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Oxidation

A Tris(triazolate) Ligand for a Highly Active and Magnetically Recoverable Palladium Catalyst of Selective Alcohol Oxidation Using Air at Atmospheric Pressure

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Abstract: High efficiency and selectivity, easy magnetic recovery and recycling, and use of air as the oxidant at atmospheric pressure are major objectives for oxidation catalysis in terms of sustainable and green processes. A tris(triazolyl) ligand, so far only used in copper-catalyzed alkyne azide cycloadditions, was found to be extremely efficient in SiO_2/γ-Fe_2O_3-immobilized palladium complexes. It was characterized by inductively coupled plasma (ICP) analysis, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectra (XPS) and found to fulfill the combined conditions for the selective oxidation of alcohols to aldehydes and ketones.

Introduction

As an essential development of organic synthesis, oxidation reactions play a pivotal role in the current chemical industry, as well as in the establishment of green and sustainable chemical processes.[1] In particular, the selective oxidation of primary or secondary alcohols to the corresponding aldehydes or ketones, which are ubiquitous precursors and intermediates in the synthesis of agrochemicals, pharmaceuticals, and fine chemicals, has been widely recognized as one of the most fundamental transformations in organic chemistry.[2] Traditionally, stoichiometric oxidizing reagents including hypervalent iodine, permanganate, dichromate, peroxides, and other heavy-metal reagents have been employed for the oxidation of alcohols.[3] These traditional procedures are quite useful in laboratory-scale reactions. These stoichiometric oxidants are somewhat expensive and/or toxic and hazardous, however, and release a considerable amount of heavy-metal wastes and byproducts. From the standpoint of green and sustainable chemistry, in addition to safety considerations, it is of particular importance to develop an alternative approach to construct a cleaner and more efficient catalytic system for the selective oxidation of alcohols. In this context, much attention has been recently paid to the development of transition-metal-catalyzed aerobic alcohol oxidations that involve Ru, Pd, Au, Co, Cu, Pt, Rh, V, Os, Ce, and Ni[4] by using "green" molecular oxygen (even air) as oxidant.[2,5] Enhanced catalytic performances in both activity and selectivity, high atom economy, and cheaper and less polluting oxidants are involved in the latter processes.

Despite this progress, there are still persistent problems in this field. In some cases, the high temperature and high oxygen pressure are essential to obtain good catalytic efficiency. The use of 1 atm of air is still limited in most of these aerobic oxidation systems. Also, numerous transition-metal catalysts do not show good tolerance to alcohol substrates. Most importantly, the economic concerns and metal contamination of carbonyl compounds are extremely restrictive as they relate to the application of homogeneous noble-metal catalysts in aerobic alcohol oxidations. To overcome these problems, the use of heterogeneous catalysts appears to be promising. Various supports including polymers, Al_2O_3, mesoporous silica, ionic liquids, resin, TiO_2, CeO_2, hydrotalcite, celite, kaolin, MgO, activated carbon, carbon nanotubes, and ZrO_2[2,6] have been widely employed to immobilize homogeneous metal catalysts or metal nanoparticle catalysts, thus forming recyclable catalytic species in the aerobic selective oxidation of alcohols. However, traditional heterogeneous catalysts usually suffer from low catalytic activity relative to their homogeneous counterparts.

Research on magnetic nanoparticles (MNPs) has become one of the hottest fields and has experienced extremely fast growth in the past few years.[7] MNPs are considered to be the

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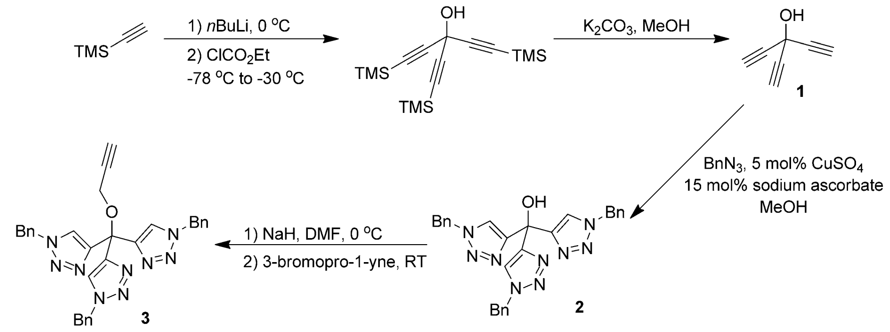
most attractive and ideal support considering their specific properties. MNPs are seemingly biocompatible and easily assembled with low preparation cost. MNP-supported catalysts generally exhibit excellent catalytic activity, selectivity, and stability owing to their nanoscale size, that is, large surface-to-volume ratio, unique interaction between the catalytic species and MNPs, and tunable characters such as size, shape, composition, electronic structure, and solubility. In addition, MNP catalysts are efficiently and easily recoverable with an external magnetic field for reuse, and they remain catalytically efficient after many repeated reactions. Therefore MNP catalysts fully embody the principles of green chemistry and sustainability.

In a related context, from both environmental and economic points of view, a few reports on the preparation and catalytic application of MNP catalysts in aerobic oxidation of alcohols have emerged.[8a,d–f] However, these MNPs that involve catalytic systems more or less showed some imperfections, such as narrow substrate scope, poor selectivity towards aldehydes or ketones, and/or the requirement of molecular oxygen with high pressure. The use of safe, clean, and available free air as oxidant is still a major significant challenge in alcohol oxidation reactions catalyzed by MNPs. Therefore, it is highly desirable to develop an efficient catalytic system that contains an MNP support for the aerobic oxidation of various alcohols at atmospheric pressure of air.



Scheme 1. Synthesis of the alkynyl-functionalized ligand tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol (**3**).

Along with our continuous efforts to develop economical and eco-friendly catalytic protocols for organic transformations from the point of view of green and sustainable chemistry,[9] herein we report the design and preparation of an MNP-immobilized tris(triazolyl)–palladium(II) catalyst and its catalytic application and recyclability in the selective oxidation of alcohols to aldehydes and ketones by air at atmospheric pressure.

