Functionalization of silicon surfaces with catalytically active Pd complexes and application to the aerobic oxidation of benzylic alcohols†

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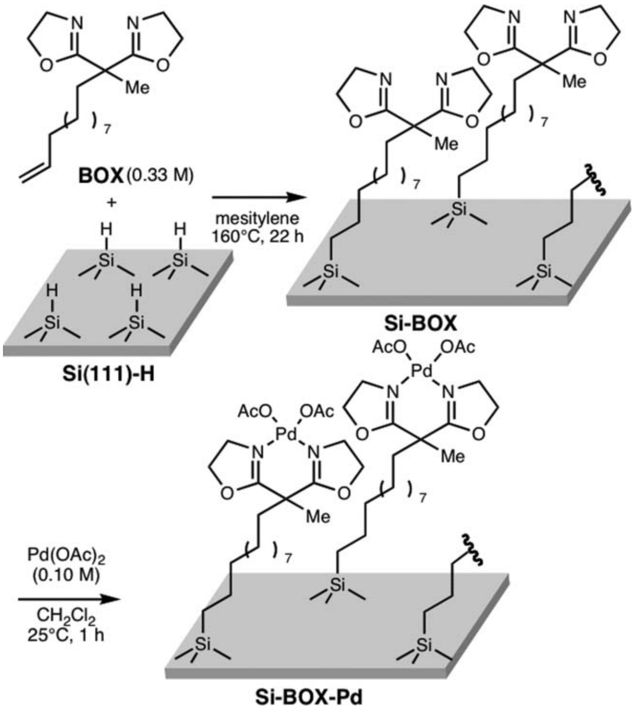
A single-crystal silicon surface was modified with a bisoxazoline–Pd molecular layer and utilized as a highly efficient (catalyst turnover number up to 780 000, 110 °C, 72 h) and recyclable catalyst in the aerobic oxidation of benzylic alcohols.

As a key material in semiconductor industry, single-crystal silicon is utilized over a wide range of scientific research. In addition to top-down fabricating techniques, bottom-up chemical modification methodologies have been developed to introduce various functionalities on the silicon substrate. It is highly anticipated that the combination of these two methodologies would contribute to the development of sophisticated silicon-based devices.

A key feature in the chemical modification of crystalline silicon surfaces with organic molecules is the strong Si–C covalent bond; accordingly, reactions between silicon surfaces and various organic molecules have been extensively examined.[1] However, the immobilization of a molecular catalyst onto crystalline silicon has yet to be widely utilized.[2] In contrast, the immobilization of catalysts on Au surface through an Au–S bond has been reported.[3] Herein, we report on the modifications of the silicon surface with bisoxazoline–Pd complexes to form a modified silicon surface that exhibited exceptionally high turnover efficiency in the aerobic oxidation of benzylic alcohols. Furthermore, the catalytically active surface can be repeatedly utilized by a simple recycle process.

As illustrated in Scheme 1, single-crystal silicon surfaces were modified by grafting a simple bisoxazoline (**BOX**) molecule, followed by the successive complexation with Pd. First, the reaction between the terminal vinyl group of the alkyl substituent of the **BOX** molecule and Si–H of the hydrogen-terminated Si(111) surface (**Si(111)–H**) was carried out *via* thermal hydrosilylation.[1] Next, The **BOX**-grafted Si(111) surface [**Si-BOX**] was treated with a solution of $Pd(OAc)_2$ in CH_2Cl_2 followed by washing with CH_2Cl_2 to form the corresponding metal complex [**Si-BOX-Pd**].

Introduction of both the ligand and the metal was confirmed using two techniques: first, attenuated total reflection infrared spectroscopy (ATR-IR) of **Si-BOX** revealed C=N stretching (1665 cm^{-1}) and C–H stretching modes of the methylene chain (2855 and 2927 cm^{-1}). ATR-IR of **Si-BOX-Pd** confirmed the inclusion of acetato ligands on the Pd atoms (three peaks at 1424, 1514 and 1562 cm^{-1}). Secondly, X-ray photoelectron spectroscopy (XPS) of **Si-BOX-Pd** indicated the Pd/N molar ratio of 0.66, which is close to the theoretical value of 0.5. Furthermore, ICP-MS measurement of **Si-BOX-Pd** indicated that Pd was incorporated at a concentration of 0.21 nmol cm^{-2}, which corresponds to a functionalization of 16% on the inherent surface Si–H groups. According to literature, 50–55% of the inherent Si–H groups can be functionalized with simple long terminal alkenes.[4] Considering the steric demand of the bisoxazoline group, it seems that the **BOX-Pd** moieties have attained almost maximum surface coverage.



