Journal of Molecular Catalysis A: Chemical 386 (2014) 114–119

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Oxidation of benzyl alcohols to aldehydes and ketones under air in water using a polymer supported palladium catalyst

Maria Michela Dell'Anna[a,*], Matilda Mali[a], Piero Mastrorilli[a,b], Pietro Cotugno[c], Antonio Monopoli[c]

[a] DICATECh, Politecnico di Bari, via Orabona 4, 70125 Bari, Italy
[b] Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), via Orabona 4, 70125 Bari, Italy
[c] Department of Chemistry, University of Bari "Aldo Moro", Via Orabona, 4, 70126 Bari, Italy

ARTICLE INFO

Article history:
Received 8 November 2013
Received in revised form 27 January 2014
Accepted 1 February 2014
Available online 11 February 2014

Keywords:
Polymer-supported palladium nanoparticles
Alcohol aerobic oxidation
Green chemistry
Recyclable catalyst
Water solvent.

ABSTRACT

This work deals with the catalytic conversion of benzyl alcohols to aldehydes or ketones using a polymer supported palladium catalyst which formed metal nanoparticles under reaction condition. The oxidation reaction was carried out on a series of substituted benzylic alcohols under air in water. The obtained results showed high selectivity also for the oxidation of primary alcohols to aldehydes without over-oxidation products. In addition, the catalyst was recycled several times with negligible metal leaching into solution.

1. Introduction

The oxidation of alcohols to aldehydes and ketones is very important from the academic and industrial point of view because compounds containing carbonyl groups are intermediates of several valuable fine chemicals such as fragrances, perfumes, flame retardants, pharmaceuticals [1]. Commonly, this reaction is obtained by adding stoichiometric amounts of inorganic oxidants ($KMnO_4$ or CrO_3) to the alcohol [2]. However, this procedure has the drawback to give pollutant and toxic by-products. With the aim to develop *greener* processes, the use of molecular oxygen as the oxidant has received growing attention in the past years [3,4], being water the only by-product of the reaction. In this regard, several methods that use molecular oxygen for the oxidation of alcohols under homogeneous and heterogeneous conditions have been exploited [5], using metal promoters such as: ruthenium [6,7], platinum [8,9], rhodium [10,11], copper [12], chromium [13], bimetallic gold–palladium [14] and gold [15–18] catalysts. During the past years there have been significant advances in palladium catalyzed oxidation reactions [19–21], and when the palladium catalyst was soluble, the use of particular ligands was crucial because it led to high selectivity and turnover numbers [22–24]. The alcohol aerobic oxidation reaction is also promoted by a variety of recyclable palladium catalysts supported onto insoluble matrices, such as SBA-15 [25], nanocrystalline starch [26], mesocellular foam [27], DNA-montmorillonite [28], poly(ethylene-glycol) [29], ionic liquid based organosilica framework [30] and graphene [31]. In these cases, the active species were found to be mostly palladium nanoparticles [26–31]. Although noticeable improvements in terms of selectivity and performance have been achieved, there is still need to develop new recoverable palladium catalysts able to work in "*greener*" reaction media, since generally the solvents employed in the aforementioned heterogeneous catalytic systems are: toluene [25,26], *p*-xylene [27], supercritical carbon dioxide [29] and α,α,α-trifluorotoluene [30]. Actually, water was used for the recyclable palladium catalyzed oxidation of several alcohols into carboxylic acids [28] and really interesting results were obtained in the aerobic oxidation of alcohols into aldehydes or ketones in water by employing: an amphiphilic resin dispersion of palladium nanoparticles [32], an aluminum hydroxide-supported palladium catalyst [33], hydroxyapatite-supported palladium nanoclusters [34]. However, in the latter cases, except for the Uozomi amphiphilic resin [32], the use of water as the solvent was limited to a marginal portion of the studies, being the activity and recyclability of the catalysts tested mostly in toluene or trifluorotoluene. The use of water as reaction media for the aerobic alcohol oxidation would be preferable and it

---

[*] Corresponding author. Tel.: +39 080 5963695; fax: +39 080 5963611.
E-mail address: mm.dellanna@poliba.it (M.M. Dell'Anna).

