, when $Pd(OAc)_2$ was used in place of PdCl₂, the benzyl alcohols with electron-withdrawing groups could also obtain good conversions and yields (Table 2, entries 18–20). Because of the competing coordination of olefin and alcohol functionalities, the oxidation of allylic alcohols remains a challenge [13]. Cinnamyl alcohol was oxidized successfully under the modified conditions to yield cinnamaldehyde (Pd(OAc)₂ in place of PdCl₂) (Table 2, entries 21, 22). Acetophenone was the major by-product. The unreactive aliphatic primary alcohol,

110 100 90 GC yield and selectivity (%) 80 70 60 50 40 30 20 -0.05 0.00 0.05 0.15 0.20 0.25 0.30 0.10 [NaOAc] (M)

Fig. 1. Reaction conditions: 2.0 mmol of 2-octanol, 0.1 mmol of PdCl₂, NaOAc, 4 mL of DMA, 80 °C, 0.1 MPa O_2 , 2 h. Conversion and selectivity were determined by GC analysis using an internal standard. GC conversion (\blacksquare), GC selectivity (\bullet).

Table 2				
Oxidation	of alcohols	catalyzed	by Pd	(II).ª

Entry	Substrate	Product	Time (h)	Conversion ^b (%)	Yield ^b (%)
1	ОН	0 	4	90	89
2	OH	O L L	4	95	95
3	OH	0 L	4	91	91
4	OH	°	4	89	89
5	он	=0	5.5	83	81
6	OH	° ()	4	95	95(89)
7	OH MeO	MeO	3	95	95 (88)
8	OH	°	4	96	91 (89)
9	OH CI	O Cl	24	46	46 (26)
10	OH	CI	6	80	79(70)
11	ОН	0	4	95	94(88)
12	ОН	0	4	97	96(75)
13	ОН	→o	4	91	88 (80)
14	МеО	MeO	4	100 (continued	94 (89) I on next page)

Table 2 (continued)

Entry	Substrate	Product	Time (h)	Conversion ^b (%)	Yield ^b (%)
15	СІ	CI	4	53	52
16 ^c	O ₂ N OH	O ₂ N O	4	45	39
17 ^c	O ₂ NOH	O ₂ N O	10	52	41
18 ^d	O ₂ N OH	O ₂ N O	7	73	68
19 ^d	O ₂ NOH	O ₂ N O	12	78	68 (63)
20 ^d	OH NO ₂	NO ₂	12	71	65
21 ^c	ОН	0	8	52	24
22 ^{d,e}	ОН	0	6	100	83
23 ^f	ОН	~~~~~¢0	0.5	>99	61

^a Reaction conditions: 2 mmol of alcohols, 0.1 mmol of PdCl₂, 0.2 mmol of NaOAc, 4 mL of DMA, 60 °C, 0.1 MPa O₂.

^b Conversions and yields are determined by GC; values parenthesis are the yields of the isolated products.

^c Reaction performed at 80 °C.

 $^{\rm d}\,$ 0.1 mmol of Pd(OAc)_2, 80 $^\circ \text{C}.$

^e 12% of acetophenone was obtained.

^f When the pressure stabilized in the apparatus, 1-octanol was added. 32% of n-caprylic acid was obtained.

caprylic alcohol could also give a yield of 61% of caprylic aldehyde (Table 2, entry 23).

2.3. O₂ pressure and O₂ uptake

The measurement of O_2 uptake during the reaction was performed with 2-octanol as a substrate to get some information about the reaction pathway. Fig. 2 indicated that the O_2 pressure decreases monotonically with an exponential decay in the course of the reaction. The relationship between O_2 uptake and the amount of 2-octanol consumed has also been investigated. As shown in Fig. 3, O_2 uptake correlates well with the amount of 2octanol consumed. It was found that 1 mmol of O_2 was consumed for converting 1 mmol of 2-octanol. The molar ratio of 2-octanol consumed to O_2 uptake was 1:1. These observations indicate that hydrogen peroxide is the initial reduction product of dioxygen.

