# Palladium Nanoparticles Supported on Titanate Nanobelts for Solvent-Free Aerobic Oxidation of Alcohols

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The solvent-free selective oxidation of alcohols by  $O_2$  without any additives has been studied using palladium nanoparticles supported on a titanate nanobelt. The catalysts were prepared by polyol reduction and impregnation with different kinds of supports. They were evaluated in oxidation reactions of benzyl alcohol. The calcined titanate nanobelt was found to be the best support for the solvent-free Pd-catalyzed oxidation of alcohols and excellent catalytic activity as well as high selectivity to the corresponding benzaldehyde could be obtained. More-

Introduction

The oxidation of alcohols to the corresponding carbonyl compounds without forming over-oxidized or undesired products is of great importance in both laboratory and industrial applications. Traditionally, the transformation was carried out by using stoichiometric, toxic, and expensive oxidants such as permanganate, chromate, bromate, chromium, or peroxy acids. More recently, numerous transition-metal-based heterogeneous and homogenous catalysts have been widely developed in an aerobic or anaerobic oxidation manner.<sup>[1]</sup> However, there are still some drawbacks in these protocols. Employing a high concentration of oxidant, base additive, or organic solvent may lead to environmental problems. The harsh reaction conditions of high oxygen pressure and/or temperature can cause operational difficulty and security issues that hinder practical application. For an ideal oxidation process, the reaction should be performed under mild conditions using oxygen or air as the oxidant in the absence of any solvent or additives.

Over the past few decades, a wide variety of heterogeneous catalysts have been developed for aerobic oxidation of alco-

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over, palladium nanoparticles immobilized on the calcined titanate nanobelt could completely suppress the formation of toluene and benzoic acid, an effect that might be caused by the enhanced basic nature and morphology of the support. The catalyst was not only active and selective towards carbonyl compounds, but also recyclable under the oxidation conditions. This catalyst was also applicable for the oxidation of other alcohols.

hols in the absence of solvent.<sup>[2]</sup> Among the reported catalysts, palladium catalysts have attracted extensive interest owing to their excellent activity and selectivity. It is well known that the composition of the catalyst support plays a crucial role in the performance of the heterogeneous catalysis. Support selection and modification has been widely studied to show its great importance for alcohol oxidation. Mori reported hydroxyapatitesupported palladium nanoclusters,<sup>[3,4]</sup> which exhibited excellent activity in the solvent-free oxidation of 1-phenylethanol to give a high turnover number (TON) of up to 236000 with an excellent turnover frequency (TOF) of 9800 h<sup>-1</sup>. PdO/Al<sub>2</sub>O<sub>3</sub> prepared by wet impregnation<sup>[5]</sup> and Pd/Al<sub>2</sub>O<sub>3</sub> prepared by adsorption<sup>[6]</sup> both showed superior activity and selectivity towards solvent-free benzyl alcohol oxidation. Moreover, a remarkable TOF of 18800 h<sup>-1</sup> for 1-phenylethanol oxidation was achieved by zeolite-supported Pd nanoparticles with a mean diameter of 2.8 nm.<sup>[7]</sup> Mesoporous SBA-16,<sup>[8]</sup> surface-modified TUD-1,<sup>[9]</sup> and amorphous MnCeO<sub>x</sub><sup>[10]</sup> also showed extraordinary activity in Pd-catalyzed solvent-free benzyl alcohol oxidation reactions, with TOF values of 14438, 18571, and 7858 h<sup>-1</sup>, respectively. In addition to the above-mentioned catalyst supports, carbonaceous materials are also promising palladium nanoparticles carriers. Pd nanoparticles supported on graphene<sup>[11]</sup> and functionalized carbon nanotubes<sup>[12]</sup> showed excellent activities for solvent-free alcohol oxidation with TOF values of 30137 and 288755 h<sup>-1</sup>. Doping mesoporous carbon with nitrogen<sup>[13]</sup> or boron<sup>[14]</sup> both gave activity and selectivity improvement compared with the original carbonaceous materials. It was suggested that the surface acido-basicity of the supports played a crucial role.