1381-1169/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molcata.2014.02.001

has several benefits, since it is cheap, nontoxic, nonflammable and allows an easy recovery of the products due to the insolubility in water of the majority of the organic compounds. Furthermore, the solubility of molecular oxygen in water is higher than in common organic solvents. With this scenario in mind, we decided to evaluate the catalytic activity of a polymer supported palladium catalyst (in the following *Pd-pol*) for the aerobic alcohol oxidation in water. The catalyst was obtained by co-polymerization of the metal-containing monomer [35] Pd(AAEMA)$_2$ [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with suitable co-monomer (ethyl methacrylate) and cross-linker (ethylene glycol dimethacrylate) [36,37] and it was already found active and recyclable in many palladium promoted reactions [38–43], even under air in water [44]. The reticular and macro porous polymeric support of *Pd-pol* is able to immobilize and stabilize palladium nanoparticles (formed under reaction conditions by reduction of the pristine Pd(II) anchored complex), suitable for the Suzuki cross coupling of arylhalides with arylboronic acids in water [44] and for the reductive amination reaction under 1 atm of H_2 [42]. Furthermore, the good swellability in water renders *Pd-pol* an ideal potential catalyst for reactions carried out in water, since the migration of the reagents to the active sites would not be hampered by the solid support.

Herein we report on the ability of *Pd-pol* in efficiently catalyzing the selective oxidation of a wide variety of alcohols into aldehydes and ketones under air as the oxidant and water as solvent.

2. Experimental

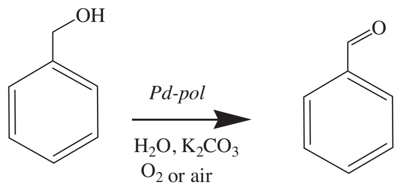
2.1. Materials

Tap water was de-ionized by ionic exchange resins (Millipore) before use. All other chemicals were purchased from commercial sources and used as received. *Pd-pol* was synthesized according to literature procedure [37]. Palladium content in *Pd-pol* was assessed after sample mineralization by atomic absorption spectrometry using a Perkin–Elmer 3110 instrument. Catalyst mineralization prior to Pd analyses was carried by microwave irradiation with an ETHOS E-TOUCH Milestone applicator, after addition of 12 mL HCl/HNO$_3$ (3:1, v/v) solution to each weighted sample.

GC-MS data (EI, 70 eV) were acquired on a HP 7890 instrument using a HP-5MS cross-linked 5% PH ME siloxane (30.0 m × 0.25 mm × 0.25 μm) capillary column coupled with a mass spectrometer HP 5973. The products were identified by comparison of their GC-MS features with those of authentic samples. Reactions were monitored by GLC or by GC-MS analyses. GLC analysis of the products was performed using a HP 6890 instrument equipped with a FID detector and a Supelcowax-10 capillary column (30.0 m × 0.25 mm × 0.25 μm). Conversions and yields were calculated by GLC analysis as moles of oxygenated product per mole of starting alcohol by using biphenyl as internal standard.

2.2. Typical oxidation of alcohols

Into a reaction vessel with a reflux condenser were placed *Pd-pol* (23.1 mg, Pd%$_w$ = 2.3), benzyl alcohol (108.1 mg, 1.0 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) and water (5 mL). The resulting mixture was stirred at 100 °C under 1 atm of air. After 6 h, the mixture was cooled down to room temperature and the organic product was extracted with ethyl acetate (3 mL). The water phase was washed with ethyl acetate (2 × 5 mL) and the organic layers were collected. GLC analysis of the ethyl acetate solution using biphenyl as an internal standard gave a 98% yield of benzyl aldehyde with >99% selectivity.



Scheme 1. Aerobic oxidation of benzyl alcohol under aerobic conditions in the presence of *Pd-pol*.

2.3. Recycling experiments

A two necked round flask was charged in air with *Pd-pol* (0.5 mol% Pd), benzyl alcohol (108.1 mg, 1.0 mmol), K_2CO_3 (138.2 mg, 1.0 mmol) and water (5 mL) and the whole system was put in a thermostated bath at 100 °C under vigorous magnetic stirring at reflux. After the minimum time needed to reach reaction completion, the mixture was cooled down to room temperature. The catalyst was recovered by filtration, washed with water, acetone, and diethyl ether and dried under high vacuum. The recovered catalyst was weighed and reused employing appropriate amounts of organic substrate and base, assuming that the palladium content remained unchanged with the recycles. Iteration of this procedure was continued for six reuses of the catalyst.