Scheme 1

The catalytic activity of **Si-BOX-Pd** was examined using the aerobic oxidation of benzyl alcohol (Scheme 2).[5] To a single chip of **Si-BOX-Pd** (5 × 5 × 0.6 mm^3, both flat sides modified, positioned at the bottom of a glass reaction tube) was added an oxygen-saturated solution (0.5 mL) of benzyl alcohol (5.4 mg, 0.050 mmol). Under these reaction conditions, the substrate/catalyst ratio (S/C) was 480 000, based on the amount of Pd. The reaction tube was purged with oxygen (8.0 mL, 0.34 mmol) and sealed using a screw cap. The reaction was carried out at 110 °C

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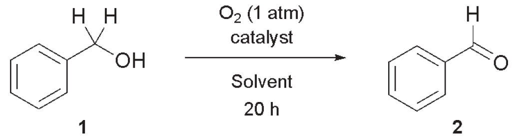


Scheme 2

for 20 h without stirring, under various solvents and conditions, as listed in Table 1. The use of toluene (entry 1) and $CF_3C_6H_5$ (entry 2) exhibited fairly high catalytic activities with turnover numbers (TONs) of 34 000 and 24 000, respectively. Polar solvents such as DMF (entry 3) and water (entry 4) afforded similar TONs of 20 000 and 24 000, respectively). Remarkably, exceptionally high catalyst turnover number was obtained when octane was used as the solvent. In the case of entry 5, the reaction proceeded nearly to completion (98%), giving an 86% yield of benzaldehyde, which corresponds to a TON of 410 000, together with $PhCO_2CH_2Ph$ (6%) and $PhCO_2H$ (1%). The high TON obtained here is among the highest value reported to date.[6]

Although lowering the reaction temperature to 80 °C retarded the reaction, a TON of 24 000 was still attained for the **Si-BOX-Pd** catalyst (entry 6). In contrast, at low catalyst loading (S/C = 200 000), neither $Pd(OAc)_2$ nor $Pd(OAc)_2$/bisoxazoline complex (homogeneous controls) showed catalytic activities. With a much higher catalyst loading (S/C = 2000, 0.05 mol%), these Pd species showed some catalytic activities, with TON of merely 1300 (entry 7) and 100 (entry 8), respectively. Catalytic activities were not observed for the control experiments with **Si-BOX** (entry 9) and with the silicon surface pretreated with a solution of $Pd(OAc)_2$ (entry 10).

When the catalytic aerobic oxidation was carried out at a 1.0-mmol scale (108 mg of benzyl alcohol) using **Si-BOX-Pd** ($20 \times 20 \times 0.6$ mm^3, S/C = 600 000) under O_2 (balloon) atmosphere, a yield of 84% was obtained after 20 h, which corresponds to a TON of 500 000 (Table 2, entry 1). Doubling the amount of benzyl alcohol (2.0 mmol, 216 mg) afforded a TON of 460 000 (38% yield, entry 2) after 20 h. A prolonged reaction time of 72 h further increased the TON to 780 000 (65% yield, entry 3). These experiments demonstrate the feasibility of scaling-up the present catalyst system. For practical purposes, chemical engineering methodologies, such as microfluidic systems, should further enhance the efficiency of our catalytic system.[7]

Table 1 Pd-catalyzed aerobic oxidation of benzyl alcohol[a]

Entry	Catalyst	Solvent	Temp/ °C	Conv./ Yield[b] (%)	TON[c]
1	**Si-BOX-Pd**	Toluene	110	7/7	34 000
2	**Si-BOX-Pd**	$CF_3C_6H_5$	110	5/5	24 000
3	**Si-BOX-Pd**	DMF	110	4/4	20 000
4	**Si-BOX-Pd**	H_2O	100	5/5	24 000
5	**Si-BOX-Pd**	Octane	110	98/86	410 000
6	**Si-BOX-Pd**	Octane	80	5/5	24 000
7	$Pd(OAc)_2$ (0.05 mol%)	Octane	110	87/67	1300
8	$Pd(OAc)_2$/**BOX** (1/1, 0.05 mol%)	Octane	110	6/6	100
9	**Si-BOX**	Octane	110	1/1	—
10	Si surface [pretreated with $Pd(OAc)_2$][d] $Pd(OAc)_2$	Octane	110	1/1	—
11	None	Octane	110	1/1	—

[a] The reaction was carried out in 0.050 mmol scale with 0.5 mL of solvent for 20 h at 110 °C in a screw-capped test tube under an alcohol/catalyst ratio of 480 000, unless noted otherwise. See ESI for details. [b] Yield of benzaldehyde. [c] Catalyst turnover number for benzaldehyde. [d] The silicon surface prepared by immersion in a solution of $Pd(OAc)_2$ in CH_2Cl_2 followed by washing with CH_2Cl_2 was used.

