# Influence of Periodic Nitrogen Functionality on the Selective Oxidation of Alcohols

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**Abstract:** An enhancement in catalytic alcohol oxidation activity is attributed to the presence of nitrogen heteroatoms on the external surface of a support material. The same Pd particles (3.1–3.2 nm) were supported on polymeric carbon–nitrogen supports and used as catalysts to selectively oxidize benzyl alcohol. The polymeric carbon–nitrogen materials include covalent tri-

azine frameworks (CTF) and carbon nitride ( $C_3N_4$ ) materials with nitrogen content varying from 9 to 58 atomic percent. With comparable metal exposure, estimated by X-ray photoelectron

**Keywords:** alcohols • nanoparticles • nitrogen functionalities • oxidation • palladium

### Introduction

Selective oxidation of alcohols with oxygen by using supported metal nanoparticles (NPs) represents a well-studied reaction because of its wide application in chemical transformations. However, up to now, scaling up a reaction that occurs in a condensed liquid phase has been rather limited and low reaction rates are usually obtained. The low rates are attributed to 1) low reaction temperatures, 2) the use of solvent(s), 3) diffusion limitations, or 4) catalyst deactivation. Catalyst deactivation is mainly due to metal leaching, sintering, overoxidation, or irreversible adsorptions.<sup>[1]</sup> The activity/selectivity of the catalyst is a function of several variables; among those variables, the role of the support has not yet been fully clarified.<sup>[2,3]</sup> A direct comparison of the various catalytic performances reported in the literature is difficult due to the different reaction conditions and materials.

The introduction of heteroatoms into supports can be beneficial for the catalytic activity of metal nanoparticles.

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spectroscopy, the activity of these catalysts correlates with the concentration of nitrogen species on the surface. Because the catalysts showed comparable acidic/basic properties, this enhancement cannot be ascribed to the Lewis basicity but most probably to the nature of N-containing groups that govern the adsorption sites of the Pd nanoparticles.

For example, the introduction of N functionalities onto the external surfaces of carbon nanotubes resulted in a 20% enhancement in the catalytic activity of Pd-supported nanoparticles (Pd NPs) relative to an unmodified surface.<sup>[4]</sup> In addition, covalent triazine framework (CTF) materials derived from aromatic nitriles with a high concentration of nitrogen functionalities<sup>[5-10]</sup> were also demonstrated to be a promising support for the liquid-phase oxidation of glycerol and benzyl alcohol.<sup>[11,12]</sup> Palladium-supported CTFs are indeed more active than activated carbon-based catalysts that do not contain any nitrogen functionalities (time of flight (TOF) of 4917  $h^{-1}$  versus 2678  $h^{-1}$  for Pd/CTF and Pd/AC, respectively, in benzyl alcohol oxidation).<sup>[12]</sup> The improved catalytic performance is attributed to a general positive effect of N species in the support. In this paper, we specifically ascribe the enhanced catalytic activity to the presence of N-containing groups and to their ability to differently adsorb the Pd NPs. Benzyl alcohol oxidation was used as a test reaction for three different Pd catalysts that differed in the number of nitrogen atoms and the chemical nature of the N functionalities borne by the support. CTF supports were obtained by a dynamic reorganization of porous polymer networks by using either para-dicyanobenzene  $(CTF_{DCB})$  or 2,6-dicyanopyridine  $(CTF_{DCP})$  as the monomer.<sup>[5,7]</sup> The third support was a carbon nitride prepared by the thermal polymerization of cyanamide in which the amount of nitrogen incorporated was the highest stoichiometrically possible (58%).<sup>[13]</sup>

### **Results and Discussion**

Elemental analysis and surface area data for the support materials are summarized in Table 1.

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Table 1.	Characterization of	the different	CTF and	$C_3N_4$	supports	by nitroger	sorption
measure	ments, combustion e	lemental ana	lysis, and	XPS.			

	Monomer	Monomer/ ZnCl <sub>2</sub>	Surface area $[m^2g^{-1}]$	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	XPS	Elemental analysis [wt %]		
					% N <sup>[a]</sup>	С	N	Н
CTF <sub>DCB</sub> C <sub>3</sub> N <sub>4</sub> CTF <sub>DCB</sub>	DCB cyanamide DCP	1:5	2814 10 1738	1.79 <sup>[b]</sup>	8 55 14	73 33 64	9 58 18	1 2 1

[a] Atomic % based on C/N/H. [b] Under detection limit.

