

DOI: 10.1002/ange.200504359

Highly Efficient Aerobic Oxidation of Alcohols Using a Recoverable Catalyst: The Role of Mesoporous Channels of SBA-15 in Stabilizing Palladium Nanoparticles**

Babak Karimi,* Sedigheh Abedi, James H. Clark, and Vitaly Budarin

Dedicated to Professor Dieter Enders
on the occasion of his 60th birthday

Ever-increasing environmental concerns has resulted in much attention being recently directed toward the development of new protocols for the aerobic oxidation of alcohols using transition-metal catalysts.^[1] Among them, palladium-based catalysts show very interesting and promising catalytic activity, and different types of palladium-based homogeneous^[2] and heterogeneous^[3] catalysts in the form of metal complexes or nanoparticles^[4] have been developed for this purpose. Accordingly, the application of palladium-based catalysts has also been well documented for the asymmetric oxidation of alcohols.^[5] Although, significant progress has been achieved in improving catalytic activity, selectivity, and substrate scope, there is still the major problem that palladium agglomeration and the formation of palladium black can cause catalyst deactivation in many cases. Recently, Tsuji and co-workers have shown that novel pyridine derivatives with 2,3,4,5-tetraphenylphenyl substituents and higher dendritic units at the 3-position significantly suppress the formation of palladium black and give the highest reported turnover numbers (TON) of 1480 in the homogeneous palladium-catalyzed oxidation of alcohols in air.^[2o] Very recently, we explored a new silica-based palladium(II) interphase catalyst for the aerobic oxidation of alcohols.^[3g] However, this method requires high catalyst concentrations (up to 5 mol%) and it suffers from the disadvantage of a significant reduction in its reactivity after three reaction cycles. Furthermore, this catalyst did not show good catalytic

activity in the aerobic oxidation of allylic alcohols. Quite recently, the use of palladium nanoparticles dispersed in an organic polymer has also been demonstrated in the aerobic oxidation of alcohols.^[4a,b] However, these heterogeneous Pd systems also suffer from high catalyst loading (typically substrate/catalyst ratios are ca. 20:1) and also the organic polymers used in these systems are potentially susceptible to oxidative degradation under aerobic oxidation conditions, thus restricting catalyst recovery over a long period. Moreover, it is well known that the small particle size as well as the high surface area of nanoparticles means they are very mobile and thermodynamically susceptible to agglomeration and the formation of larger inactive particles.^[6] Ordered mesoporous structures (such as MCM-41^[7] and SBA-15^[8]) with regular channel structures and pore diameters in the range of 2 to 30 nm, their easy separation from the reaction mixtures, and their relatively high surface area, would seem to be ideal for forming a scaffold in which three-dimensional dispersions of metal nanoparticles could be supported. Furthermore, because the majority of the nanoparticles are usually formed inside the channels of ordered porous materials, the support prevents agglomeration while providing the inherent advantages of a heterogeneous catalyst such as easy recovery and product separation. For these reasons, the preparation^[9] and the use^[10] of metal nanoparticles deposited on such porous materials have received much attention in recent years. However, despite these attractive features, to our knowledge there is no report on the use of metal nanoparticles supported on mesoporous materials for the aerobic oxidation of alcohols. We disclose herein a simple procedure for the preparation of a new type of palladium catalyst immobilized on functionalized SBA-15 and its application as a heterogeneous catalyst for the aerobic oxidation of alcohols. Transmission electron microscopy (TEM) before and after catalysis indicates the involvement of Pd nanoparticles confined inside the channels of SBA-15 as a reservoir of active species for catalysis. SBA-15 was obtained from pluronic P123 (EO₂₀PO₇₀EO₂₀ (EO = ethylene oxide, PO = propylene oxide), M_{Av} = 5800, Aldrich) and (EtO)₄Si under acidic conditions following the reported procedure.^[8] The resulting SBA-15 was functionalized with a bipyridylamide ligand followed by complexation with Pd(OAc)₂ to afford the corresponding immobilized palladium catalyst **1**.^[11] The TEM

[*] Prof. Dr. B. Karimi, S. Abedi
Department of Chemistry
Institute for Advanced Studies in Basic Sciences (IASBS)
PO. Box 45195-1159, Gava Zang, Zanjan (Iran)
Fax: (+98) 241-424-9023
E-mail: karimi@iasbs.ac.ir
Prof. Dr. J. H. Clark, Dr. V. Budarin
Clean Technology Centre
University of York
York YO105DD (UK)

[**] This work was supported by the IPM and IASBS Research Councils. We also acknowledge Dr. E. Shams for the atomic absorption analysis of the samples, and we thank the referees for their valuable comments.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