2.4. Mechanistic aspects

It is well-known that in the palladium-catalyzed alcohol oxidation the Pd (II) was first reduced to Pd (0) and then Pd (0) was reoxidized to Pd (II). The Pd (0) species is prone to aggregation to Pd black with concomitant loss of catalytic activity [22-24]. In our catalytic system, the solution was clear brown without Pd black observed after reaction. Although Kaneda has demonstrated that DMA could prevent palladium catalyst precipitation into inactive Pd black and promote the reoxidation of the Pd (0) by oxygen in the Wacker oxidation from the study of cyclic voltammetry, kinetics, and X-ray absorption fine structure data [25,26]. We decided to further gain insight into the effect of DMA on the present oxidation process with transmission electron microscopy analysis. Transmission electron microscopy examination of a mixture of PdCl₂/ NaOAc in DMA stirred for 1 h at 60 °C, revealed the presence of dispersed Pd nanoparticles in the solution (Fig. 4a). After reaction, the Pd nanoparticles are still highly dispersed uniformly (Fig. 4b).



Fig. 2. A representative kinetic time-course for the PdCl₂-catalyzed oxidation of 2octanol obtained by gas-uptake methods. Reaction conditions: 2.0 mmol of 2octanol, 0.1 mmol of PdCl₂, 0.2 mmol of NaOAc, 4 mL of DMA, 80 °C, 0.1 MPa O_2 .

From TEM images, the generation of Pd nanoparticles had a homogeneous size distribution of ca. 1-4 nm diameter. These results showed that the transient Pd (0) did not aggregate to form Pd black during the oxidation process. We speculate that the smooth conduct of oxidation is probably attributed to facilitating reoxidation of the Pd nanoparticles [27], which could be stabilized by DMA. It is worth mentioning that DMA could be used to stabilize palladium nanoparticles for the cross-coupling of the silanes R₃SiH with phenyl and vinyl thioethers [28].

It was reported that Pd sponge could be oxidized to a homogenous Pd (II) species under O_2 at 80 °C in the solution of DMA [25]. In our case, the Pd nanoparticles were also oxidized by O_2 to Pd (II) under the reaction conditions and then Pd (II) catalyzed the alcohols to form the carbonyl compounds. The Pd (II) works as the catalytically active species throughout the reaction. The proposed catalytic mechanism was shown in Scheme 1. It is well-known that only Pd (II) can efficiently catalyze Wacker oxidation [24]. Control experiment was performed to support the mechanism (Scheme 2). The experiment was carried out using 4-methylpentan-2-ol as a substrate under the standard reaction conditions. After reaction, 1-octene and 0.5 mL H₂O was added to the reaction solution. The



Fig. 3. Time profile of the oxidation of 2-octanol. The relation of conversion and O_2 uptake. Reaction conditions: 2.0 mmol of 2-octanol, 0.1 mmol of PdCl₂, 0.2 mmol of NaOAc, 4 mL of DMA, 80 °C, 0.1 MPa O_2 . GC conversion (\Box), O_2 uptake (\bullet).

reaction was carried out under 0.6 MPa O_2 at 80 °C for 4 h. 2-Octanone was obtained in 75% yield. This result indicated that the Pd (II) was existent during the alcohol oxidation reaction process. However, in our catalytic system the possibility of direct catalyzing the alcohol oxidation by Pd nanoparticles could not be totally excluded.

2.5. Recycling catalyst

The recyclability of the catalytic system using the oxidation of 4methylpentan-2-ol was investigated (Fig. 5). The recovery and reuse of the catalytic system were readily accomplished after extraction of the products with n-heptane. The active Pd species in the residual DMA solution could be recycled. The result in Fig. 5 showed that this system could run three times with only a slight drop in activity. The conversion of the fourth run was significantly lower, which might be due to the extraction of a bit of palladium nanoparticles into n-heptane phase. This result was consistent with the experimental phenomena. It was found that the color of the solution changed from brown to light yellow.

3. Conclusions

In summary, a new PdCl₂/DMA catalytic system for the oxidation of various alcohols into corresponding carbonyl compounds using molecular oxygen as the sole oxidant under mild aerobic conditions has been developed. The results demonstrated that our catalytic system is superior to the Pd(OAc)₂/DMSO system (efficient for benzylic and allylic alcohols but the reactions are slow) and PdCl₂/ethylene carbonate system (only efficient for saturated secondary alcohols). In this catalytic system, palladium nanoparticles generated in situ and stabilized by DMA were considered to facilitate its reoxidation. The advantage of this catalytic system is no additional cocatalysts or ligands. Most importantly, the catalytic system is very easy to handle and can be reused for three runs without significant loss of catalytic activity.