Table 2 Aerobic oxidation of benzyl alcohol catalyzed by **Si-BOX-Pd**[a]

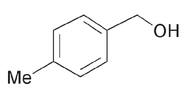
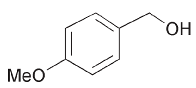
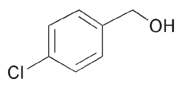
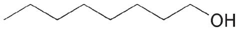
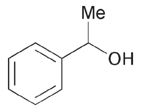
Entry	Benzyl alcohol/ mmol mg^{-1}	Alcohol/ Catalyst	Time/h	Yield[b] (%)	TON[c]
1	1.0/108	600 000	20	84	500 000
2	2.0/216	1 200 000	20	38	460 000
3	2.0/216	1 200 000	72	65	780 000

[a] The reaction was carried out using **Si-BOX-Pd** with dimensions of $20 \times 20 \times 0.6$ mm^3 in 7.0 mL of octane at 110 °C. [b] Yield of benzaldehyde. [c] Catalyst turnover number for benzaldehyde.

As listed in Table 3, the **Si-BOX-Pd** catalyst chip was utilized for the oxidation of other benzylic alcohols. For *p*-methylbenzyl alcohol (entry 1), a TON of 370 000 was obtained, whereas for *p*-methoxybenzyl alcohol (entry 2) and *p*-chlorobenzyl alcohol (entry 3), larger catalyst chips were required to afford reasonable amounts of the corresponding aldehydes (62% at S/C = 48 000 and 6% at S/C = 24 000, respectively). For aliphatic alkanols (S/C = 24 000; entry 4), catalytic activity was not detected. Finally, the oxidation of 1-phenylethanol (entry 5) to the corresponding ketone proceeded smoothly to afford a TON of 110 000.

Due to the flat shape of the catalyst, recycling can be readily achieved by physically transferring the used catalyst chip into the reaction vessel for the next run. As shown in Table 4, the catalytic activity of **Si-BOX-Pd** is maintained during repeated uses. Furthermore, upon removal of the catalyst chip, the reaction immediately ceases, indicating that the active species is not released into solution but remains on the catalyst surface.

Table 3 Aerobic oxidation of benzylic alcohols catalyzed by **Si-BOX-Pd**[a]

Entry	Alcohol	Alcohol/Catalyst	Yield (%)	TON[b]
1		480 000	79	370 000
2[c,d]		48 000	62	30 000
3[c]		24 000	6	1400
4[c]		24 000	0	0
5		480 000	24	110 000

[a] The reaction was carried out in 0.050 mmol scale at 110 °C in a screw-capped test tube. [b] Catalyst turnover number for aldehyde or ketone. [c] The reaction was carried out with a $25 \times 20 \times 0.6$ mm^3 of **Si-BOX-Pd** and 2.0 mL of octane under O_2 (balloon) atmosphere. [d] 0.10 mmol of alcohol was used.

Table 4 Recycle of **Si-BOX-Pd** in the catalytic aerobic oxidation of benzyl alcohol[a]

Run	Yield (%)	Catalyst TON
1st run	85	410 000
2nd run	85	410 000
3rd run	30	140 000
4th run	30	140 000
Total (four runs)	—	1 100 000

[a] The reaction was carried out in 0.050 mmol scale at 110 °C in a screw-capped test tube under the alcohol/catalyst ratio being 480 000.

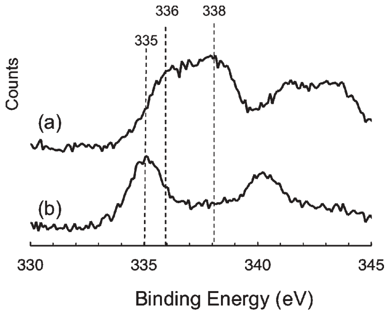


Fig. 1 XPS spectra of Pd 3d region of **Si-BOX-Pd** (a) before and (b) after the catalytic reaction. Another experiments showed that the peak at 338 eV in spectrum (a) shifted to the peak at 336 eV upon the prolonged acquisition time. See ESI† for details.

In the present system, extremely small amounts of a metal species, which was grafted onto a flat silicon chip surface, was shown to exhibit high catalytic efficiency. Detailed XPS analysis (Fig. 1) of a freshly prepared sample indicated that the Pd species on **Si-BOX-Pd** existed as Pd(II).[8] After the first run, however, the Pd species was found to be those of Pd(0), which may be mononuclear bisoxazoline–Pd species or could be equivalent to the recently reported nano-sized Pd clusters for supported systems on clays, organic polymers, *etc*.[6,9] Assuming the formation of such Pd clusters, and judging from the extent of the change in Pd intensity in XPS measurements, the size of the clusters can be estimated as less than 1.5 nm.[10] Further studies to gain insight into the mechanism of our highly efficient catalyst system are currently underway.

In summary, a single-crystal silicon surface was utilized to immobilize a bisoxazoline–Pd molecular layer. The modified surface exhibited exceptionally high turnover efficiency in the aerobic oxidation of some benzylic alcohols albeit with a narrow substrate scope. The catalytically active surface can be repeatedly utilized *via* a simple recycle process. Efforts aimed at further developing efficient catalytic systems based on the functionalization of silicon surfaces are ongoing in our laboratory.

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