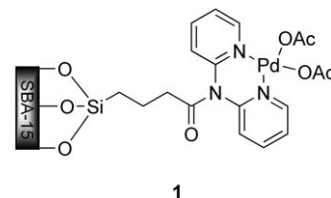


image of catalyst **1** is shown in Figure 1 a and b, and reveals the absence of any palladium particles inside the channels. An interesting point is that the nanoarchitecture of the catalyst (SBA-15 channel) largely survived even after prolonged reflux at 150°C in concentrated sulfuric acid during the preparation procedure.^[11] A typical nitrogen adsorption/

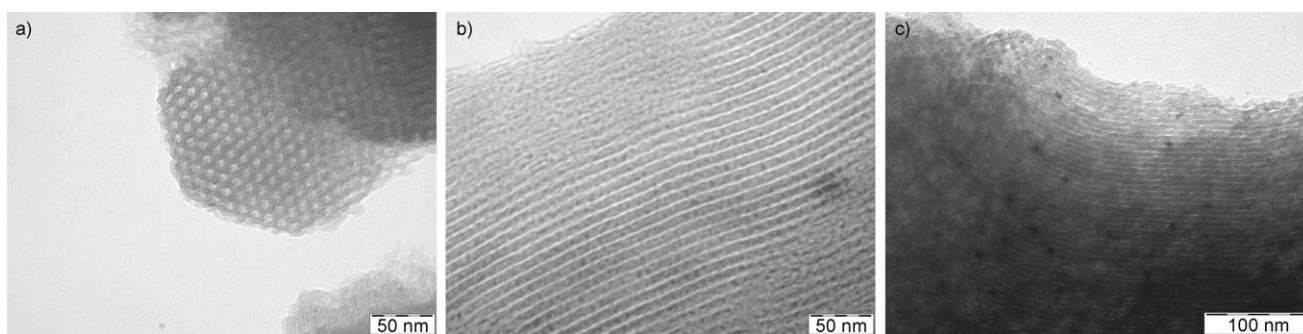


Figure 1. TEM images of **1**: a) perpendicular to the ordered channels, b) across the ordered mesoporous channels, and c) after the first recovery.

desorption type IV profile with a sharp hysteresis loop, which is characteristic of the highly ordered mesoporous materials, was obtained for **1** (see the Supporting Information).^[11]

A BET surface area of 455 m² g⁻¹ and a total pore volume of 0.76 cm³ g⁻¹ were measured for the material. These values are smaller than those for the starting SBA-15 (864 m² g⁻¹). BJH calculations showed an average pore diameter of 7.6 nm for **1**, a value which is in good agreement with the pore diameter estimated from the TEM image (Figure 1 a,b).^[11]

As summarized in Table 1, **1** (ca. 0.004 equiv) is an efficient heterogeneous catalyst for the aerobic oxidation of a wide range of alcohols. A number of different solvents for the oxidation reaction were investigated, and both toluene and trifluorotoluene (TFT) led to high yields of the products.

Table 1: Aerobic oxidation of alcohols using **1**.

Entry	R ¹	R ²	t [h]		Yield [%] ^[a,b,c]	
			O ₂	air	O ₂	air
1	Ph	H	3.5	5.5	> 99 (83)	> 99
2	4-MeC ₆ H ₄	H	3.5	5	> 99	> 99
3	2-MeC ₆ H ₄	H	8	–	25	–
4	2-ClC ₆ H ₄	H	12	–	35	–
5	4-MeOC ₆ H ₄	H	2.5	2.5	> 99	> 99
6	4-ClC ₆ H ₄	H	12	13	> 99	> 99
7	4-NO ₂ C ₆ H ₄	H	14	15	> 99	> 99
8	Ph	Me	15	17	> 99 (91)	96
9	Ph	Et	15	17	> 99	93
10	PhCO	Ph	12	12	> 99 (95)	94
11	Ph	Ph	20	20	> 99	> 99
12	PhCH=CH-	H	5	6	98	97
13	PhCH=CH-	Me	6	7	> 95	94
14	(CH ₃) ₂ C=CHCH-	H	6	6.5	> 99	> 99
15	CH ₃ (CH ₂) ₄	CH=CH ₂	6	6	93	93
16	cyclohexenol		7	8	> 95	92
17	CH ₃ (CH ₂) ₃	H	24	–	> 99 ^[d]	–
18	CH ₃ (CH ₂) ₅	H	24	–	> 99 ^[d]	–
19	PhCH ₂ CH ₂	H	24	–	> 99 ^[d]	–
20	PhCH ₂ CH ₂ CH ₂	H	24	–	> 99 ^[d]	–
21	4-phenylcyclohexanol		16	–	53	–
22	4- <i>tert</i> -butylcyclohexanol		16	–	45	–

[a] GC yield based on an internal-standard method unless otherwise stated. [b] Yields in parentheses refer to isolated pure products. [c] The molar ratios of substrate/**1** are 1:0.004. [d] Conversions refer to the corresponding esters.