Figure 1 reports the pore-size distribution of the two CTF supports estimated by the nonlocal density functional theory (NLDFT) method. The samples have both micro- and meso-



Figure 1. NLDFT pore-size distribution for the samples  $\mathrm{CTF}_{\mathrm{DCB}}$  and  $\mathrm{CTF}_{\mathrm{DCP}}$ 

pores with pore diameters less than 5.5 nm for  $\text{CTF}_{\text{DCB}}$  and 4 nm for  $\text{CTF}_{\text{DCP}}$  as shown in earlier studies.<sup>[6,8]</sup> The surface area of  $\text{CTF}_{\text{DCB}}$  is higher (2814 m<sup>2</sup>g<sup>-1</sup>) than that of  $\text{CTF}_{\text{DCP}}$  (1738 m<sup>2</sup>g<sup>-1</sup>). C<sub>3</sub>N<sub>4</sub> has a very low surface area (10 m<sup>2</sup>g<sup>-1</sup>) with nontextured pores. In this latter case, we expected that the lack of porosity would confine the Pd particles to the external surface of the support and avoid diffusion limitations.

The N1s and C1s X-ray photoelectron spectroscopy (XPS) data are shown in Figures 2 and 3, respectively, for



Figure 2. XPS measurements on the three catalysts (N1s XPS data).

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the native support material. Analysis of the C1s XPS data for the CTF<sub>DCB</sub> and CTF<sub>DCP</sub> support materials showed the presence of a high concentration of C-C and C-H species (≈284.8 eV) and smaller concentrations of C–O ( $\approx$ 286.5 eV); C=O and C– N (-288.3 eV); and C=C species ( $\approx$ 290.8 eV). Similar analysis of the C1s data obtained for C3N4 showed a high concentration of C-N moieties (288.0 eV) with a much smaller concentration of C-C and C-H species ( $\approx 4\%$  at 284.8 eV). N1s data collected for the support materials showed the presence of C<sub>2</sub>NH ( $\approx$ 398.3 eV), C<sub>3</sub>N ( $\approx$ 400.1 eV), and NH (402 eV) species on the surface of the support materials. Analysis of the relative fraction of C<sub>3</sub>N and C<sub>2</sub>NH species showed an increase in C<sub>2</sub>NH species on the surface of the  $C_3N_4$  material, which is consistent with a higher concentration of the species based on the molecular structure with cross-linked tri-s-triazine units.

Comparison of carbon and nitrogen elemental analysis data with surface concentrations estimated by XPS were in excellent agreement (less than 6% difference) with the exception of the surface carbon content measured for CTF<sub>DCP</sub> which showed an increase in the concentration of carbon. Elemental analysis clearly shows an increase in N concentration that is consistent with the addition of pyridine to the cyanobenzene building block for the CTF<sub>DCB</sub> and CTF<sub>DCP</sub> support materials (9 and 18%, respectively). The N content in the  $C_3N_4$  was determined to be 58 atomic percent (Table 1). The N content determined by XPS in the case of C<sub>3</sub>N<sub>4</sub> is consistent with theoretically predicted N concentrations in this compound (C/N 42:57%); however, bulk N/C ratios were lower due to total oxygen content. Analysis of O1s XPS data showed that the surface of the  $C_3N_4$  contained a small concentration of O (1.5 at %, primarily in C-O moieties at 532 eV).<sup>[14]</sup> The CTF<sub>DCB</sub> and CTF<sub>DCP</sub> supports had much higher concentrations of surface oxygen (11 and 8%, respectively) primarily due to C-O (532 eV) and C=O spe-

cies (530.7 eV) for the  $\text{CTF}_{\text{DCP}}$  support. However, studies on unwashed, freshly prepared  $\text{CTF}_{\text{DCB}}$  (i.e., which still contained  $\text{Zn}^{2+}$  catalyst) had low oxygen content (<1.2%), thus indicating that the addition of oxygen to these support materials occurs during storage in air or the removal of zinc.

TEM data collected for all the as-prepared Pd-loaded support materials (Figure 4a (Pd/  $CTF_{DCP}$ ) and Figure 4b (Pd/  $C_3N_4$ )) reveal the homogeneous distribution of Pd particles on the support surfaces with the same average particle sizes and deviations (3.09–3.18 nm). This particle size is slightly larger



Figure 3. XPS measurements on the three catalysts (C1s XPS data).