4. Experimental

4.1. Reagents

All chemicals used in this study were analytical grade, commercially available and used without further purification unless otherwise noted. $PdCl_2$, $Pd(OAc)_2$ and $Pd(OCOCF_3)_2$ were purchased from Shenyang Research Institute of Nonferrous Metals. $Pd(PPh_3)_4$ [29], $PdCl_2(CH_3CN)_2$ [30], $Pd_2(dba)_3$ [31], (dba = diben zylideneacetone) were synthesized by the literature methods.

4.2. General procedures

All experiments were carried out in a Teflon-lined 316 L stainless steel autoclave equipped with a magnetic stirring. Prior to the experiment, the air in the autoclave was exchanged ten times with oxygen. GC calculations of conversions and yields were performed on an Agilent 7890A with a flame ionization detector. All products were confirmed by GC–MS with Agilent 6890N GC/5973 MS detector and the comparison of their GC retention time with those of authentic samples. ¹H NMR and ¹³C NMR spectrum were recorded on a 400 MHz NMR spectrometer using CDCl₃ as the solvent with TMS as an internal reference. ¹H and ¹³C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane (CDCl₃: δ C = 77.0 ppm; residual CHCl₃ in CDCl₃: δ H = 7.26 ppm). Transmission electron micrographs (TEM) were acquired on a FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV.



Fig. 4. TEM images of Pd nanoparticles: (a) before reaction, (b) after reaction.

4.3. General chromatographic analysis conditions

SE-54 capillary column, $30 \text{ m} \times 250 \text{ }\mu\text{m} \times 1 \text{ }\mu\text{m}$; FID detector, 300 °C; injection: 250 °C; carrier gas: nitrogen; carrier gas rate: 2.8 mL/min. All substrates and their corresponding products unless otherwise noted were detected under a condition as: column temperature: 100 °C for 7 min, raising to 250 °C in a rate of 15 °C/min. 2-Pentanol and its corresponding product were detected under a condition as: column temperature: 30 °C for 7 min, raising to 250 °C in a rate of 15 °C/min. 4-Methyl-2-pentanol and its corresponding product were detected under a condition as: column temperature: 30 °C for 7 min, raising to 250 °C in a rate of 15 °C/min.

4.4. A typical example for alcohol oxidation

The reaction was carried out in a 150 mL Teflon-lined 316 L stainless steel autoclave and a magnetic stirrer. A mixture of 0.1 mmol of PdCl₂, 0.2 mmol of NaOAc, 2 mmol of 2-octanol and 4 mL of DMA were placed in the 150 mL Teflon-lined 316 L stainless steel autoclave and stirred for 5 min. Then, 0.1 MPa of O₂ was introduced. The mixture was stirred for 4 h at 60 °C. After the reaction, the reactor was quickly cooled to room temperature. The excess of O₂ was depressurized slowly. GC analysis of the solution using biphenyl as an internal standard gave a 89% yield of 2-octanone with >99% selectivity.

4.5. General procedures for obtained isolated yield

After reactions, the products were extracted using a 1:1 diethyl ether/water mixture (2×30 mL). The diethyl ether layers containing the products were dried over MgSO₄, filtrated and concentrated under reduced pressure. The resultant crude mixture



Scheme 1. Proposed catalytic mechanism.

was purified by column chromatography (silica gel) with a mixture of EtOAc/hexane as eluent.

Acetophenone: light yellow liquid, ¹H NMR (400 MHz, CDCl₃): δ 2.57 (s, 3 H), 7.43 (t, ${}^{3}J_{H,H}$ = 7.44 Hz, 2H), 7.53 (t, ${}^{3}J_{H,H}$ = 7.36 Hz, 1H), 7.93 (d, ${}^{3}J_{H,H}$ = 7.16 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 198.1, 137.1, 133.1, 128.6, 128.3, 26.6.

4′-Methylacetophenone: white crystal, ¹H NMR (400 MHz, CDCl₃): δ 2.46 (s, 3H), 2.29 (s, 3H). 7.75 (d, ³J_{H,H} = 8.0 Hz, 2H), 7.14 (d, ³J_{H,H} = 7.88 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 197.7, 143.8, 134.7, 129.2, 128.7, 128.4, 26.4, 21.6.

2'-Chloroacetophenone: colorless liquid, ¹H NMR (400 MHz, CDCl₃): δ 2.64 (s, 3 H), 7.54 (d, ³*J*_{H,H} = 7.76 Hz, 1H); 7.29–7.41 (m, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 200.9, 139.7, 132.6, 131.8, 131.2, 129.9, 127.5, 31.2.