Results and Discussion

Since Fokin et al. pioneered the synthesis of tris(triazolyl) fragments,[10] these compounds have been shown to be excellent ligands with copper salts in Cu^I-catalyzed alkyne–azide cycloaddition (CuAAC).[10,11] To our surprise, however, tris(triazolyl) ligands have not been used in any other reaction. It was thus of interest to functionalize, immobilize, and metalize a tris(triazolyl) ligand, and evaluate the catalytic property of its palladium complexes in aerobic alcohol oxidation.

Synthesis of a SiO_2@γ-Fe_2O_3-immobilized tris(triazolyl) ligand

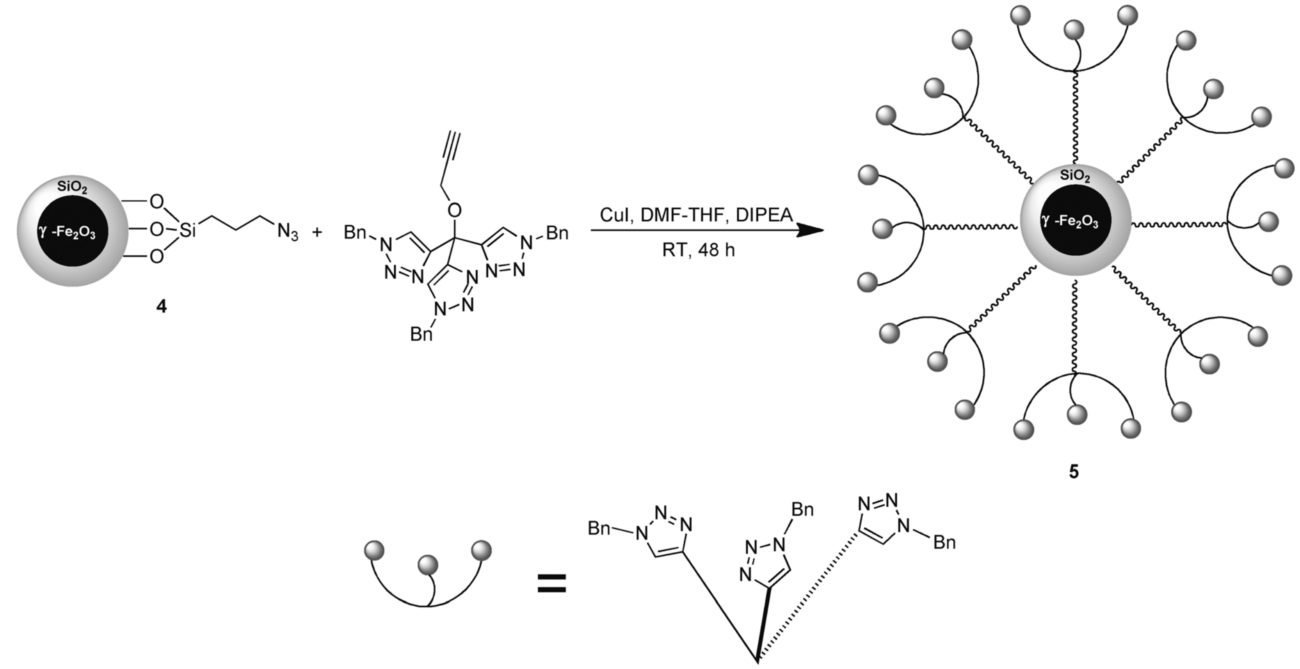
In the primary steps, tris(alkynyl)carbinol intermediate **1** was synthesized by the addition of trimethylsilylacetylide to ethyl chloroformate, followed by removal of the trimethylsilyl groups. Then, CuAAC reactions of **1** with three equivalents of benzyl azide were conducted in the presence of copper sulfate and sodium ascorbate. It provided tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol (**2**), which underwent further propargylation with NaH and propargyl bromide to give alkynyl-functionalized tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol ligand **3** (Scheme 1).[11b]

The pre-synthesized azido-functionalized magnetic nanoparticles (**4**) were obtained through the immobilization of 3-azidopropyltriethoxysilane on the surface of robust SiO_2/γ-Fe_2O_3 by means of heterogenization with the Si–OH binding sites of SiO_2/γ-Fe_2O_3.[9b,c,12] The CuAAC reaction was then successfully carried out between **4** and an excess amount of **3** using CuI/*N*,*N*-diisopropylethylamine (DIPEA) as catalyst in mixed DMF/THF at room temperature (RT) to produce MNP-anchored tris(triazolyl) ligand **5** (Scheme 2). The reaction was monitored by FTIR spectroscopy as indicated by the almost complete disappearance of the IR signal of the azide group at 2102 cm^{-1} (Figures S1–S3 in the Supporting Information). The determination of the nitrogen content (C, H, N elemental analysis) showed that the tris(triazolyl) ligand loading was approximately 0.51 mmol g^{-1}.

Preparation and characterization of MNP-immobilized Pd catalysts

Complexation of **5** with $Pd(OAc)_2$ (1.2 equiv) was conducted overnight in toluene at 45 °C, and resulted in the assembly of MNP-immobilized tris(triazolyl)–$Pd(OAc)_2$, **Cat. 1**. For comparison, the highly water-dispersible **Cat. 1** was reduced by the addition of $NaBH_4$ (10 equiv per Pd atom) in water to form MNP-supported PdNPs,[13] **Cat. 2** (Scheme 3). Both Pd catalysts were characterized by transmission electron microscopy (TEM), inductively coupled plasma (ICP) analysis, and X-ray photoelectron spectroscopy (XPS).

ICP analysis revealed that the Pd loadings of **Cat. 1** and **Cat. 2** are 0.24 and 0.21 mmol g^{-1}, respectively, which means that the Pd species was partially released from the initial Pd^{II} complex during the preparation of the PdNPs. The TEM images



Scheme 2. Synthesis of tris(triazolyl) fragment-modified SiO_2@γ–Fe_2O_3 nanoparticles.

indicated that the average diameter of the NPs of **Cat. 1** was approximately 30 nm and ranged from 15 to 40 nm, which is similar to the sizes of both unloaded MNP SiO_2/γ-Fe_2O_3 and **Cat. 2** (Figure 1a–c). Moreover, the mean size of formed PdNPs loaded onto the surface of MNP in **Cat. 2** was around 4 nm (Figure 1c).

