Tetrahedron Letters 52 (2011) 4954-4956

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Solid-supported Pd(0): an efficient heterogeneous catalyst for aerobic oxidation of benzyl alcohols into aldehydes and ketones *

Bandna¹, Nidhi Aggarwal¹, Pralay Das^{*}

Natural Plant Products Division, Institute of Himalayan Bioresource Technology (Council of Scientific and Industrial Research), Palampur 176061, H.P., India

ARTICLE INFO

ABSTRACT

activities.

Article history: Received 8 June 2011 Revised 13 July 2011 Accepted 17 July 2011 Available online 22 July 2011

Keywords: Aerobic oxidation Heterogeneous catalyst Nano- and microparticles Solid supported palladium

The oxidation of alcohols into the corresponding carbonyls is a very important and useful organic transformation¹ since aldehydes and ketones of industrial significance are used as intermediates in the manufacture of dyes and pharmaceuticals.² The use of transition metals in selective catalytic oxidation with environmentally benign oxidants has emerged as a very interesting alternative to the conventional waste-producing oxidation procedures which require stoichiometric amounts of toxic inorganic salts, in the past years.^{3,4} Recently, aerobic oxidation processes have received increasing attention. The use of oxygen has great benefits from both the economic and green chemistry view points, because oxygen is relatively cheap and produces water as the only byproduct. Thus due to the wide scope of the development of catalysts, suitable active metals for both homo- and heterogeneous catalyzed oxidations with molecular oxygen have been explored which include Fe,⁵ Ru,⁶ Co,⁷ Cu,⁸ Mn,⁹ Os,¹⁰ and Pd.¹¹ Solid supported transition metal nanoparticles have found immense interest in recent years for the development of new synthetic methodologies due to its high catalytic activity and reusability.¹² Few recent reports showed that heterogeneous nanoparticles of palladium are capable of aerobic oxidation of aromatic alcohols.¹³

Recently our group described the synthesis of solid supported nano/microparticles of Pd(0) (SS-Pd(0)) and its application in Suzuki-Miyaura cross coupling reaction.¹⁴ Herein, we have investigated the scopes of SS-Pd(0) catalyst in the oxidation of benzyl

alcohols to the corresponding aldehydes and ketones using molecular oxygen as the oxidant. Primary and secondary benzyl alcohols yielded the corresponding products in good yields. Moreover, the catalyst system could be recycled up to five runs without significant loss of activity.

© 2011 Elsevier Ltd. All rights reserved.

Solid-supported nano- and microparticles of Pd(0) (SS-Pd) were used as heterogeneous catalysts for aer-

obic oxidation of benzyl alcohols. Primary and secondary benzyl alcohols gave the corresponding prod-

ucts in good yields. In addition, the catalysts could be reused up to five runs without significant loss of

We investigated the oxidation of 2-ethoxybenzylalcohol 1a as the model substrate. The progress of reaction was monitored by

Catalyst O₂

Table 1

Effect of catalysts and solvents for the oxidation of 2-ethoxybenzylalcohol

OH Catalyst,O2 Solvent, 110 °C					
	✓ `OC₂H₅	5h		OC_2H_5	
	Ia		2a		
Entry	Catalyst (mol % Pd)	Solvent	Yield (%) ^a	TON	TOF h^{-1}
1	SS-Pd(1)	Toluene	11	1100	220
2	SS-Pd(3)	Toluene	68	2266	453
3	SS-Pd(5)	(i) Toluene	80	1600	320
		(ii) THF	9	180	36
		(iii) Dioxane	3	60	12
		(iv) C ₆ H ₆	55	1100	220
		(v) CH_3CN	23	460	92
4	SS-Pd(6)	Toluene	80	1333	267
5	$Pd(OAc)_2(5)$	Toluene	69	1380	276
6	Pd/C(5)	Toluene	2	40	8
7	$Pd_2C_6H_{10}Cl_2(10)$	Toluene	1	20	4
8	$Pd_2(dba)_3(10)$	Toluene	20	400	80
9	$Pd[P(C_6H_5)_3]_4(5)$	Toluene	39	780	156

TON = % conversion \times mmole of substrate/mmole of catalyst, TOF = TON/time. Determined by means of GC, based on the 2-ethoxy benzyl alcohol.