Extensive research on TiO<sub>2</sub> materials has resulted in TiO<sub>2</sub>-derived one-dimension (1 D) nanostructures prepared by a hydrothermal alkali treatment attracting great attention since the pioneering work by Kasuga et al.<sup>[15,16]</sup> Among various potential



applications, efforts have also been made to employ these structures as supports for catalytic transformations. Mostly as a result of their high specific surface area and crystallinity, titanate nanotubes have been extensively used to immobilize metal nanoparticles for catalytic reactions such as benzyl alcohol oxidation,<sup>[17]</sup> reduction of NO,<sup>[18]</sup> phenol hydrogenation,<sup>[19]</sup> double-bond migration,<sup>[20]</sup> and tetralin hydrogenation.<sup>[21]</sup> Chang et al. investigated the morphology-dependent CO oxidation by titanate nanotubes, nanosheets, and their derived Pd catalysts.<sup>[22]</sup> The Pd-loaded sheet-like catalyst showed higher activity in spite of smaller specific surface area. TiO2nanobelt-supported noble metal catalysts for aerobic oxidation of alcohols has been largely explored;<sup>[23, 24]</sup> however, there are few reports about using titanate nanosheets or nanobelts as catalyst supports. For example, Shen et al. reported NO<sub>x</sub> storage and reduction over a potassium titanate nanobelt-based catalyst.<sup>[25]</sup> To the best of our knowledge, there are no reports about solvent-free alcohol oxidation with palladium nanoparticles immobilized on titanate nanobelts.

Herein, we report that titanate and  $\text{TiO}_2$  nanobelts hydrothermally produced in alkali solution can be loaded with Pd nanoparticles by polyol reduction. The catalytic performance for aerobic alcohol oxidation in the absence of solvent and additives was evaluated to show that titanate nanobelts are a highly efficient support for Pd-catalyzed solvent-free oxidation of various alcohols.

# **Results and Discussion**

Figure 1 shows the XRD patterns of the as-synthesized nanobelt support. Complete conversion of commercial TiO<sub>2</sub> to a layered titanate structure was observed with the typical strong diffraction peak around  $2\theta = 10^{\circ}$ , which indicated a interlayer distance of approximately 8.85 Å. The synthesized titanates could be assigned to mainly sodium trititanate (JCPDs No. 31-1329) with the general formula Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·nH<sub>2</sub>O with small admixtures of Na<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>(JCPDs No. 33-1294) and Na<sub>2</sub>Ti<sub>9</sub>O<sub>19</sub> (JCPDs No. 33-1293).<sup>[26,27]</sup> After calcination at 500 °C, the interlayer distance was shortened to approximately 7.24 Å with a diffraction peak at about  $2\theta = 12^{\circ}$ . This could be ascribed to the loss of



**Figure 1.** X-ray diffraction patterns of: a) commercial  $TiO_2$ , b) titanate nanobelts, and c) titanate nanobelt sample calcined at 500 °C.

intercalated water and partial conversion into hexatitanate.<sup>[28,29]</sup> Thermogravimetric analysis (TGA) of the titanate nanobelt (TNB) is also presented (see the Supporting Information, Figure S1). About 5.3% weight loss below 125 °C was seen, which could be caused by loss of physically adsorbed water. A further weight loss of about 6.2% between 125 and 400 °C could be attributed to the loss of interlayer and structural water, which was consistent with the XRD results. The morphology of the titanate nanobelt was discovered to be uniform, several micrometres in length, approximately 30–400 nm in width, and  $\approx$ 10 nm in thickness (Figure 2A). The morphology and structure



**Figure 2.** A) SEM and B) HR-TEM images of Pd nanoparticles deposited on calcined titanate nanobelts. C) EDX spectrum and D) size distribution profile of the catalyst.

ture were found to be well maintained after calcination (see the Supporting Information, Figure S2). The nitrogen adsorption–desorption analysis showed that the specific surface areas of the as-prepared titanate nanobelt and calcined sample were 13.6 and 15.3 m<sup>2</sup>g<sup>-1</sup>, respectively (see the Supporting Information, Figure S3).