The elemental composition was measured by energy-dispersive X-ray spectroscopy (EDX) analysis and the results, shown in Figure 2, indicate Si, O, Fe, and Pd signals that are produced by **Cat. 2**. For further characterization of the sample, scanning transmission electron microscopy (STEM)-coupled quantified energy-dispersive X-ray spectroscopy (EDX) mapping of **Cat. 2** was also determined (Figure 3). On the compositional maps of Si, Fe, Pd, and the combined composition images, the presence of the iron oxide nanoparticles is clearly distinguished in the core of the MNP that is encapsulated by the silicon oxide shell, whereas the palladium nanoparticle is localized at the border of the MNP.

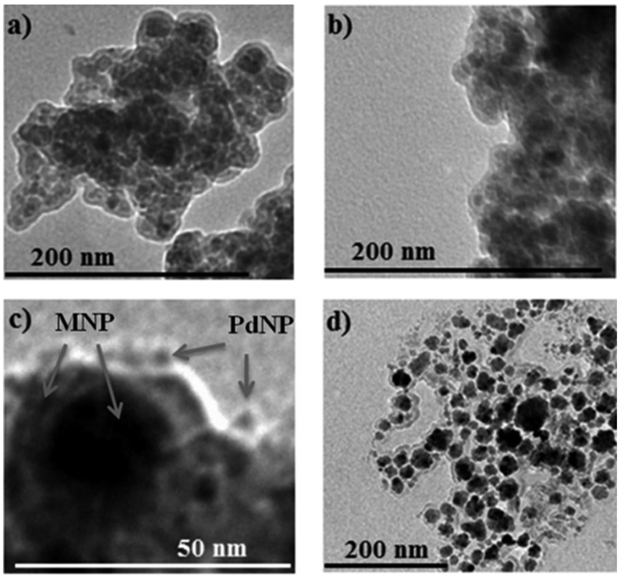
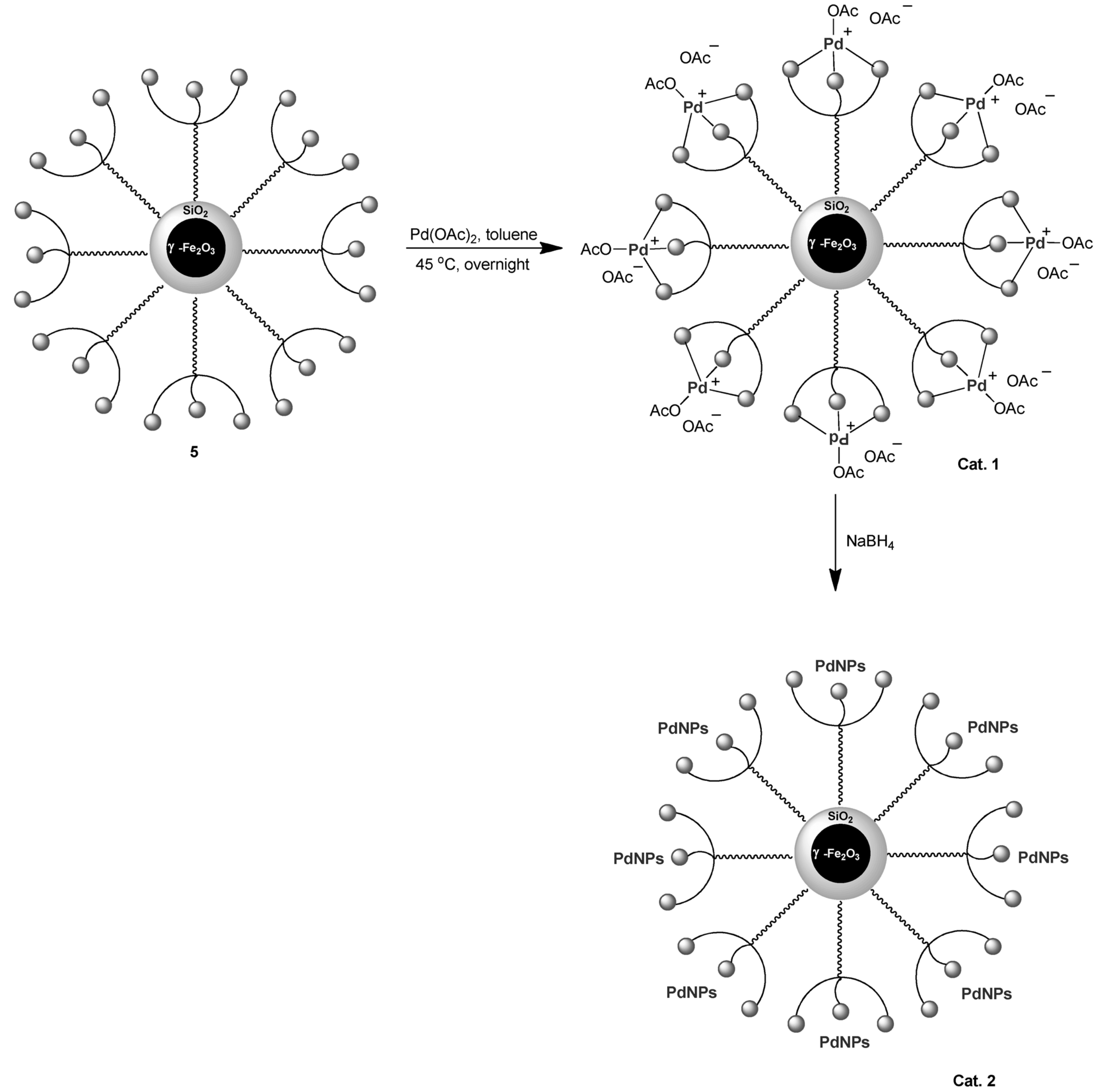


Figure 1. a) TEM image of SiO_2/γ–Fe_2O_3 nanoparticles. b) TEM image of **Cat. 1**. c) TEM image of **Cat. 2**. d) TEM image of **Cat. 1** after four reaction cycles in the aerobic oxidation of benzyl alcohol.