3. Results and discussion

The aerobic oxidation of benzyl alcohol was used as the model reaction in the presence of *Pd-pol* as the catalyst (Scheme 1).

The reaction was significantly affected by different parameters, such as reaction temperature and presence of the base. After the explorative experiments summarized in Table 1, the best conditions were found to be those employed in entry 5, that is: benzyl alcohol (1.0 mmol), *Pd-pol* (0.5 mol% of Pd), K_2CO_3 (1.0 mmol), air (1 atm) in water (5 mL) at 100 °C for 6 h.

The reported results revealed that in the absence of base at room temperature the conversion into benzyl aldehyde was poor both under air and under 1 atm pressure of O_2 (entries 1 and 2), while at 100 °C it increased under air up to 57% in 16 h (entry 3) with a 77% selectivity in benzyl aldehyde, being benzoic acid and its benzyl ester the over oxidation side-products. The reaction performed at 100 °C under dioxygen in the absence of base gave better results (entry 4) giving a 75% conversion into benzyl aldehyde in 6 h, and the presence of the base at 100 °C (entry 5) increased the catalytic activity of the system avoiding the use of 1 atm pressure of O_2.

The best conditions reported in entry 5 of Table 1 were applied in the same oxidation reaction carried out in the absence of the palladium catalyst (entry 6). No oxidation of the model substrate occurred at all, even after 12 h stirring.

Using the optimized reaction conditions, the activity and the scope of the catalyst was explored in the aerobic oxidation of a variety of different primary and secondary alcohols (Table 2).

Table 2 summarizes the most significant results. Both electron rich (entries 1–3) and electron deficient (entries 4 and 5) derivatives of benzyl alcohol showed excellent reactivity and afforded the corresponding aldehydes in quantitative yields. As expected, secondary alcohols were more difficult to oxidize. In fact, 1-phenylethanol (entry 6) and 1-phenylpropanol (entry 7) furnished excellent yields of corresponding ketones under optimized reaction conditions, though it was necessary to increase the reaction times to 16 h to ensure complete conversion. It is also noteworthy that, under the same conditions, the aerobic oxidation of benzyl alcohol promoted by a palladium(II) soluble catalyst extensively used in these kind of reactions,[24] such as palladium acetate (entry 8) gave only 40% conversion of the substrate into benzylaldehyde

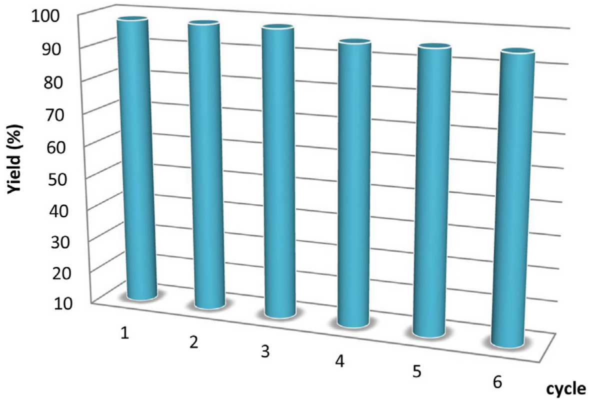


Fig. 1. Recyclability of *Pd-pol* (0.5 mol% of Pd) in the aerobic oxidation in water of benzyl alcohol in the presence of K_2CO_3 (1 eq) at 100 °C (t = 6 h).

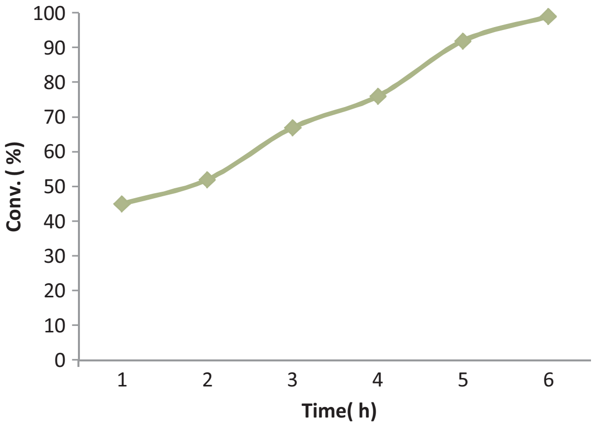


Fig. 2. Time course for the oxidation of benzyl alcohol catalyzed by *Pd-pol*. Reaction conditions: *Pd-pol* (0.5 mol% of Pd), benzyl alcohol (1.0 mmol), K_2CO_3 (1.0 mmol), water (5 mL), 100 °C, under air (1 atm).