Palladium nanoparticles could be easily deposited on the titanate nanobelts by the polyol reduction. However, no clear artifacts assignable to any palladium compounds were observed in the XRD pattern after the reduction. A mean size of 2.43 nm was observed in the high-resolution transmission electron microscopy (HR-TEM) image (Figure 2B,D). From the HR-TEM image, a lattice fringe of approximately 0.22 nm was clearly displayed, which is consistent with the (111) plane of palladium nanocrystals. The energy dispersive X-ray spectroscopy (EDX) pattern is shown in Figure 2C, which confirms the existence of Pd in the sample. Moreover, Na, Ti, and O signals were also found, which verifies the formation of the titanate nanostructure. This was further confirmed by the XPS survey spectrum (Supporting Information, Figure S4), which clearly showed the characteristic peaks of Na1s ( $\approx$ 1071 eV), O1s  $(\approx$  530 eV), Ti 2p ( $\approx$  458 and 464 eV), and Pd 3d ( $\approx$  337 and



342 eV). The deposited palladium species were investigated by XPS spectroscopy and found to be metallic Pd.

The catalytic activities of different Pd catalysts were evaluated in the solvent-free oxidation of benzyl alcohol and the results are listed in Table 1. All Pd catalysts exhibited excellent

<b>Table 1.</b> Catalytic effect of Pd catalysts on different supports in the solvent-free benzyl alcohol oxidation. <sup>[a]</sup>											
Entry	Catalyst <sup>[b]</sup>	Pd content [wt%]	Conv. <sup>[c]</sup> [%]	Selec Benzaldehyde	TOF <sup>[e]</sup> [h <sup>-1</sup> ]						
1	Pd/TiO <sub>2</sub> -NB	2.88	44.5	71.7	20.7	7.6	5563				
2	Pd/TNT	3.12	45.5	67.7	30.2	2.1	5688				
3	Pd/TNB-u	2.66	30.2	88.4	5.0	6.6	3775				
4	Pd/TNB	2.17	45.2	98.5	n.d. <sup>[f]</sup>	1.5	5650				
5	Pd/TNB-im	3.72	25.5	99.2	n.d.	0.8	3188				
6	PdO/TNB	3.53	27.7	96.8	n.d.	3.2	3463				
7	TNB	-	0.1	100	n.d.	n.d.	-				
8	no catalyst	-	8.3	81.9	n.d.	18.1	-				
[a] Reaction conditions: Renzyl alcohol (50 mmol) Pd $(4 \times 10^{-3} \text{ mmol})$ O											

[a] Reaction conditions: Benzyl alcohol (50 mmol), Pd ( $4 \times 10^{-3}$  mmol), O<sub>2</sub> (20 mLmin<sup>-1</sup>), 120 °C, 1 h. [b] Titanate nanobelts with or without calcination, and titanate nanotubes are denoted as TNB, TNB-u, and TNT, respectively. Pd/TNB-im represented calcined TNB-supported Pd catalyst by impregnation. [c] Determined by GC analysis. [d] Including benzyl benzoate and hydrobenzoin. Benzoic acid was not detected in the specified reaction time. [e] The turnover frequency was calculated by the moles of substrate converted per mole of Pd in the whole catalyst per hour. [f] Not detected.