XPS analysis was performed on both **Cat. 1** and **Cat. 2** to investigate their composition and the oxidation states of the Pd atoms. As shown in Figure 4c, the signals of Si, C, N, O, Fe, and Pd were clearly observed in the XPS spectrum of **Cat. 1**, thus proving the presence of the magnetic iron core coated with a silica shell that is functionalized with C/N/Pd species. Two binding energies (BEs) were observed for Pd 3d at 335.7 eV (29.6%) and at 337.7 eV (70.4%), which indicate the presence of both Pd^0 and Pd^{II}, respectively (Figure 4a, Table S1 in the Supporting Information). With the BE of the $Pd(OAc)_2$ alone being 338.4 eV, the BE of 337.7 eV belongs to Pd^{II} linked to the triazole rings. It seems reasonable that some neutral Pd species are released in situ from the initially formed tris(triazolyl)–palladium(II) complexes owing to the treatment in toluene overnight at 45 °C. The XPS spectrum of **Cat. 2** showed the predominance of Pd^0 (56%) over Pd^{II} (44%) (Figure 4b, Table S1 in the Supporting Information). The relatively high amount of Pd^{II} could be attributed either to the insufficient amount of reducing agent used for the reduction of all the Pd^{II} to Pd^0, or to the re-oxidation of the catalyst by air during storage and analysis.



Scheme 3. Preparation of MNP-immobilized Pd catalysts **Cat. 1** and **Cat. 2**.

Investigation of the activity, selectivity, recyclability, and substrate scope of MNP-immobilized Pd catalysts

The Pd-catalyzed oxidation of alcohols using oxygen as the oxidant has been recognized as a potentially powerful transformation for organic synthesis.[6a, 14] With the MNP-supported palladium catalysts in hand, the catalytic properties were investigated for alcohol oxidation using benzyl alcohols as probe substrate (Table 1). In these preliminary experiments, the reaction was conducted in the presence of 40 mg of **Cat. 1** (1.9 mol% of [Pd]) and K_2CO_3 in toluene at 85–90 °C using 1 atm of air as oxidant. It was found that the reaction was completed within 4.5 h, with 93% selectivity and 84% isolated yield towards desired aldehyde compound **6** (Table 1, entry 2). In addition, the selectivity of **6** decreased to 82% with increasing reaction time in the range of 3–5.5 h (Table 1, entries 1–3). In these processes, the corresponding acid **7** and ester **8** were also observed as side products. Under the same conditions, the replacement of **Cat. 1** by **Cat. 2** caused clear decreases in both conversion and selectivity towards **6** (Table 1, entry 4) to 76 and 85%, respectively. The oxidation of benzyl alcohol also proceeded when Pd(OAc)$_2$ was used as catalyst, but the conversion was much lower than that of **Cat. 1** (Table 1, entry 5). Thus, the tris(triazolyl) group apparently played the role of an activating ligand for the catalytic activity of the Pd atoms. Moreover, the results of contrast tests showed that unloaded γ-Fe$_2$O$_3$@SiO$_2$ nanoparticles were not active at all in this trans-

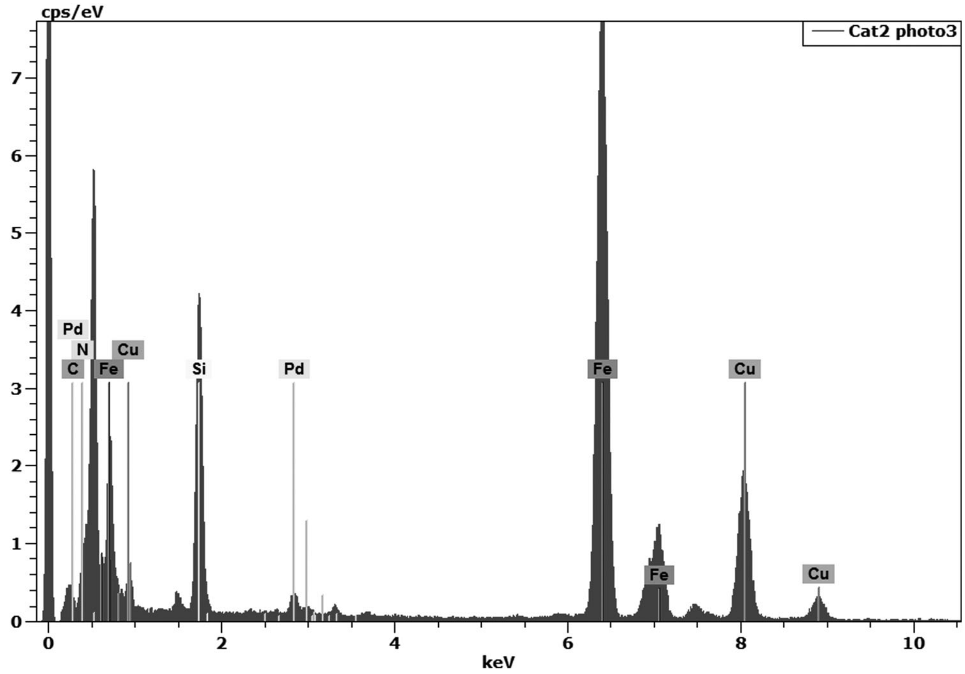


Figure 2. EDX spectrum of **Cat. 2**.

formation. The mixture of γ-Fe_2O_3@SiO_2 and $Pd(OAc)_2$ provided moderate conversion but poor recyclability (Table 1, entry 7).

As a key issue for the evaluation of the heterogeneous catalysts, the recyclability of MNP-anchored Pd catalysts was investigated (Table 2). After the completion of the first reaction cycle, both **Cat. 1** and **Cat. 2** were readily removed from the reaction medium by using an external magnet, and new reactions were then performed with fresh reactants under the same conditions. Remarkably, **Cat. 1** was recycled for at least five reaction runs without significant decrease in both activity and selectivity. On the contrary, a clear decrease in the reaction conversion was observed after two cycles in the case of **Cat. 2**. ICP analysis indicated that the amount of Pd leaching after four cycles from the initial **Cat. 1** was negligible. The TEM image revealed that the morphology and size of **Cat. 1** changed over time, and a particle aggregation problem emerged after four reaction cycles (Figure 1d).