^{*} IHBT Communication No. 2200

^{*} Corresponding author. Fax: +91 1894 230433.

E-mail address: pdas@ihbt.res.in (P. Das).

¹ These authors contributed equally to this work.

^{0040-4039/\$ -} see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2011.07.073

Table 2
Oxidation of primary and secondary benzyl alcohols to aldehydes and ketones



Entry	Substrate	\mathbb{R}^1	R ²	Time (h)	Product	Yield (%) ^a	TON /TOF ^{-h}
1	1a	2-0C ₂ H ₅	Н	5	2a	78	1560/312
2	1b	Н	CH₃	5	2b	96	1963/393
3	1c	4-NO ₂	Н	3	2c	70	1400/467
4	1d	3-OMe	Н	3	2d	90	1800/600
5	1e	4-Br	Н	3	2e	80	1600/533
6	1f	4-Cl	Н	3	2f	83	1660/553
7	1g	2-Br	Н	3	2g	85	1700/567
8	1h	4-Me	CH ₃	5	2h	90	1800/360
9	1i	2,4-0Me	CH ₃	5	2i	93	1860/372
10	1j	2,5-OMe	CH ₃	5	2j	90	1800/360
11	1k	4-OMe	CH ₃	5	2k	90	1800/360
12	11	4-Cl	C ₆ H ₅	5	21	74	1480/296
13	1m	4-Br	CH ₃	5	2m	90	1800/360

^a Isolated yield.

TLC and GC analysis. Initially optimization of the solvent and catalytic system was carried out (Table 1). Different loadings of SS-Pd with 1, 3, 5, and 6 mol % Pd were also tested for optimization of the reaction condition. Highest turnover number (TON, 2266) and turnover frequencies (TOF, 453 h⁻¹) were calculated when SS-Pd (3 mol % Pd) was used for the oxidation reaction of **1a** (Table 1, entry 2). However, only 68% yield of **2a** was observed by GC analysis. SS-Pd with 5 mol % Pd in toluene showed 80% yield of **2a** and TON/TOF was calculated as $1600/320 h^{-1}$ (Table 1, entry 3). No further improvement of yield was observed by enhancing the catalyst loading up to 6 mol % Pd (Table 1, entry 4). Hence SS-Pd (5 mol % Pd) and toluene solvent were found to be optimum under the reaction conditions. Comparative studies of different catalytic systems were also performed (Table 1, entries 5–9) and the best result was obtained using SS-Pd under the same reaction condition.

Further investigations were performed to enhance the scopes of oxidation reactions in different substituted primary and secondary benzyl alcohols. Both the primary and secondary benzyl alcohols on oxidation gave satisfactory to good yields of the corresponding aldehydes and ketones. Secondary benzyl alcohol was also found to be reactive toward oxidation under the same reaction condition and the product **2b** was obtained in excellent yield¹⁵ (Table 2, entry 2). Primary benzyl alcohols with electron donating and withdrawing groups afforded products **2c** and **d** in good yields (Table 2, entries 3 and 4).