activities towards oxidation of benzyl alcohol and benzaldehyde was revealed to be the main product. Pd supported on the TiO<sub>2</sub> nanobelt showed conversion of 44.5% and TOF of 5563 h<sup>-1</sup> at 120 °C for benzyl alcohol oxidation (Table 1, entry 1). However, the selectivity of benzaldehyde was rather low (71.7%), which was mainly due to the dehydrogenation reaction. Pd supported on titanate nanotube showed similar conversion and selectivity (45.5% and 67.7%, respectively; Table 1, entry 2). When the uncalcined titanate nanobelt precursor of the TiO<sub>2</sub> nanobelt was employed as the catalyst support, the oxidation of benzyl alcohol was reduced, but the selectivity for benzaldehyde improved and the amount of toluene as byproduct was inhibited from 20.7% to 5.0% (Table 1, entry 3). After calcination at 500 °C, high activity with a TOF value of 5650 h<sup>-1</sup>could be obtained over Pd/TNB catalyst (Table 1, entry 4). In addition, 98.5% benzaldehyde selectivity was achieved and the production of toluene was completely suppressed even after reaction for 5 h. It is well known that an alkaline environment is beneficial to achieve high selectivity in the oxidation of benzyl alcohol. For example, Au-Pd bimetallic catalysts supported on ZnO and MgO resulted in no formation of toluene.<sup>[30]</sup> The basic nature of the titanate nanobelts makes the catalyst particularly useful, especially compared with the extensive and more complicated efforts involving base addition<sup>[31-33]</sup> and support modification.<sup>[8-10,34]</sup> After full water removal by calcination, partial hydrolysis and Na<sup>+</sup> exchange in the titanate nanobelts could be completely inhibited to strengthen the basicity of the support. Based on these results Pd/TNB was shown to be the most active and selective catalyst of the as-prepared samples for benzyl alcohol oxidation. For comparison, Pd and PdO nanoparticles were immobilized on titanate nanobelts by impregnation and they both showed high benzaldehyde selectivity with no formation of toluene (Table 1, entries 5 and 6). However, the conversion of benzyl alcohol decreased significantly as a result of the larger metal particle sizes of about 5.04 nm (Figure S5 in the Supporting

Information).

Blank experiments were also carried out. Only 8.3% conversion, with 81.9% benzylaldehyde selectivity, was achieved in the absence of any catalyst (Table 1, entry 8). The main byproducts were benzyl benzoate and hydrobenzoin. When only the titanate nanobelts were added, the conversion was very slow but benzaldehyde was found to be the sole product (Table 1, entry 7). Even if reacted for 16 h, the conversion was still as low as 0.3%. This phenomenon has also been observed with porous carbon supports.<sup>[13]</sup> It indicated that without the Pd active phase, the titanate support showed a similar negative effect on the oxidation of benzyl alcohol, which might be caused by the enhanced oxygen adsorption on the supports and limited oxygen diffusion in the solution.

A recycling study was also carried out with Pd/ TNB. After each reaction the catalyst was easily recovered by centrifugation and used again directly. In this case, the conversion of benzyl alcohol was 45.2, 40.3, and 36.8% for the three cycles with a reaction time

of 1 h each, conversion values that indicated that the catalyst remained active under the reaction conditions. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis of the reaction solution revealed that 5.4% Pd content was leached each cycle. Moreover, the tendency of Pd nanoparticles to grow larger was also observed in the TEM image of recovered catalyst (Figure S6 in the Supporting Information).

The temperature effect on the solvent-free oxidation of benzyl alcohol with Pd/TNB catalyst was also examined. Figure 3 shows the time-dependent conversion, selectivity, and TOF of the reaction at different temperatures (100, 120, 140, and 160 °C). Both conversion and TOF were expected to increase with elevated reaction temperature. In spite of the higher catalytic activity at higher temperature, the selectivity for the corresponding benzaldehyde was found to be worse. For example, selectivity dramatically dropped to about 85% with a conversion of more than 90% at 140 or  $160^{\circ}$ C. However, when the reaction was performed at 120°C, greater than 95% selectivity was observed throughout the oxidation process. After 5 h, a selectivity of 95.6% was achieved with an alcohol conversion of about 92.8%. Notably, benzoic acid was not detected at any point during the required reaction time at any of the tested temperatures. This suggested that titanate nanobelt could suppress the over-oxidation of benzyl alcohol. The origin of this phenomenon is still under investigation.