However, the high cost and toxicity of TFT resulted in us choosing toluene for the subsequent studies. High catalytic activity for both benzylic and allylic alcohols was observed and afforded the corresponding carbonyl compounds in excellent yields.

In particular, the catalyst showed excellent activity for the selective oxidation of various types of allylic alcohols to afford the corresponding α,β -unsaturated carbonyl compounds in excellent yields (Table 1, entries 12–16). Interestingly, the oxidation of primary aliphatic alcohols under the same reaction conditions furnished the corresponding esters in excellent yields in all cases (Table 1, entries 17–20). However, the oxidation of secondary aliphatic alcohols only produced moderate yields of the corresponding ketones (Table 1, entries 21 and 22).

It is worth mentioning that the reaction in air proceeded at a rate comparable to that in pure oxygen, thus indicating that the reaction is not retarded by the concentration of oxygen dissolved in the solvent. However, the oxidation of 2-substituted benzylic alcohols gave the corresponding aldehydes in only low yields (Table 1, entries 3 and 4). A TEM image of the catalyst **1** after the oxidation reaction showed that Pd nanoparticles with a relatively regular size of about 7 nm were mostly formed inside the regular mesoporous channels (Figure 1c). The low conversion of 2-substituted benzylic alcohols can be ascribed to steric hindrance by the quasi-two-dimensional surface of the nanoparticles.^[12]

Moreover, after the first use of catalyst **1** in the aerobic oxidation of benzyl alcohol (Table 1, entry 1) to give benzaldehyde in 83 % yield, the recovered catalyst was successfully used in 12 subsequent reactions and exhibited consistent catalytic activity (total TON \approx 3000). All recycling runs gave a product purity of greater than 99 % by GC analysis (see the Supporting Information).^[13] To rule out the contribution of homogeneous catalysis the reaction with benzyl alcohol was also conducted in the presence of catalyst **1** for one hour to obtain a conversion of 37 %. The solid was then hot-filtered off and transferred to another Schlenk flask containing K₂CO₃ in toluene at 80 °C under O₂. The catalyst-free solution was then left for 12 hours, but no further reaction took place. Furthermore, analysis of the solution by atomic absorption indicated that no Pd species had leached into the reaction. Nevertheless, it is difficult at this stage to attribute the actual catalytic activity solely to the ligand-bound Pd or to the Pd nanoparticles. It would also not be a surprise if the Pd

nanoparticles stabilized inside the channels of SBA-15 serve as a reservoir for a trace and nondetectable number of Pd particles to react through a homogeneous pathway.^[13] Further studies on this particular area are currently underway and the results will be published in due course.

It is also noteworthy that the N₂ adsorption/desorption analysis of the recovered catalyst showed very similar isotherms to those of the fresh catalyst **1**, with relatively sharp adsorption and desorption branches in the P/P_0 range of 0.5:1–0.8:1. This observation strongly indicates a relatively narrow size distribution of the mesopores, even in the recovered catalyst (see the Supporting Information), even though the total pore volume decreased from 0.76 to 0.57 cm³ g^{−1}. This observation accompanied by the TEM results suggests that most of the nanometer-scale void space and the channels of the host SBA-15 remain open, although a small portion of the channels may be blocked by Pd nanoparticles (see the Supporting Information).

To better clarify the role of the bipyridyl ligands in our protocol we set up two sets of control experiments. First, we prepared a new catalyst in which SBA-15 without any organic ligands was loaded with Pd(OAc)₂ at the same Pd loading as in **1**. The oxidation of benzyl alcohol was then conducted under the same reaction conditions as before, but using this catalyst. Interestingly, we found that the corresponding benzaldehyde was produced in greater than 99% conversion after 5 h in the first experiment. However, the catalyst activity decreased dramatically when it was used in two further oxidations of benzyl alcohol. The significant deactivation of the catalyst along with a color change to dark grayish is presumably a consequence of the formation of large palladium clusters (palladium black) on the outer surface of SBA-15. In the second experiment, SBA-15 modified with 3-cyanopropyl groups was loaded with Pd(OAc)₂ and the resulting pale yellow solid was tested for its catalytic activity in the same reaction as above. In this case, the solid catalyst showed a high degree of leaching and also the corresponding benzaldehyde was produced in low (less than 25%) conversion after 5 h as a result of the rapid formation of palladium black. Therefore, we believe that the bipyridyl ligands in catalyst **1** might indeed provide a means of uniformly distributing the mononuclear palladium species throughout the solid support to ensure the controlled formation of nanoparticles mostly inside the ordered mesoporous channels of SBA-15. It may also be concluded that the presence of the bipyridyl ligand in the size-restricted mesopores of the parent SBA-15 is effective for preventing both the leaching and the agglomeration of coordinated palladium nanoparticles to form huge particles of palladium black, and this results in the high durability and recycling characteristics of **1**.