Primary benzyl alcohols bearing halogen groups were also successfully oxidized to benzaldehydes 2e-g with satisfactory yields (Table 2, entries 5-7). Secondary benzyl alcohols with electron donating groups afforded products **2h**-**k** in good yields (Table 2, entries 8-11) and halogen substituted secondary benzyl alcohols also gave products 21 and m in satisfactory yields without any dehalogenation products (Table 2, entries 12 and 13). Evaluation of recyclability was done on the same test substrate 1a. After completion of reaction, the product was extracted with ethyl acetate and the recovered catalyst was washed with acetone, dried, and used for further reactions. The catalytic activity of SS-Pd remained almost the same upto five runs as indicated by the yields of the corresponding aldehyde 2a (Table 3). Gradual decrease in yields was encountered after six to seven runs of SS-Pd catalyst. As shown in Table 3, on recycling, from the first to the seventh run the TONs drop from 1600 to 1000 and total turnover number over the seven cycles was 10400.

Table 3	
Recyclability experiments of 2a using SS-Pc	l

Run	1st	2nd	3rd	4th	5th	6th	7th
Yield (%) ^a	80	80	79	79	78	74 ^b	50 ^b
TON	1600 TTON over seven cycles	1600	1580	1580	1560	1480	1000 10400

TTON = total turnover number; procedure followed as described for 2a.

^a Determined by means of GC.

^b Isolated yield.

In conclusion, aerobic oxidation of benzyl alcohols using SS-Pd has been developed. Different primary and secondary benzyl alcohols afforded the corresponding products in good yields. Due to the stability of the SS-Pd catalyst in moisture and air, it is very easy to handle under reaction conditions. This methodology will find interest in both academic as well as industry due to its atom-economy and cost-effective process by using heterogeneous nano and microparticles as. ligand free catalysts.

Acknowledgments

Authors are grateful to Dr. P. S. Ahuja, Director IHBT for providing necessary facilities during the course of the work. We gratefully acknowledge financial assistance from the Department of Science & Technology (Nano Mission), New Delhi (Grant No. SR/NM/NS-95/2009). Bandna (SRF) thanks CSIR, New Delhi for awarding senior research fellowships.

Supplementary data

Supplementary data (general experimental procedures and characterization data for all compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.07.073.

References and notes

 (a) Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. *Catal. Today* **2000**, *57*, 157; (b) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis*, 2nd ed.; Wiley-VCH, 2004; (c) Brink, G.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287*, 1636.

- (a) Sheldon, R. A.; Kochi, J. K. Metal-Catalyzed Oxidations of Organic Compounds; Academic Press: New York, 1981; (b) Pillai, U. R.; Sahle-Demessie, E. Appl. Catal. A: Gen. 2003, 245, 103; (c) Hudlicky, M. Oxidations in Organic Chemistry; ACS: Washington, DC, 1990.
- Backvall, J. E. Modern Oxidation Methods; Wiley-VCH, 2004; (b) Mallat, T.; Baiker, A. Chem. Rev. 2004, 104, 3037.
- (a) Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Chelle-Regnaut, I.; Gautier, A.; Dumeunier, R.; Philippart, F.; Doda, K.; Mutonkole, J. L.; Brown, S. M.; Urch, C. J. *Adv. Inorg. Chem.* **2004**, *56*, 211; (b) Sheldon, R. A.; Arends, I. W. C. E.; Ten Brink, G. J.; Dijksman, A. Acc. Chem. Res. **2002**, *35*, 774; (c) Zhan, B. Z.; Thompson, A. *Tetrahedron* **2004**, *60*, 2917.
- 5. Martin, S. E.; Suarez, D. F. Tetrahedron Lett. 2002, 43, 4475.
- (a) Yamaguchi, K.; Mizuno, N. Angew. Chem., Int. Ed. 2002, 41, 4538; (b) Marko, I.; Paul Giles, R.; Tsukazaki, M.; Chelle-Regnaut, I.; Urch, C. J.; Brown, S. M. J. Am. Chem. Soc. 1997, 119, 12661; (c) Choi, E.; Lee, C.; Na, Y.; Chang, S. Org. Lett. 2002, 4, 2369.
- (a) Sharma, V. B.; Jain, S. L.; Sain, B. *Tetrahedron Lett.* **2003**, 44, 383; (b) Gilhespy, M.; Lok, M.; Baucherel, X. *Chem. Commun.* **2005**, 1085.
- (a) Naik, R.; Joshi, P.; Deshpande, R. K. *Catal. Commun.* **2004**, *5*, 195; (b) Gamez, P.; Arends, I. W. C. E.; Reedijk, J.; Sheldon, R. A. *Chem. Commun.* **2003**, 2414; (c) Ragagnin, G.; Betzemeier, B.; Quici, S.; Knochel, P. *Tetrahedron* **2002**, *58*, 3985; (d) Tsai, W.; Liu, Y. H.; Peng, S. M.; Liu, S. T. *J. Organomet. Chem.* **2005**, *6*, 415; (e) Marko, I. E.; Gautier, A.; Dumeunier, R.; Doda, K.; Philippart, F.; Brown, S. M.; Urch, C. J. *Angew. Chem.* **2004**, *116*, 1614.
- Son, Y. C.; Makwana, V. D.; Howell, A. R.; Suib, S. L. Angew. Chem. 2001, 113, 4410.
 (a) Shapley, P. A.; Zhang, N.; Allen, J. L.; Pool, D. H.; Liang, H. C. J. Am. Chem. Soc.
- **2000**, *122*, 1079; (b) Coleman, K. S.; Coppe, M.; Thomas, C.; Osborn, J. A.