The scope of alcohols was examined for oxidation to aldehydes and ketones using 1.9 mol% of the supported palladium catalyst **Cat. 1** under aerobic conditions. Representative results are summarized in Scheme 4. The substituted primary alcohols were oxidized smoothly under standard reaction conditions and afforded the corresponding aldehydes **9a** and **9b** in excellent conversions and selectivities. This protocol was extended to primary alcohols that contained other electron-withdrawing or electron-donating groups. When 2,3-dimethoxybenzyl alcohol and 3-nitrobenzyl alcohol were employed, the corresponding aldehyde products **9b** and **9c** were obtained with lower conversions and excellent selectivity. The catalyst was also effective for the oxidation of secondary benzylic alcohols with electron-donating or electron-withdrawing groups under prolonged reaction times. A series of ketones **9e**–**9j** were obtained with excellent conversions and selectivity, in the range of 81–97 and 86–91%, respectively. The results show that no direct correlation can be drawn between the electronic nature of the alcohols and the outcome of the reactions; in addition, primary alcohols exhibited higher reactivity than secondary alcohols.

Mechanistic explanations for Pd-catalytic aerobic oxidation of alcohols have recently been sought in several studies.[3e,15] Briefly, three steps were included in the catalytic cycle, which are the coordination of the alcohol with Pd atom to form a Pd alkoxide, β-hydride elimination of the Pd alkoxide to produce a carbonyl compound and a Pd hydride, and oxidation of the Pd hydride by molecular oxygen to give the initial Pd catalyst for the next cycle. In particular, in this transformation, Pd catalysts are known to aggregate easily and form inactive Pd black. To suppress the formation of Pd black, the use of both an excess amount of ligand and sufficient oxygen partial pressure rather than air are generally necessary. With **Cat. 1**, the tris(triazolyl) moieties act as a strong ligand to stabilize Pd^{II} and Pd^0 intermediates, thus forming sufficiently stable Pd complexes, which results in the inhibition of Pd atom aggregation. Chelated cage structures that involve the formation of six-membered rings[11a,16] are expected to lead to remarkable catalytic performance in air at atmospheric pressure, as well as good recyclability.

Conclusion

Considering the increasing environmental and economic concerns in large-scale preparation, the oxidation of alcohols using dioxygen from air at atmospheric pressure over supported transition-metal catalysts is particularly attractive.

In this report, the catalytic oxidation of alcohols was achieved in air by using a novel MNP-immobilized tris(triazolyl)–Pd^{II} catalyst that was designed and assembled with the aim of using it as a magnetically recyclable and efficient catalyst. This catalyst provided impressive and superior performances with regard to activity, selectivity, and recyclability relative to its PdNP counterpart. A series of primary and secondary benzyl alcohols were smoothly oxidized to afford the corresponding aldehydes and ketones in the presence of the magnetic tris(triazolyl)–Pd^{II} catalyst (1.9 mol%) at 85–90 °C in toluene with 81–97% conversions and 86–92% selectivity. In addition, the catalyst was easily recoverable and reusable for at least five cycles with only a slight decrease in catalytic performance.