after 6 h, leading to quantitative conversion only after 16 h reaction, thus exhibiting a catalytic activity much lower than *Pd-pol*. On the other hand, it was reported [34] that the aerobic oxidation of benzyl alcohol with commercially available heterogeneous palladium catalysts, such as Pd/C, Pd/SiO_2 and Pd/Al_2O_3 gave unsatisfactory results in terms of both activity and selectivity, because they do not bear palladium nanoparticles of appropriate size and shape [45,46].

Unfortunately, *Pd-pol* based catalytic system was inactive with aliphatic alcohols. In fact, β-citronellol and 1-butyl-1-octanol were reluctant to react, giving the corresponding carbonyl compounds in 10% and 5% yields for 7 h, respectively, even under 1 atm O_2.

The *Pd-pol* recyclability was explored in the oxidation of benzyl alcohol. After the first use, the supported catalyst was recovered by simple filtration and reused in the next run after a washing workup. The recovered catalyst was successfully employed in the subsequent five cycles with a high catalytic activity, giving the product in excellent yields (93–98%, Fig. 1).

To determine the true nature of the active species in *Pd-pol* catalytic system, a hot filtration test was performed. To do this, the solid catalyst was filtered off after the aerobic oxidation of benzyl alcohol had run for 1 h and the conversion reached 40% *ca*. The clear filtrate was then stirred under standard reaction conditions at 100 °C. After 16 h, the analysis of the catalyst-free reaction showed that the conversion had stopped at the initial value (40% *ca*). In addition, the atomic adsorption analysis carried out on the digested filtered catalyst revealed a palladium content in the recovered *Pd-pol* equal to that found in the catalyst before use. Also the *Pd-pol* recovered after 6 h reaction had a palladium amount equal to that found in the pristine catalyst, within the experimental error. However, it is very important to note that the absence of catalytic activity in the solid-free filtrate does not always imply no leaching of Pd species and the amount of leached palladium after each partial or total catalytic run may be below the detection limit. In fact, atomic adsorption analysis carried out on the catalyst recovered after six runs revealed a slight decrease of the palladium amount, being 90% of the initial content.

To gain insight into the kinetics of the reaction, the time course for the oxidation of benzyl alcohol was monitored periodically, as shown in Fig. 2, revealing a pseudo-first order reaction with respect to the benzyl alcohol. *Pd-pol* seemed to have a negligible induction period compared to the overall reaction time. However, a fast color change of the catalyst from yellow to dark gray was observed at the beginning of the reaction, suggesting that the reaction medium transforms the pre-catalyst into the active species, *i.e.* palladium nanoparticles.