Several aromatic alcohols were selected to be tested in the catalysis and the results are listed in Table 2. All the alcohols could be oxidized to their corresponding carbonyl compounds smoothly in the absence of any solvent and additive under an atmosphere of oxygen. However, the catalytic activity differed



Figure 3. Time-dependent catalytic activity at different temperature: squares, 100 °C; circles, 120 °C; triangles, 140 °C; diamonds, 160 °C.

depending on the type and position of the substituent. Generally, aromatic alcohols bearing an electron-donating group exhibited higher activity than those with an electron-withdrawing group. p-Methylbenzyl alcohol and p-methoxylbenzyl alcohol presented high activity with initial TOF values of 10550 and 7700 h<sup>-1</sup>, respectively, and both could be oxidized to their corresponding aldehydes with good conversion after a short period of reaction (Table 2, entries 2 and 3). However, the Pd catalyst showed very poor catalytic activity in the oxidation of p-nitrobenzyl alcohol even after 20 h at 140 °C (Table 2, entry 6). As can be seen from Table 2, m-methoxylbenzyl alcohol exhibited almost the same catalytic activity as *p*-methoxylbenzyl alcohol (Table 2, entry 4). However, significant activity decrease was observed in the oxidation of o-methoxylbenzyl alcohol (Table 2, entry 5). It is thought that the oxidation pathway might undergo a chemisorption of alcohol on the metalsupport surface. Hence, increasing steric hindrance might hinder the interaction of reactant with the active sites.

<b>Table 2.</b> Catalytic performance of various alcohols over Pd catalyst with molecular $O_{2^{\text{[a]}}}$										
	ОН 	ł	Pd/TNE		0					
	$R^1 R^2$	1:	20 °C, (	$O_2$	$R^1 R^2$					
Entry	R <sup>1</sup>	R <sup>2</sup>	<i>T</i> [b]	Conv. [%]	Selectivity	TOF				
			[11]	[/0]	[,0]	[11]				
1	Ph	н	0.5	24.2	99.6	6050				
•			5	92.8	95.6	2320				
2	4-MePh	Н	0.5	42.2	98.3	10550				
			6	82.6	93.5	1721				
3	4-MeOPh	н	0.5	30.8	90.9	//00				
			6	/3.6	94.2	1533				
4	3-MeOPh	Н	0.5	25.9	86.5	64/5				
			24	83.5	77.4	435				
5	2-MeOPh	Н	0.5	2.9	82.8	/25				
			24	31.1	47.6	162				
6 <sup>[b]</sup>	4-NO₂Ph	Н	0.5	2.4	100	600				
			20	9.9	/5.8	02 2775				
7	PhCH=CH	Н	0.5	100	87.8	2002				
			0	100	84.1 100	2083				
8	Ph	Me	0.5	40.5	100	1040				
		Me	05	00.4 17.9	100	22,000				
9 <sup>[c]</sup>	Ph		6	100	100	23 900 4167				
[a] Reaction conditions: Aromatic alcohol (50 mmol), Pd (4×10 <sup>-3</sup> mmol), O <sub>2</sub> (20 mLmin <sup>-1</sup> ), 120 °C. Conversion and selectivity was determined by GC analysis. [b] 140 °C. [c] 160 °C, Pd (2×10 <sup>-3</sup> mmol).										

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The catalyst was also effective for the solvent-free oxidation of cinnamyl alcohol (Table 2, entry 7). The conversion reached 15.1% with an initial TOF value of 3775 h<sup>-1</sup> after half an hour and complete conversion with selectivity of 84.1% could be obtained after 6 h. The main byproduct was found to be benzal-dehyde, with a selectivity of 10.2%. Enhanced catalytic activity was also observed in the oxidation of 1-phenylethanol. Quantitative transformation to acetophenone was observed after 6 h at 160 °C with a high initial TOF value of 23 900 h<sup>-1</sup> (Table 2, entry 9).

# Conclusions

We have demonstrated that palladium nanoparticles immobilized on titanate nanobelts are highly efficient nanocatalysts in the solvent-free oxidation of various alcohols. The polyol reduction resulted in small nanoparticles with a size of 2.4 nm, which led to good catalytic performance. The selectivity could be greatly strengthened by removal of water from the titanate nanobelts. The enhanced basic nature and morphology of the support are probably responsible for this effect. Titanate nanobelts act as a superior support for Pd-catalyzed alcohol oxidation compared with other TiO<sub>2</sub> derivatives.