In conclusion, we have described a new highly recoverable and efficient palladium-based catalyst for the aerobic oxidation of alcohols. We have also demonstrated that the combination of an organic ligand and ordered mesoporous channels resulted in an interesting synergistic effect that led to enhanced activity, the prevention of the agglomeration of the Pd nanoparticles, and the generation of a durable catalyst. This approach may find potential applications in other types

of nanocatalyzed reactions involving transition metals. Further applications of this new approach on other transition-metal-based nanoparticles are currently ongoing.

Experimental Section

A mixture of K₂CO₃ (1 mmol) and **1** (0.18 g, ca. 0.4 mol % of Pd) in toluene (5 mL) was prepared in a two-necked flask. The flask was then evacuated (water aspirator) and refilled with pure oxygen three times (balloon filled). A solution of the alcohol (1 mmol) in toluene (1 mL) was then injected into the solution and the resulting mixture was stirred at 80 °C under oxygen or air (for the time indicated in Table 1). After completion of the reaction, the mixture was filtered off and the catalyst rinsed twice with CH₂Cl₂ (5 mL). The excess solvent was then removed under reduced pressure to give the corresponding carbonyl compounds (Table 1).

Received: December 8, 2005

Revised: May 4, 2006

Published online: June 23, 2006

Keywords: aerobic oxidation · alcohols · mesoporous materials · nanoparticles · palladium

- [1] a) R. A. Sheldon, I. W. C. E. Arend, A. Dijkman, *Catal. Today* **2000**, 57, 157; b) B. Z. Zhan, A. Thompson, *Tetrahedron* **2004**, 60, 2917; c) R. A. Sheldon, *Green Chem.* **2000**, 2, G1; d) P. T. Anastas, L. B. Bartlett, M. M. Kirchhoff, T. C. Williamson, *Catal. Today* **2000**, 55, 11.
- [2] a) K. Kaneda, Y. Fujii, K. Morioka, *J. Org. Chem.* **1996**, 61, 4502; b) K. Kaneda, Y. Fujii, K. Ebitani, *Tetrahedron Lett.* **1997**, 38, 9023; c) K. P. Peterson, R. C. Larock, *J. Org. Chem.* **1998**, 63, 3185; d) T. Nishimura, T. Onoue, K. Ohe, S. Uemura, *Tetrahedron Lett.* **1998**, 39, 6011; e) T. Nishimura, T. Onoue, K. Ohe, S. Uemura, *J. Org. Chem.* **1999**, 64, 6750; f) G.-J. T. Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, 287, 1636; g) K. Hallman, C. Moberg, *Adv. Synth. Catal.* **2001**, 343, 260; h) M. J. Schultz, C. C. Park, M. S. Sigman, *Chem. Commun.* **2002**, 3034; i) D. R. Jensen, M. J. Schultz, J. A. Mueller, M. S. Sigman, *Angew. Chem.* **2003**, 115, 3940; *Angew. Chem. Int. Ed.* **2003**, 42, 3810; j) G.-J. T. Brink, I. W. C. E. Arends, R. A. Sheldon, *Adv. Synth. Catal.* **2002**, 344, 355; k) T. Nishimura, S. Uemura, *Synlett* **2004**, 201; l) S. Paavola, K. Zetterberg, T. Privalov, I. Csöreg, C. Moberg, *Adv. Synth. Catal.* **2004**, 346, 237; m) T. Iwasawa, M. Tokunaga, T. Obora, Y. Tsuji, *J. Am. Chem. Soc.* **2004**, 126, 6554; n) M. J. Schultz, S. S. Hamilton, D. R. Jensen, M. S. Sigman, *J. Org. Chem.* **2005**, 70, 3343; o) T. Iwasawa, M. Tokunaga, Y. Obora, Y. Tsuji, *J. Am. Chem. Soc.* **2004**, 126, 6554; p) for a recent excellent review on the palladium-catalyzed oxidation of alcohols, see: J. Muzart, *Tetrahedron* **2003**, 59, 5789; for a recent excellent review on the palladium-catalyzed aerobic oxidation of organic chemicals, see: q) S. S. Stahl, *Angew. Chem.* **2004**, 116, 3400; *Angew. Chem. Int. Ed.* **2004**, 43, 3480; r) T. Nishimura, S. Uemura, *Catal. Surv. Jpn.* **2000**, 4, 135; s) B. A. Steinhoff, A. E. King, S. S. Stahl, *J. Org. Chem.* **2006**, 71, 1861.
- [3] a) T. Nishimura, N. Kakiuchi, M. Inoue, S. Uemura, *Chem. Commun.* **2000**, 1245; b) N. Kakiuchi, Y. Maeda, T. Nishimura, S. Uemura, *J. Org. Chem.* **2001**, 66, 6620; c) N. Kakiuchi, M. Nishimura, M. Inoue, S. Uemura, *Bull. Chem. Soc. Jpn.* **2001**, 74, 165; d) K. Moroi, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2002**, 124, 11572; e) K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, 126, 10657; f) U. R. Pillai, E. Sahle-Demessie, *Green*