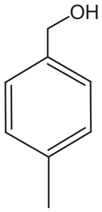
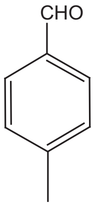
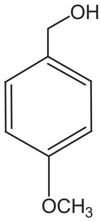
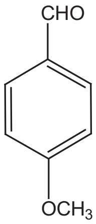
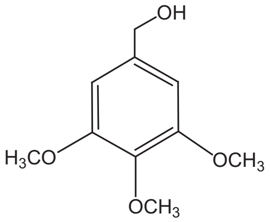
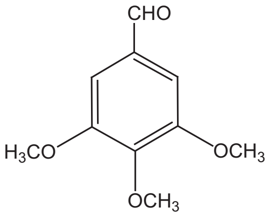
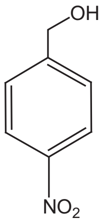
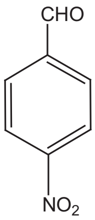
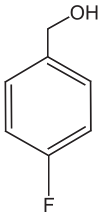
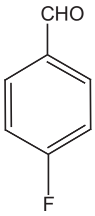
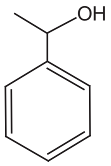
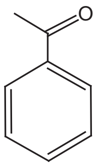
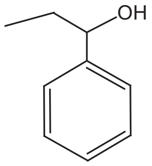
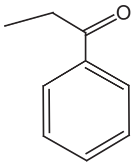
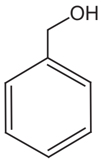
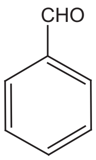
In fact, the polymeric support of *Pd-pol* was proven to stabilize palladium nanoparticles (with diameters ranging from 2 to 10 nm) formed under air in water at 100 °C, as revealed by TEM analysis [44]. From the above results, it can be concluded that the catalytically active species are not the original monomeric Pd(II) species, *i.e.* $[Pd(AAEMA)_2]$, but the *in situ* generated palladium nanoparticles formed by thermal decomposition at 100 °C, in accordance with the simulated process proposed by Rozenberg et al. [47]. The lacking of formation of these Pd nanoparticles may be responsible for the low activity of *Pd-pol* in the aerobic alcohol oxidation at room temperature (Table 1, entries 1 and 2). The reaction pathway could be thus similar to the one proposed by Kaneda and co-workers [34] starting with an oxidative addition of the alcohol to the coordinately unsaturated palladium(0) at the nanoparticle edge, affording Pd(II)-alcoholate intermediate, which undergoes a β-hydride elimination to produce the corresponding carbonyl compound and a Pd-hydride species. The reaction of the palladium(II) hydride with O_2 regenerates the initial palladium(0) species (Scheme 2) and produces H_2O_2, which fast decomposes into H_2O and O_2. The base

Table 1
The effect of the oxidant, reaction temperature and base in the aerobic oxidation of benzyl alcohol using *Pd-pol* catalyst.[a]

Entry	T (°C)	Oxidant[b]	Pd (mol%)	Base[c]	Time (h)[d]	Conv. (%)[e]	Selectivity (%)[e]
1	25	air	0.5	No	7	10	>99
2	25	O_2	0.5	No	7	13	>99
3	100	air	0.5	No	16	57	77
4	100	O_2	0.5	No	6	75	>99
5	100	air	0.5	K_2CO_3	6	>99	>99
6	100	air	no	K_2CO_3	16	0	0

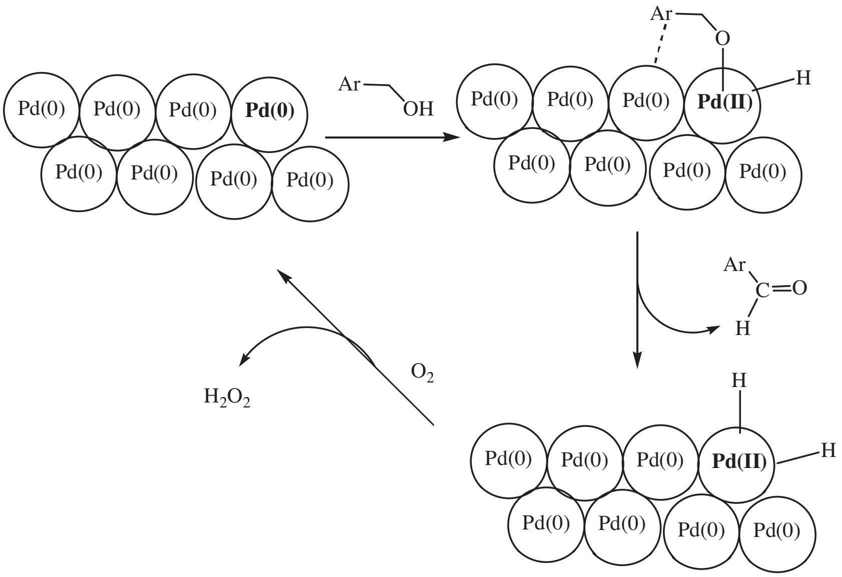
[a] Reaction conditions: benzyl alcohol (1.0 mmol), water (5 mL).
[b] Under 1 atm of O_2 or air.
[c] 1.0 mmol when present.
[d] Minimum time needed to reach reaction completion.
[e] Assessed by GLC with the internal standard (biphenyl) method.