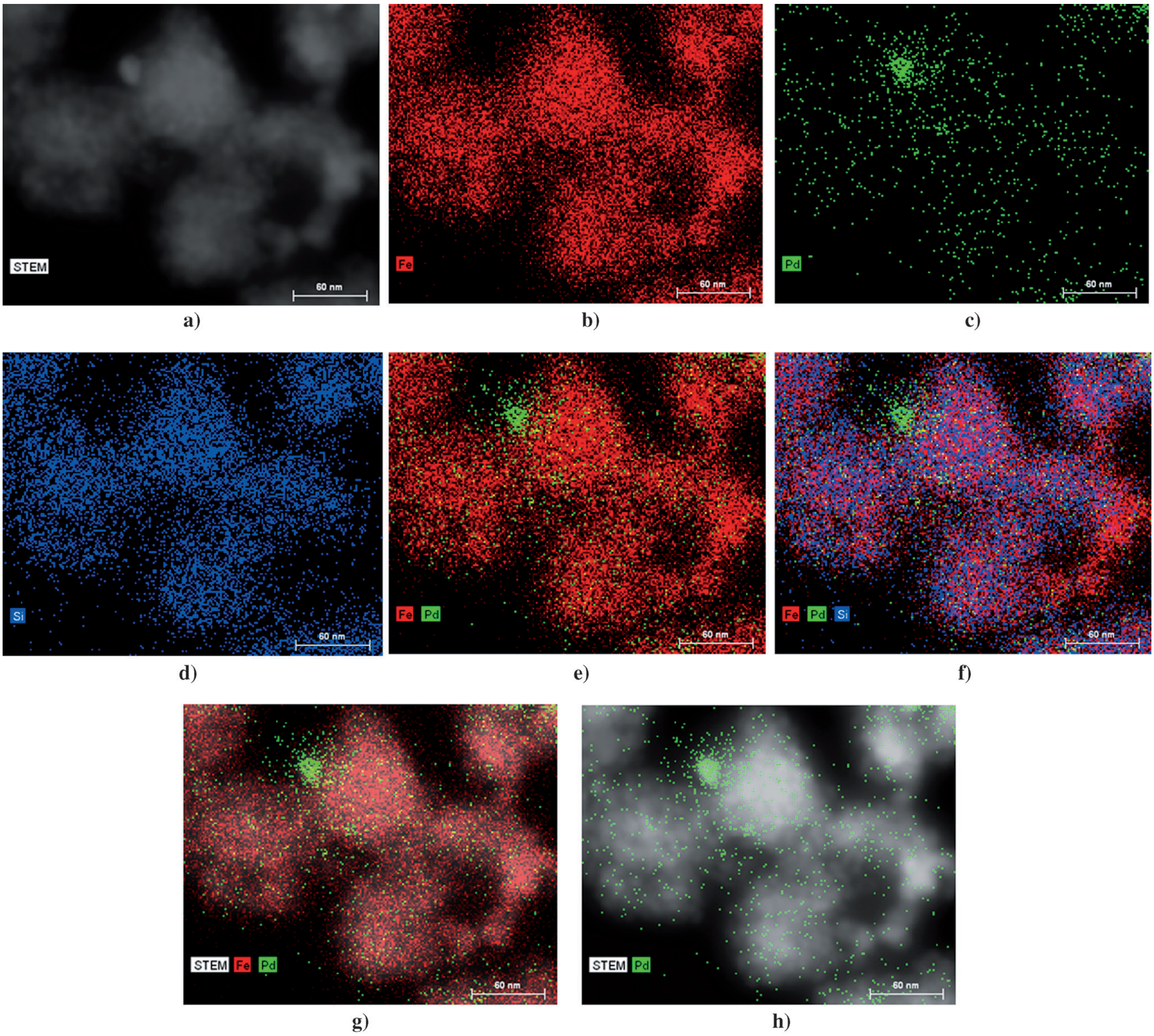


Figure 3. a) STEM dark-field image; elemental maps of **Cat. 2** for b) Fe, c) Pd, d) Si, and e) mixtures of Fe and Pd, f) Fe, Pd, and Si. h) STEM dark-field image-elemental maps of Pd and g) a mixture of Fe and Pd obtained by EDX. All scale bars = 60 nm.

Positive effects of this catalytic system in terms of cost as well as associated safety and environmental benefits makes it an ideal protocol for the selective oxidation of alcohols. This work should significantly contribute to the development of clean technology and establishing green and sustainable chemical processes.

Experimental Section

General

All reactions were performed under nitrogen by using standard Schlenk techniques unless otherwise noted. Toluene was dried over Na foil and freshly distilled under nitrogen immediately prior to use. THF was dried over Na foil and freshly distilled from sodium benzophenone under nitrogen immediately prior to use. All commercially available reagents were used as received, unless indicated otherwise. Flash column chromatography was performed using silica gel (300–400 mesh). ^{1}H NMR spectra were recorded by using a 300 MHz spectrometer, and ^{13}C NMR spectra were recorded at 75 MHz by using a 300 MHz spectrometer. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France. The infrared spectra were recorded using an ATI Mattson Genesis series FTIR spectrophotometer. The inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses were carried out using a Varian ICP-OES 720ES apparatus. Room temperature throughout the paper is 23–25 °C.

Synthesis of tris(trimethylsilylethynyl)methanol[11a]

A solution of trimethylsilylacetylene (4.6 mL, 33.2 mmol) in anhydrous THF (40 mL) was added into a flame-dried round-bottomed flask, and the mixture was cooled to −78 °C. Then, 2.5 M *n*BuLi in hexane (12.2 mL, 30.4 mmol) was added dropwise, and the solu-

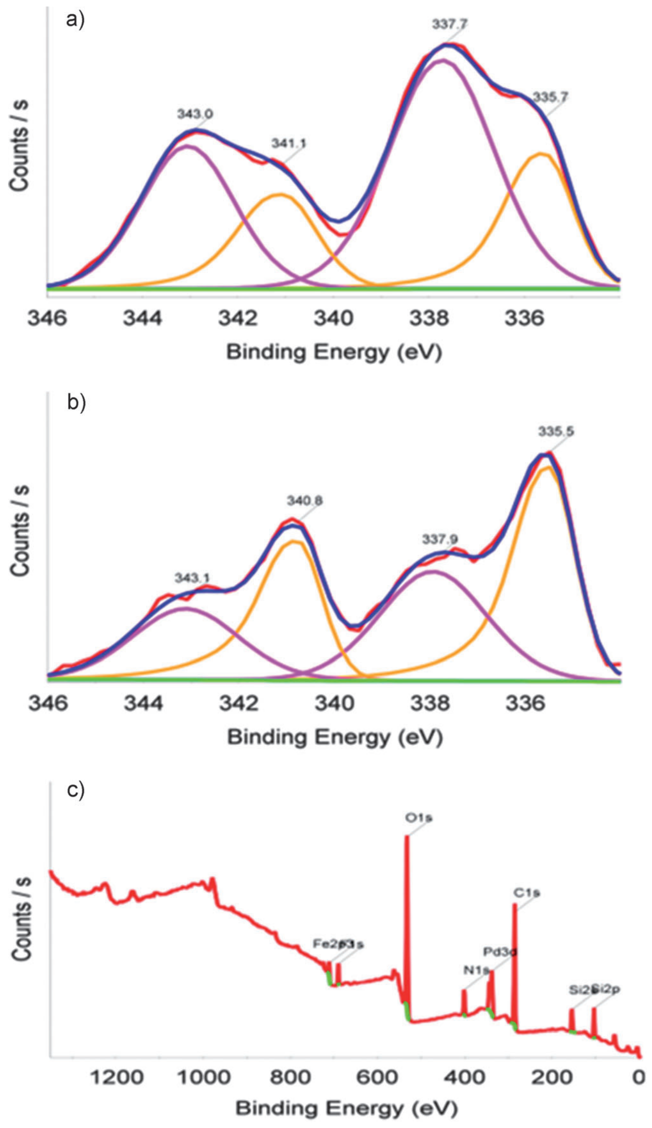


Figure 4. a) XPS Pd 3d spectrum of **Cat. 1**. b) XPS Pd 3d spectrum of **Cat. 2**. c) XPS survey of **Cat. 1**.

Table 2. Investigation of the recyclabilities of MNP–Pd catalysts in the aerobic oxidation of benzyl alcohol.[a]

	Cat. 1		**Cat. 2**	
	Conversion[b]	Selectivity towards **6**[b]	Conversion[b]	Selectivity towards **6**[b]
Cycle 1	100	93	76	85
Cycle 2	97	93	70	85
Cycle 3	92	93	50	72
Cycle 4	92	90	–	–
Cycle 5	86	91	–	–

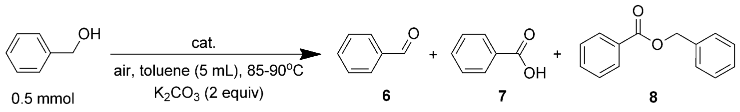
[a] The reaction was carried out with benzyl alcohol (0.5 mmol) in the presence of freshly prepared or recycled Pd catalyst (**Cat. 1** or **Cat. 2**) and K_2CO_3 (1 mmol) in toluene (5 mL) at 85–90 °C in air at atmospheric pressure. [b] Both conversion and selectivity towards **6** were measured by ^1H NMR spectroscopic analysis.

tion was stirred for 2 h. Ethyl chloroformate (884 μL, 9.12 mmol) was subsequently added, and the reaction was stirred overnight (15 h) while warming to −30 °C. The reaction was quenched with saturated NH_4Cl solution, diluted with water, and extracted with Et_2O (3×60 mL). The combined organic phase was dried over Na_2SO_4, and the solvent was removed under vacuum. Purification by flash chromatography on a short pack of silica gel eluting with hexanes and hexanes/ethyl acetate (90:10) afforded tris(trimethylsilylethynyl)methanol in 67 % yield (1.9 g). The product was recrystallized from hexane at 0 °C. ^1H NMR (300 MHZ, $CDCl_3$): $\delta = 2.84$ (s, 1 H), 0.24 ppm (s, 27 H).