4'-Chloroacetophenone: white liquid, ¹H NMR (400 MHz, CDCl₃): δ 2.58 (s, 3H), 7.44 (d, ³*J*_{H,H} = 9.84 Hz, 2H), 7.88 (d, ³*J*_{H,H} = 8.4 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 197.3, 140.1, 135.9, 130.3, 129.4, 27.1.

Benzaldehyde: colorless oil liquid, ¹H NMR (400 MHz, CDCl₃): δ 7.51 (t, ³J_{H,H} = 7.6 Hz, 2H), 7.61 (t, ³J_{H,H} = 7.2 Hz, 1H), 7.86 (d, ³J_{H,H} = 7.6 Hz, 2H), 9.99 (s, 1H); ¹³C NMR (100.6 MHz, CDCl₃): δ 192.0, 136.0, 134.1, 129.4, 128.7.

3-Methylbenzaldehyde: colorless liquid, ¹H NMR (400 MHz, CDCl₃): δ 9.97 (s, 1H), 7.66 (d, ³*J*_{H,H} = 6, 2H), 7.44–7.38 (m, 2H), 2.41 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃): δ 192.6, 138.9, 136.5, 135.3, 130.0, 128.9, 127.3, 21.2.

4-Methylbenzaldehyde: colorless liquid, ¹H NMR (400 MHz, CDCl₃): δ 2.44 (s, 3H), 7.33 (d, ³ $J_{\rm H,H}$ = 8.0 Hz, 2H), 7.77 (d, ³ $J_{\rm H,H}$ = 8.0 Hz, 2H), 9.96 (s, 1H); ¹³C NMR (100.6 MHz, CDCl₃): δ 192.6, 146.1, 134.8, 130.4, 130.3, 22.5.

4-Methoxybenzaldehyde: colorless liquid, ¹H NMR (400 MHz, CDCl₃): δ 3.85(s, 3H), 6.98 (d, ³*J*_{H,H} = 8.80 Hz, 2H), 7.81 (d, ³*J*_{H,H} = 8.80 Hz, 2H), 9.86 (s, 1H); ¹³C NMR (100.6 MHz, CDCl₃): δ 190.9, 164.7, 132.1, 130.1, 114.5, 55.7.



Scheme 2. Control experiment.



Fig. 5. Recyclability of active catalyst in the oxidation of 4-methylpentan-2-ol.

4-Nitrobenzaldehyde: light yellow acicular crystal, ¹H NMR (CDCl₃, 400 MHz): δ 8.09 (d, ³*J*_{H,H} = 7.2 Hz, 2H), 8.41 (d, ³*J*_{H,H} = 6.8 Hz, 2H), 10.18 (s, 1H); ¹³C NMR (100.6 MHz, CDCl₃): δ 191.0, 151.7, 140.7, 131.2, 124.9.

4.6. Gas-uptake kinetics for the PdCl₂/NaOAc/DMA system

A typical reaction was conducted as follows. 0.1 mmol of PdCl₂, 0.2 mmol of NaOAc and 4 mL of DMA were added to the 150 mL Teflon-lined 316 L stainless steel autoclave. The autoclave was attached to an apparatus with a pressure transducer designed to measure the gas pressure. The air in the autoclave was exchanged ten times with oxygen, and then filled with oxygen to 0.1 MPa. The autoclave was put into an oil bath which was preheated to 80 °C. When the pressure stabilized in the apparatus, 2 mmol of 2-octanol was added via syringe through a septum. The amount (mmol) of oxygen that reacted was calculated using volume, actual temperature and pressure from the ideal gas equation. The conversion was determined by gas chromatography analysis.

4.7. Recycling experiments for the oxidation of 4-methylpentan-2-ol

Fresh reaction using 2 mmol of 4-methylpentan-2-ol, 0.1 mmol of PdCl₂, 0.2 mmol of NaOAc, 4 mL of DMA were carried out at 80 °C under 0.1 MPa O₂. After 2 h, the reaction mixture was cooled to a room temperature, and washed with *n*-heptane (5 mL × 6). The *n*-heptane phase was decanted, and another portion of 2 mmol of 4-methylpentan-2-ol and 0.2 mmol of NaOAc was successively added

into the Pd-DMA phase, followed by stirring under identical reaction conditions.

Acknowledgment

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No 20643006), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry and the National Basic Research Program of China (2009CB623505).

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