Table 2
Aerobic oxidation of alcohols using *Pd-pol* catalyst in water under air.[a]

Entry	Substrate	Product	Time (h)	Yield[b] (%)
1			6	98
2			6	98
3			8	95
4			8	98
5			8	98
6			16	98
7			16	98
8[c]			6 16	40 92

---

[a] Conditions: Alcohol (1.0 mmol), *Pd-pol* (0.5 mol%), K_2CO_3 (1.0 mmol), water (5 mL), at 100 °C.
[b] GLC yields using internal standard (biphenyl) method.
[c] In the presence of $Pd(OAc)_2$ (0.5 mol%).



Scheme 2. Possible reaction mechanism for the oxidation of alcohols promoted by *Pd-pol*.

may favor the formation of palladium-alkoxide species and/or the eliminations [48,49].

Several studies already showed that the C—H bond cleavage (β-hydride elimination) is the rate-determining step of the benzyl alcohol oxidation reaction promoted by noble metal catalysts [34,48–52]. To get more insights into the mechanism of the present catalytic reaction, the relative rates of the oxidation of *para*-substituted benzyl alcohols (CH_3O, CH_3, H and NO_2 groups) were examined. The initial rates were measured for the first 15 min for each reaction [48] and the corresponding kinetic constants (k) were calculated. A good linearity between the log k_X/k_H values and the Hammett constant (σ) parameters for the oxidation of different *para*-substituted benzyl alcohols was obtained (Fig. 3) [53]. The resulting Hammett parameter ρ was −0.927, suggesting that the reaction is substituent-sensitive and carbocation species are involved. The negative ρ value indicates a positive charge buildup in the transition state (Scheme 3), further supporting rate-limiting β-hydride elimination. Electron-donating groups can stabilize carbocation species which are more easily oxidized.

It is noteworthy that *Pd-pol* is superior in terms of palladium leaching and recyclability in the aerobic alcohol oxidation in water compared with a catalyst similar to it, *i.e.* palladium nanoparticles supported onto soluble *N,N*-dimethylacrylamide based cross-linked polymers, obtained by grafting $Pd(OAc)_2$ onto the pre-formed resin, followed by metal reduction [54]. It seems that synthesizing a polymer supported catalyst starting from a metal containing monomer (as in the case of *Pd-pol*) allows to obtain better retained active species compared to the classical way of synthesis (preparation of the organic support followed by the anchoring of the metal complex onto it).

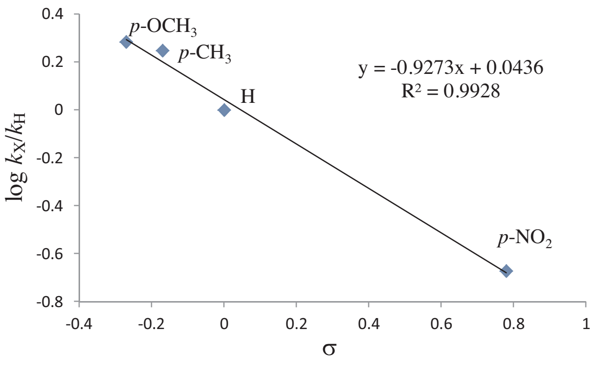
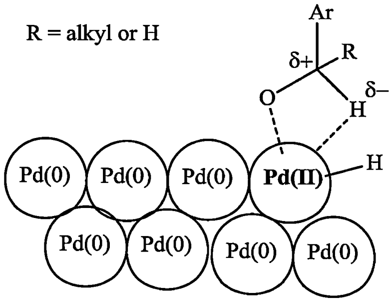


Fig. 3. Hammett plot for the oxidation of benzylic alcohols at 100 °C. Conditions: *Pd-pol* (0.5 mol% of Pd), benzyl alcohol (1.0 mmol), K_2CO_3 (1.0 mmol), water (5 mL), 100 °C, under air (1 atm).



Scheme 3. Plausible transition state of the β C—H bond cleavage step.

4. Conclusions

In conclusion, we have demonstrated the significant efficiency of a reticular and porous methacrylic material in the stabilization of active palladium species (nanoparticles) in the oxidation of alcohols in water by air. Several types of primary and secondary aromatic alcohols could be oxidized to their corresponding carbonyl compounds in the presence of a low loading of palladium (0.5 mol%) at relatively short reaction times (ranging from 6 to 16 h). Moreover, the catalyst could be easily recovered and reused to give quantitative yield of carbonyl adducts up to six cycles. The hot filtration test suggested that the catalyst operated through a heterogeneous pathway, even if atomic spectroscopy analyses revealed a less than 3% palladium leaching after each cycle.