## **Experimental Section**

## Characterization

X-Ray powder diffraction patterns (XRD) of the products were obtained on a Japan Rigaku DMax- $\gamma$ A rotation anode X-ray diffrac-

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tometer equipped with graphite-monochromated CuKR radiation ( $\lambda = 1.54178$  Å). X-Ray photoelectron spectroscopy (XPS) was conducted on an ESCALab MKII X-ray photo electron spectrometer using MgK<sub>a</sub> radiation exciting source. Scanning electron microscope (SEM) measurements were performed using a Zeiss Supra 40 microscope. Transmission electron microscope (TEM) photographs were taken on a Hitachi model H-800 transmission electron microscope at an accelerating voltage of 200 kV. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was recorded using an Atomscan Advantage (Thermo Jarrell Ash Corporation, U.S.A.) instrument. TGA was measured on Q500IR. Nitrogen physisorption isotherms were measured at -196 °C on Tristar II 3020m. Prior to each measurement, the sample was degassed at 250 °C for 12 h under high vacuum. The specific surface area was calculated by the Brunauer–Emmett–Teller method.

## Preparation of the catalysts

Titanate and TiO<sub>2</sub> nanobelts were synthesized as reported in the literature<sup>[35,36]</sup> with slight modification. Typically, commercially available TiO<sub>2</sub> powder (mainly anatase, 1 g) was suspended in NaOH aqueous solution (50 mL, 10 M) and stirred for 30 min. Then, the resulted milky solution was transferred to a Teflon-lined stainless steel autoclave with a volume of 80 mL. The autoclave was sealed and subsequently heated at 200°C for 24 h. After cooling to room temperature, the slurry was centrifuged and washed thoroughly with deionized water. The titanate nanobelts were obtained by drying the collected precipitate at 60°C and calcination in air at 500°C for 3 h. The as-synthesized uncalcined and calcined titanate nanobelt supports are designated as TNB-u and TNB, respectively. For comparison, the TiO<sub>2</sub> nanobelts were prepared by further suspending in HCl (0.1 M) overnight followed by drying and calcination at 700°C. This support was denoted as TiO<sub>2</sub>-NB.

Pd nanoparticles were immobilized on these supports by a simple polyol reduction. The nanobelt supports (0.2 g) were immersed in ethylene glycol (30 mL) and stirred at 110 °C in an oil bath for 30 min. Then, ethylene glycol solution (6 mL) containing Na<sub>2</sub>PdCl<sub>4</sub> (18.0 mg) was added dropwise. The solution was further heated for another 4 h. After cooling to room temperature the products were centrifuged (10000 rpm, 5 min), washed several times with deionized water and ethanol, and dried 60 °C.

## Catalytic alcohol oxidation

The selective alcohol oxidation over supported Pd catalysts in the absence of solvent was performed under atmospheric conditions. Typically, a 25 mL three-necked glass flask was precharged with the catalyst sample (20 mg) and benzyl alcohol (50 mmol) and fitted with a reflux condenser. The mixture was heated and stirred vigorously (800 rpm) at 120 °C in an oil bath with a continuous oxygen stream bubbled in at a flow-rate of 20 mLmin<sup>-1</sup>. After the desired reaction time, the catalyst sample was removed by centrifugation and the organic products were analyzed by gas chromatography (Agilent 7890A series) equipped with a FID detector and a HP-5 column (30 mm×0.32 mm×0.25  $\mu$ m). The structure of the product was confirmed by comparison with a standard sample and by GC-MS (Agilent GC-MS 6890/5973).

## **Recycling study**

After the reaction period was over, the reaction mixture was cooled to room temperature and centrifuged. The solid catalyst

was collected and fresh reactant was added. To analyze Pd leaching during the reaction, the mixed solvent of centrifugate was evaporated under reduced pressure and the residue was dissolved in aqua regia (conc. HCI:conc. HNO<sub>3</sub>=3:1, v/v) and H<sub>2</sub>O. This solution was then analyzed by ICP-AES.

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