Figure 4. TEM image of a) Pd/CTF<sub>DCP</sub> and b) Pd/C<sub>3</sub>N<sub>4</sub>.

than the size of the unsupported Pd particles (2.81 nm), which indicates a slight coarsening during the immobilization on the support material (Table 3). The large concentration of Pd NPs on  $C_3N_4$  is because of its low surface area and same total Pd concentration versus the other catalysts. Due to the low surface area and variation in support morphology, which will affect the fraction of material sampled in the TEM, there is an apparent higher areal concentration of Pd nanoparticles. Pd XPS data collected on the catalysts revealed the presence of similar concentrations of Pd<sup>2+</sup> (24–

Table 2. Atomic % and Pd oxidation state data as determined by XPS.

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35%) and Pd<sup>0</sup> on each sample (Figure 5, Table 2). On Pd/C<sub>3</sub>N<sub>4</sub> and Pd/CTF<sub>DCB</sub> PdO was also detected in the O1s spectra. These species are likely generated by exposure of the metal to air and often occur in Pd catalysts that progressively deactivate (O<sub>2</sub> poisoning effect). However, in the catalytic tests we did not observe any deactivation.

Despite the similar Pd particle sizes and oxidation states, significant differences in catalytic activity were observed for the oxidation of benzyl alcohol over the three catalysts (Table 4).  $Pd/C_3N_4$  is more

Table 3. Median size of Pd nanoparticles immobilized on different supports before reaction.

	Statistical median [nm]	Standard deviation [nm]
Pd NPs	2.81	0.5
Pd/CTF <sub>DCB</sub>	3.18	0.6
Pd/C <sub>3</sub> N <sub>4</sub>	3.16	1.1
Pd/CTF <sub>DCP</sub>	3.09	0.9

active than Pd/CTF<sub>DCB</sub> which is more active than Pd/ CTF<sub>DCB</sub> (converted mol (molPd)<sup>-1</sup>h<sup>-1</sup>=14131, 8025, and 4917 h<sup>-1</sup>, respectively). Blank experiments using bare supports showed total inactivity, thereby proving the compulsory need of Pd for catalysis. It should be noted that  $C_3N_4$  has been recently reported to be an active metal-free catalyst under UV-assisted conditions for benzyl alcohol oxidation;<sup>[15]</sup> however, since we are not using a UV source, this should not be an issue.

It is known that microporosity could limit the activity of metal NPs in liquid-phase oxidation.<sup>[16,17]</sup> Therefore a comparison of the catalyst activities was carried out by using XPS and surface-area data, which provided a direct measurement of exposed active metal-site accessibility. This ena-

Sample	Atomic %	Binding energy [eV] (fraction Pd [%])				
		Pd–O	$Pd^0$	Pd <sup>2+</sup>		
CTF <sub>DCB</sub>	C 72.1, N 16.5, O 11.4	_	_	_		
Pd/CTF <sub>DCB</sub>	C 63.8, N 7.0, O 26.2	-	335.25	337.37		
	Pd 3.0	-	(64.8)	(35.2)		
CTF <sub>DCP</sub>	C 77.8, N 13.8, O 8.4	-	_	_		
Pd/CTF <sub>DCP</sub>	C 41.1, N 29.6, O 22.2	537.90	335.56	337.90		
	Pd 7.1	(7.3)	(76.4)	(23.6)		
$C_3N_4$	C 41.6, N 56.9, O 1.5	_	_	_		
Pd/C <sub>3</sub> N <sub>4</sub>	C 38.8, N 27.8, O 26.3	537.80	335.18	337.20		
	Pd 7.1	(7.9)	(65)	(35)		

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Figure 5. Pd XPS data collected on the catalysts; concentrations of  $Pd^{2+}$  (24–35%) and  $Pd^{0}$  on each sample

Catalyst <sup>[a]</sup>	Converted mol $(mol Pd)^{-1}h^{-1}$	Selectivity <sup>[b]</sup>					
		Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Unknown	
Pd/ CTF <sub>DCB</sub>	4917	31	66	1	1	1	
Pd/C <sub>3</sub> N <sub>4</sub>	14131	35	62	0.5	2	0.5	
Pd/ CTF <sub>DCP</sub>	8025	26	71	1.5	1	0.5	

[a] Reaction conditions. Alcohol/metal: 5000, T=80 °C,  $pO_2=2$  atm, benzyl alcohol/cyclohexane ratio 50:50. [b] Selectivity calculated at 90% conversion as mol of products (mol converted)<sup>-1</sup>×100.

bled us to identify trends on materials with different surface areas and structures.