Acknowledgement

The authors thank Italian MIUR (project PRIN 2010-2011 n. 2010FPTBSH_001) for financial support.

References

[1] M.I. Fernandez, G. Tojo, Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice, Springer, New York, 2006.
[2] J. March, Advanced Organic Chemistry: Reactions Mechanisms, and Structure, 4th ed., John Wiley & Sons, New York, 1992.
[3] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037–3058.
[4] B.-Z. Zhan, A. Thompson, Tetrahedron 60 (2004) 2917–2935.
[5] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329–2364.
[6] N. Komiya, T. Nakae, H. Sato, T. Naota, Chem. Commun. (2006) 4829–4831.
[7] R.A. Sheldon, I.W.C.E. Arendes, G.–J.T. Brink, A. Dijksman, Acc. Chem. Res. 35 (2002) 774–781.
[8] L. Tonucci, M. Nicastro, N. d'Alessandro, M. Bressan, P. D'Ambrosio, A. Morvillo, Green Chem. 11 (2009) 816–820.
[9] A. Frassoldati, C. Pinel, M. Besson, Catal. Today 173 (2011) 81–88.
[10] T. Zweifel, J.–V. Naubron, H. Grützmacher, Angew. Chem. Int. Ed. 48 (2009) 559–563.
[11] L. Liu, M. Yu, B.B. Wayland, X. Fu, Chem. Commun. 46 (2010) 6353–6355.
[12] Z. Hu, F.M. Kerton, Appl. Catal. A: Gen. 413–414 (2012) 332–339.
[13] W. Amer, K. Abdelouahdi, H.R. Ramananarivo, M. Zahouily, E.M. Essassi, A. Fihri, A. Solhy, Curr. Org. Chem. 17 (2013) 72–78.
[14] P. Miedziaka, M. Sankara, N. Dimitratosa, J.A. Lopez-Sancheza, A.F. Carleya, D.W. Knighta, S.H. Taylora, C.J. Kielyb, G.J. Hutchingsa, Catal. Today 164 (2011) 315–319.
[15] H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi, Angew. Chem. Int. Ed. 46 (2007) 4151–4154.
[16] C. Shang, Z.-P. Liu, J. Am. Chem. Soc. 133 (2011) 9938–9947.
[17] N. Asao, N. Hatakeyama, Menggenbateer, T. Minato, E. Ito, M. Hara, Y. Kim, Y. Yamamoto, M. Chen, W. Zhangi, A. Inouei, Chem. Commun. 48 (2012) 4540–4542.
[18] D. Tsukamoto, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, J. Am. Chem. Soc. 134 (2012) 6309–6315.
[19] M.J. Schultz, C.C. Park, M.S. Sigman, Chem. Commun. (2002) 3034–3035.
[20] S.S. Stahl (Ed.), Angew. Chem. Int. 43 (2004) 3400–3420.
[21] L.-Y. Wang, J. Li, Y. Lv, H.-Y. Zhang, S. Gao, J. Organomet. Chem. 696 (2011) 3257–3263.
[22] B.P. Buffin, J.P. Clarkson, N.L. Belitz, A. Kundu, J. Mol. Catal. A: Chem. 225 (2005) 111–116.
[23] I.W.C.E. Arends, G.-J. ten Brink, R.A. Sheldon, J. Mol. Catal. A: Chem. 251 (2006) 246–254.
[24] K.M. Gligorich, M.S. Sigman, Chem. Commun. (2009) 3854–3867.
[25] G. Zhang, Y. Wang, X. Wen, C. Ding, Y. Li, Chem. Commun. 48 (2012) 2979–2981.
[26] S. Verma, D. Tripathi, P. Gupta, R. Singh, G.M. Bahuguna, L.N. Shivakumar, R.K. Chauhan, K.S. Saranb, S.L. Jain, Dalton Trans. 42 (2013) 11522–11527.
[27] E.V. Johnston, O. Verho, M. Shakeri, C.–W. Tai, P.P. Almgren, K. Eriksson, S. Oscarsson, J.–E. Bäckvall, Chem. Eur. J. 18 (2012) 12202–12206.