- Chem.* **2004**, *6*, 161; g) B. Karimi, A. Zamani, J. H. Clark, *Organometallics* **2005**, *24*, 4695.
- [4] a) Y. Uozumi, R. Nakao, *Angew. Chem.* **2003**, *115*, 204; *Angew. Chem. Int. Ed.* **2003**, *42*, 194; b) Z. Hou, N. Theyssen, A. Brinkmann, W. Leitner, *Angew. Chem.* **2005**, *117*, 1370; *Angew. Chem. Int. Ed.* **2005**, *44*, 1346; c) M. S. Kwon, N. Kim, C. M. Park, J. S. Lee, K. Y. Kang, J. Park, *Org. Lett.* **2005**, *7*, 1077.
- [5] a) E. M. Ferreira, B. M. Stoltz, *J. Am. Chem. Soc.* **2001**, *123*, 7725; b) J. T. Bagdanoff, E. M. Ferreira, B. M. Stoltz, *Org. Lett.* **2003**, *5*, 835; c) S. K. Mandal, D. R. Jensen, J. S. Pugsley, M. S. Sigman, *J. Org. Chem.* **2003**, *68*, 4600; d) J. T. Bagdanoff, B. M. Stoltz, *Angew. Chem.* **2004**, *116*, 357; *Angew. Chem. Int. Ed.* **2004**, *43*, 353.
- [6] a) D. R. Rolison, *Science* **2003**, *299*, 1698; b) M. Moreno-Mañas, R. Pleixats, S. Villarroja, *Organometallics* **2001**, *20*, 4524.
- [7] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710; b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- [8] a) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548; b) D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.
- [9] a) C. Yang, P. Liu, Y. Ho, C. Chiu, K. Chao, *Chem. Mater.* **2003**, *15*, 275; b) J. Zhu, Z. Konya, V. F. Puentes, I. Kiricsi, C. X. Miao, J. W. Ager, A. P. Alivisatos, G. A. Somorjai, *Langmuir* **2003**, *19*, 4396; c) J. He, T. Kunitake, A. Nakao, *Chem. Mater.* **2003**, *15*, 4401; d) T. F. Baumann, J. H. Satcher, *Chem. Mater.* **2003**, *15*, 3745.
- [10] a) S. D. Jackson, G. D. McLellan, G. Webb, L. Conyers, B. T. Keegan, S. Matter, S. Simpson, P. B. Wells, D. A. Whan, R. Whyman, *J. Catal.* **1996**, *162*, 10; b) G. Jacobs, F. Ghadiali, A. Pisanu, A. Borgna, W. Alvarez, D. E. Resasco, *Appl. Catal. A* **1999**, *188*, 79; c) S. Mandal, D. Roy, R. V. Chaudhari, M. Sastry, *Chem. Mater.* **2004**, *16*, 3714.
- [11] See the Supporting Information for details.
- [12] a) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, *J. Am. Chem. Soc.* **2005**, *127*, 9374; b) H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, *Langmuir* **2004**, *20*, 11 293.
- [13] For recent examples of metal colloids as reservoirs for homogeneous metal species, see: a) S. Tasler, B. H. Lipshutz, *J. Org. Chem.* **2002**, *67*, 1190; b) I. W. Davis, L. Matty, D. L. Hughes, P. J. Reider, *J. Am. Chem. Soc.* **2001**, *123*, 10139.