XPS elemental analysis data reveals that the nanometers at the top of the C<sub>3</sub>N<sub>4</sub> and CTF<sub>DCP</sub> support material contain the same concentration of Pd (7.1%; Table 2). By considering the similar Pd particle sizes, weight loading, and nonporosity of C<sub>3</sub>N<sub>4</sub>, we can estimate that all of the Pd of the CTF<sub>DCP</sub> support materials are located on the external surface in an eggshell-like configuration. This location of Pd on the external surface of the CTF<sub>DCP</sub> material is consistent with the small pore size of the  $\text{CTF}_{\text{DCP}}$  material estimated by  $N_2$  physisorption (Figure 1), which would be too small for the 3.1-3.2 nm Pd particles to condense into, particularly if one considers the remaining polyvinyl alcohol (PVA) on the Pd particles, evidenced by the XPS data (described below), which probably enlarged their effective diameters. On the contrary, the Pd concentration determined on CTF<sub>DCB</sub> showed a much lower Pd content (3%) than the  $CTF_{DCP}$ and C<sub>3</sub>N<sub>4</sub>-based materials (Table 2). This reduction in Pd trapped on the top nanometer of support material is probably due to the larger pore diameters (Figure 1) that are large enough to trap 3 nm-sized Pd particles from the external surface of the support and therefore not sampled by XPS.

Therefore, a realistic comparison of the catalytic activity could be made only between Pd on  $C_3N_4$  and  $CTF_{DCB}$  which presented the same Pd particle size and the same Pd exposure. Due to the similar concentration and the similar size of Pd particles on the external surface of the support material, we can assume that all the catalytic reactions in the liquid phase of the Pd/CTF<sub>DCP</sub> and Pd/C<sub>3</sub>N<sub>4</sub> catalysts are occurring on the external surface of the support materials. Furthermore, we can assume that the large micropore volume of the Pd/CTF<sub>DCP</sub> catalyst will be inconsequential toward the diffusion of reactants under reaction conditions. This is due to the large difference in reactant volume (30 mL) versus pore volume of the catalyst (1.05 mLg<sup>-1</sup>, 0.0985 g catalyst) used in the reaction, which means most of the reactants are flowing around the outside of the support where the Pd clusters are located. Therefore the difference in surface area between the two supports did not play a significant role. However, the large difference in activity between Pd/ CTF<sub>DCP</sub> and Pd/C<sub>3</sub>N<sub>4</sub> indicates that other factors are influ-

> encing catalytic activity. To exclude factors related to Pd exposure mediated by residual PVA, we performed TGA measurements. PVA decomposes in a temperature range between 300 and 350 °C. In the same range, Pd/CTF<sub>DCP</sub> and Pd/C<sub>3</sub>N<sub>4</sub> lose 0.15 and 0.18 wt%, respectively, thus indicating that a comparable and rather low amount of PVA (about 10 wt% of the total employed) is still present on the catalysts. Thus the possible shielding of the Pd particles by residual PVA should be similar in both cases. The TGA, however, did not provide any information about the location of the PVA. As the catalytic tests are performed in the presence of a

solvent, which can play an important role in reaction kinetics, we evaluated the active surface of Pd by chemisorption. The samples were treated with  $H_2$ , purged with He, and then dosed with  $O_2$ .  $O_2$  was chemisorbed in a similar range (0.45–0.43 mol  $O_2$  per mol Pd) in both cases. These experiments definitely demonstrated that Pd NPs on  $CTF_{DCP}$  and  $C_3N_4$  presented a similar Pd exposure, thus confirming the findings of XPS measurements above.