[28] L. Tang, X. Guo, Y. Li, S. Zhang, Z. Zha, Z. Wang, Chem. Commun. 49 (2013) 5213–5215.
[29] Z. Hou, N. Theyssen, A. Brinkmann, W. Leitner, Angew. Chem. Int. Ed. 44 (2005) 1346–1349.
[30] B. Karimi, D. Elhamifar, J.H. Clark, A.J. Hunt, Org. Biomol. Chem. 9 (2011) 7420–7426.
[31] G. Wu, X. Wang, N. Guan, L. Li, Appl. Catal. B: Environ. 136–137 (2013) 177–185.
[32] Y. Uozumi, R. Nakao, Angew. Chem. Int. Ed. 42 (2003) 194–197.
[33] M.S. Kwon, N. Kim, C.M. Park, J.S. Lee, K.Y. Kang, J. Park, Org. Lett. 7 (2005) 1077–1079.
[34] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 126 (2004) 10657–10666.
[35] M.M. Dell'Anna, G. Romanazzi, P. Mastrorilli, Curr. Org. Chem. 17 (2013) 1236–1273.
[36] M.M. Dell'Anna, P. Mastrorilli, A. Rizzuti, G.P. Suranna, C.F. Nobile, Inorg. Chim. Acta 304 (2000) 21–25.
[37] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, in: P.J.H. Scott (Ed.), Solid-Phase Organic Syntheses, 2, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2012, pp. 79–86.
[38] M.M. Dell'Anna, M. Gagliardi, P. Mastrorilli, C.F. Nobile, J. Mol. Catal. A: Chem. 158 (2000) 515–520.
[39] M.M. Dell'Anna, P. Mastrorilli, F. Muscio, C.F. Nobile, G.P. Suranna, Eur. J. Inorg. Chem. 8 (2002) 1094–1099.
[40] M.M. Dell'Anna, P. Mastrorilli, F. Muscio, C.F. Nobile, in: M. Anpo, M. Onaka, H. Yamashita (Eds.), Science and Technology in Catalysis, Elsevier, Amsterdam, 2002, pp. 133–136.
[41] M.M. Dell'Anna, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. A: Chem. 201 (2003) 131–135.
[42] M.M. Dell'Anna, A. Lofu, P. Mastrorilli, V. Mucciante, C.F. Nobile, J. Organomet. Chem. 691 (2006) 131–137.
[43] M.M. Dell'Anna, P. Mastrorilli, A. Rizzuti, C. Leonelli, Appl. Catal. A: Gen. 401 (2011) 134–140.
[44] M.M. Dell'Anna, M. Mali, P. Mastrorilli, A. Rizzuti, C. Ponzoni, C. Leonelli, J. Mol. Catal. A: Chem. 366 (2013) 186–194.
[45] Y. Pereza, M.L. Ruiz–Gonzalez, J.M. Gonzalez–Calbet, P. Concepcion, M. Boronat, A. Corma, Catal. Today 180 (2012) 59–67.
[46] J. Chen, Q. Zhang, Y. Wang, H. Van, Adv. Synth. Catal. 350 (2008) 453–464.
[47] A.S. Rozenberg, A.A. Rozenberg, G.I. Dzardimalieva, A.D. Pomogailo, Colloid J. 67 (2005) 63–71.
[48] J.A. Mueller, C.P. Goller, M.S. Sigman, J. Am. Chem. Soc. 126 (2004) 9724–9734.
[49] L.C. John, A. Gunay, A.J. Wood, M.H. Emmert, Tetrahedron 69 (2013) 5758–5764.
[50] A. Abad, A. Corma, H. Garcia, Chem. Eur. J. 14 (2008) 212–222.
[51] F. Wang, W. Ueda, J. Xu, Angew. Chem. Int. Ed. 51 (2012) 3883–3887.
[52] M. Wang, F. Wang, J. Ma, M. Li, Z. Zhang, Y. Wang, X. Zhang, J. Xu, Chem. Commun. 50 (2014) 292–294.
[53] σ values were taken from T.H. Lowry, K.S. Richardson, Mechanism and Theory in Organic Chemistry, 3rd ed., Harper and Row, New York, 1987, pp. 144.
[54] A. Biffis, L. Minati, J. Catal. 236 (2005) 405–409.