Synthesis of benzyl azide

In a Schlenk tube, benzyl bromide (10 mmol) and sodium azide (12 mmol) were added to DMSO (40 mL), and the mixture was stirred at RT for 24 h. Then H_2O (40 mL) was added to quench the azidation reaction. The aqueous solution was extracted with diethyl ether (3×20 mL), the combined organic phase was dried over Na_2SO_4 and filtered, and the filtrate was removed under vacuum to obtain the crude product that was further purified by silica-gel chromatography (using pentane/ethyl acetate as eluent) to yield benzyl azide.

Table 1. Optimization of the oxidation of benzyl alcohol using Pd catalysts in air.[a]

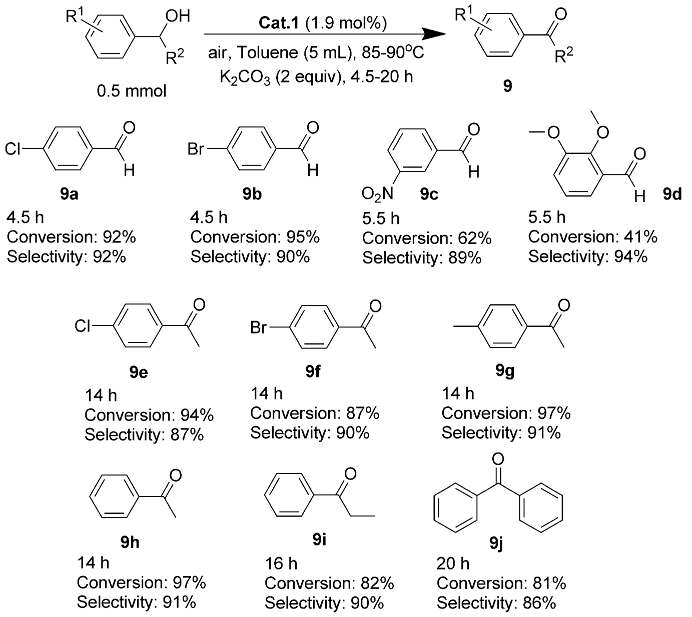


Entry	Cat. [mol %]	t [h]	Conversion [%][b]	Selectivity [%][b]		
				6	7	8
1	**Cat. 1** (1.9)	3	90	>96	1	2
2	**Cat. 1** (1.9)	4.5	100	93	3	4
3	**Cat. 1** (1.9)	5.5	100	82	4	14
4	**Cat. 2** (1.9)	4.5	76	85	6	9
5	$Pd(OAc)_2$ (5)	4.5	55	87	3	10
6	γ-Fe_2O_3@SiO_2[c]	4.5	NR	0	0	0
7	γ-Fe_2O_3@SiO_2[c]/$Pd(OAc)_2$ (5)	4.5	49, 12[d]	89	5	6

[a] The reaction was carried out with benzyl alcohol (0.5 mmol) in the presence of the listed catalysts and K_2CO_3 (1 mmol) in toluene (5 mL) at 85–90 °C in air at atmospheric pressure. [b] Both conversion and selectivity towards **6** were measured by ^1H NMR spectroscopic analysis. [c] γ-Fe_2O_3@SiO_2 (40 mg). [d] Conversion of the second recycle.

Synthesis of tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol (2)[11a]

In a round-bottomed flask, tris(trimethylsilylethynyl)methanol (1.5 g) in methanol (15 mL) was stirred in the presence of K_2CO_3 (8.0 g) at RT for 4 h. The solution was filtered to remove an excess amount of K_2CO_3 and added to a solution of benzyl azide (1.9 g) in methanol (15 mL). $CuSO_4{\cdot}5H_2O$ (60 mg) and sodium ascorbate (150 mg) were added, and the mixture was stirred for 72 h. Solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (CH_2Cl_2; 75 mL) and washed with a saturated Na_2CO_3 solution (5×45 mL). At the end of the extraction, the aqueous phase was not blue (the color of copper salts) any longer. The organic phase was dried over Na_2SO_4, and the solvent was removed under vacuum. A yield of 1.2 g (52 %) of the desired crude product **2** was obtained after a very short silica-gel chromatography to remove the excess amount of benzyl azide. The crude product was



Scheme 4. Investigation of the substrate scope in the presence of **Cat. 1** in the oxidation of alcohols.

not further purified, and it was used directly for the next step. ^{1}H NMR (300 MHZ, $CDCl_3$): $\delta = 7.63$ (s, 3 H), 7.36–7.38 (m, 9 H), 7.27–7.30 (m, 6 H), 5.49 (s, 6 H), 4.71 ppm (s, 1 H).

Synthesis of 3-[tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-propyne (3)[11b]

A solution of **2** (503 mg, 1.0 mmol) in DMF (2 mL) was added dropwise at 0 °C to a flame-dried flask that contained a suspension of NaH (80 mg, 60 % in oil, 2.0 mmol) in DMF (2 mL). After stirring for 2 h at RT, the suspension became a clean solution that was cooled again to 0 °C. Then, a commercial solution of propargyl bromide in toluene (0.220 mL, 80 % solution in toluene, 2.0 mmol) was added dropwise. The reaction mixture was allowed to warm to RT and stirred for an additional 14 h. Water (10 mL) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3×10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum. Traces of DMF were removed by dissolving the crude product in an ethyl acetate/hexane (4:1) mixture (40 mL) and washing the solution with water (3×20 mL). The organic phase was dried over Na_2SO_4 and concentrated under vacuum to afford crude **3**, which was further purified by flash column chromatography using ethyl acetate as the eluent. The product was obtained as a thick orange oil or pumiceous solid (0.46 g, 86 %). ^{1}H NMR (300 MHZ, $CDCl_3$): $\delta = 7.88$ (s, 1 H), 7.29–7.41 (m, 15 H), 5.53 (s, 6 H), 4.15 (d, $J = 2.4$ Hz, 2 H), 2.08 ppm (t, $J = 2.4$ Hz, 1 H).