Tetrahedron Lett. **1999**, 40, 3723; (c) Dobler, C.; Mehltretter, G. M.; Sundermeier, U.; Eckert, M.; Militzer, H. C.; Beller, M. Tetrahedron Lett. **2001**, 42, 8447.

- (a) Buffin, B. P.; Clarkson, J. P.; Belitz, N. L.; Kundu, A. J. Mol. Catal. A: Chem. 2005, 225, 111; (b) Pillai, U. R.; Sahle-Demessie, E. Green Chem. 2004, 6, 161; (c) Caravati, M.; Grunwaldt, J. D.; Baiker, A. Phys. Chem. Chem. Phys. 2005, 7, 278; (d) Muzart, J. Tetrahedron 2003, 59, 5789; (e) Caravati, M.; Grunwaldt, J. D.; Baiker, A. Catal. Today 2004, 91–92, 1.
- 12. (a) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757; (b) Ikegami, S.; Harmamoto, H. *Chem. Rev.* **2009**, *109*, 583.
- (a) Karimi, B.; Abedi, S.; Clark, J. H.; Budarin, V. Angew. Chem., Int. Ed. 2006, 45, 4776; (b) Mifsud, M.; Parkhomenko, K. V.; Arends, I. W. C. E.; Sheldon, R. A. Tetrahedron 2010, 66, 1040; (c) Feng, B.; Hou, Z.; Yang, H.; Wang, X.; Hu, Y.; Li, H.; Qiao, Y.; Zhao, X.; Huang, Q. Langmuir 2010, 26, 2505.
- 14. Das, P.; Sharma, D.; Shil, A. K.; Kumari, A. Tetrahedron Lett. 2011, 52, 1176.
- 15. 2-Phenyl ethanol (**2b**). A mixture of **1b** (100 mg, 0.818 mmol), SS-Pd (918 mg, 0.04 mmol Pd) and 3 ml of toluene was purged with molecular oxygen and stirred at 110 °C for 5 h. The progress of reaction was monitored on TLC. After completion of reaction, the reaction was cooled, diluted with ethyl acetate and filtered through cotton bed. The combined organic layer was evaporated under reduced pressure and crude residue was purified by silica gel (mesh 60–120) column chromatography (Hexane/EtOH 95:5) afforded **2b** as colorless liquid (94 mg, 96%).¹H NMR (300 MHz, CDCl₃) δ 2.59 (s, 3H), 7.44–7.55 (m, 3H), 7.93–7.96 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 26.49, 128.22 (2C), 129.48 (2C), 133.01, 137.06, 198.07.