Synthesis of MNP-immobilized azide

The $Si(OMe)_3$-functionalized azido compound was freshly pre-synthesized through a classic azidation method by using redistilled DMF as solvent at 45 °C. Under an atmosphere of nitrogen, the obtained $Si(OMe)_3$-functionalized azido compound (350 mg) was added to a suspension of MNPs $SiO_2/\gamma\text{-}Fe_2O_3$ (0.3 g) in anhydrous toluene (30 mL). The mixture was then stirred at 110 °C under a nitrogen atmosphere for 24 h. The dark brown solid material obtained was magnetically separated, washed repeatedly with toluene (2×10 mL), CH_2Cl_2 (10 mL), a diluted aqueous solution of ammonia and a saturated Na_2CO_3 solution (until there was no blue color in the solution), H_2O (2×20 mL), and acetone (2×10 mL) to remove any unanchored species and then dried under vacuum.

Synthesis of the MNP-immobilized tris(triazolyl) ligand by CuAAC reaction

The MNP-immobilized azide (600 mg) and tris(triazolyl) compound **3** (300 mg) were mixed with Cu^I (8 mg) in DMF/THF (1:1, 20 mL) under nitrogen. *N*,*N*-Diisopropylethylamine (2 mL) was injected into the mixture, which was then sonicated for approximately 30 min and stirred at RT for 48 h. The reaction was monitored by FTIR as indicated by the almost complete disappearance of the IR signal of the azido group at 2102 cm^{-1}. Then the mixture was submitted to magnetic separation, and the MNPs were washed sequentially with DMF (10 mL), THF (10 mL), CH_2Cl_2 (10 mL), diluted aqueous ammonia solution and saturated Na_2CO_3 solution (until there was no blue color in the solution), H_2O (2×10 mL), and acetone (10 mL), and finally dried under vacuum.

Synthesis of MNP-immobilized tris(triazolyl)Pd$(OAc)_2$ complex (Cat. 1)

Under a nitrogen atmosphere, toluene (30 mL) was mixed with MNP-immobilized tris(triazolyl) ligand (500 mg; the ligand loading, 0.51 mmol g^{-1}, was determined by elemental analysis) and $Pd(OAc)_2$ (1.2 equiv, 0.61 mmol, 16.2 mg). The mixture was then sonicated for approximately 30 min and stirred at 45 °C overnight. After cooling to RT, the solution was colorless. Then the mixture was submitted to magnetic separation, and the MNPs were washed sequentially with DMF (10 mL), THF (10 mL), CH_2Cl_2 (10 mL), H_2O (2×10 mL), and acetone (10 mL), and finally dried under vacuum. The obtained catalyst was kept in N_2 for further applications.

Synthesis of the MNP-immobilized Pd nanoparticles (Cat. 2)

Under a nitrogen atmosphere, in a Schlenk flask, the suspension of MNP–Pd complex **Cat. 1** (200 mg) in Milli-Q H_2O (20 mL) was sonicated for approximately 20 min under nitrogen. An aqueous solution (10 mL) that contained 1.26 mmol of $NaBH_4$ was then injected. The mixture was stirred at RT for 2 h, and the color of the mixture changed from brown to black, which indicated the reduction of Pd^{2+} to Pd^0 and PdNP formation. The mixture was submitted to magnetic separation, the MNPs were washed with Milli-Q H_2O (2×10 mL) and acetone (10 mL) under nitrogen, and the catalyst was dried at 45 °C for at least 4 h under vacuum and stored under nitrogen before use.

General procedures for the Cat. 1-catalyzed oxidation of benzyl alcohol

A dried Schlenk tube equipped with a magnetic stirring bar was charged with the MNP-immobilized tris(triazolyl) $Pd(OAc)_2$ complex (**Cat. 1**, 40 mg), benzyl alcohol (0.5 mmol), K_2CO_3 (1 mmol), and toluene (10 mL). The mixture was sonicated for approximately 20 min and stirred at 85–90 °C for 4.5 h in air. The catalyst was collected by using a magnet and washed successively with toluene (2 mL), CH_2Cl_2 (10 mL), and acetone (5 mL) with the protection of N_2, then dried at 45 °C under vacuum. The combined organic phase was dried over Na_2SO_4 and filtered, and the filtrate was removed under vacuum (vacuum 40 mbar, 70 °C) to obtain the crude product. This product was analyzed by ^1H NMR spectroscopy, which showed 100% conversion and 93% selectivity toward benzaldehyde. The crude product was further purified by silica gel chromatography (using pentene as eluent) to yield the desired benzaldehyde. The recovered catalyst was kept in N_2 before use for the next reaction cycle.

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FULL PAPER

Oxidation

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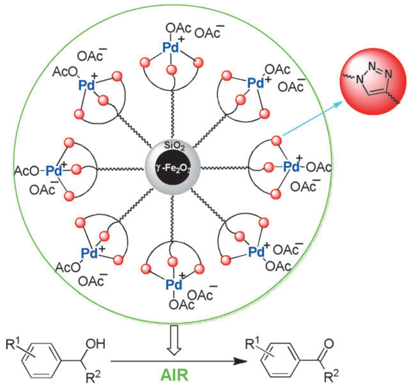
■■ – ■■

A Tris(triazolate) Ligand for a Highly Active and Magnetically Recoverable Palladium Catalyst of Selective Alcohol Oxidation Using Air at Atmospheric Pressure



Coming up for air: A tris(triazolyl) ligand, so far only used in Cu-catalyzed alkyne azide cycloadditions, was found to be extremely efficient in SiO_2/γ-Fe_2O_3-immobilized palladium complexes (see scheme). It was characterized by several methods and found to fulfill the combined conditions for the selective oxidation of alcohols under air.