Based on the logic described above, the result strongly indicates that nitrogen surface chemistry of the catalytic support mediates catalytic activity. In fact, the increase in catalytic activity closely parallels the increase in N content measured by XPS and elemental analysis (Figure 6). This trend is further confirmed by comparison of the activity of similarly sized Pd particles (4.0 nm) supported on nitrogen-free activated carbon (converted mol (mol Pd)<sup>-1</sup>h<sup>-1</sup>=2678 h<sup>-1</sup>).<sup>[12]</sup>



Figure 6. Activity of the catalyst as a function of the nitrogen concentration.  $^{\left[ 12\right] }$ 

Recent theoretical calculations by Zope et al. have shown that the support can play an active role in liquid-phase alcohol oxidation to improve the formation of alcoholate by means of O-H scission.<sup>[18]</sup> Thus, a possible explanation of the correlation between the N content and the activity could involve the basic properties of N-containing groups. However, the two catalysts showed only a slight difference in the generated pH (5.45 for  $\text{CTF}_{\text{DCP}}$  and 6.0 for  $C_3N_4$ ), thus highlighting a very low basicity. This finding was confirmed by a negligible amount of adsorbed CO<sub>2</sub> revealed by attenuated total reflectance (ATR)-IR measurements. The low difference in the basicity of the two catalysts could also explain the negligible difference in terms of selectivity to benzaldehyde found (Table 4). In fact, it should be expected that an increase in basicity would increase the overoxidation to benzoic acid.

As shown in Table 4, in all cases the main byproduct of the reaction was toluene. Toluene has been shown to derive from a disproportionation pathway beside the oxidation pathway that produces benzaldehyde.<sup>[19,20]</sup> It has also been reported that the support and the reaction media can play an important role in the ratio of products between the two different pathways. However, in the present cases we observed very small differences in the selectivity of all the catalysts toward toluene. Therefore, because the tests were carried out in the same solvent, we were able to conclude that in the present case a negligible influence of the support is present in determining the preferential reaction pathway.

Moreover, O1s and C1s XPS data collected for the samples show an increase in C–O species due to the alcohol on the PVA (Table 5). The surface PVA reduces the surface concentrations of C and N significantly due to blocking of these species. Indeed, after deposition of Pd–PVA NPs, we detected by XPS almost the same C/N/O distribution (41:30:22 for Pd/CTF<sub>DCP</sub> and 39:28:26 for Pd/C<sub>3</sub>N<sub>4</sub>; Table 2). Furthermore, after the deposition of Pd NPs, the generated pH decreased (4.27 for CTF<sub>DCP</sub> and 5.35 for C<sub>3</sub>N<sub>4</sub>). Therefore the huge difference in the catalytic activity between Pd/CTF<sub>DCP</sub> and Pd/C<sub>3</sub>N<sub>4</sub> cannot merely be ascribed to the considerable amount of nitrogen heteroatoms, but most probably also to the nature of N-containing groups.

An indication of the impact of nitrogen-containing groups has been revealed by studying the changes in the nitrogen functionality of the catalyst compared to the original support material by means of XPS (Table 5). For both  $CTF_{DCP}$ and  $C_3N_4$  support materials, there is a decrease in  $C_3N$  functionality with the addition of Pd. This strongly indicates that the Pd associates with these sites. This point can be also supported by looking at XPS results for the less active catalyst,  $CTF_{DCB}$ . In that case, there is an increase in N–H and  $C_2NH$ functionality, thus indicating that during the liquid-phase

Table 5. Summary of binding energies [eV] and moiety fraction [%] data as determined by XPS.

Sample				C 1s			
	С–С,		С-О	C–N,	C	`=C	C+
	C-H			C=O	л	ι—π	C=N
CTF <sub>DCB</sub> [eV]	284.78	2	86.47	288.47	29	1.22	_
[%]	66.0		19.7	8.3	(	5.0	_
Pd/CTF <sub>DCB</sub> [eV]	284.89	2	86.56	288.52	29	1.18	_
[%]	60.1		24.6	10.0	-	5.3	_
CTF <sub>DCP</sub>	284.66	2	86.18	288.10	29	0.65	292.94
[%]	61.3		19.1	12.0	1	5.6	2.0
Pd/CTF <sub>DCP</sub> [eV]	284.78	2	86.95	288.40		-	-
[%]	26.7		36.3	37.0		-	-
$C_3N_4$ [eV]	284.80		-	288.00		-	293.36
[%]	4.3		-	93.0		-	2.7
$Pd/C_3N_4$ [eV]	284.84		-	288.00		-	293.36
[%]	33.7		-	64.8		-	1.5
Sample		N	1s			O1s	
	$C_2NH$	$C_3N$	NH	$NO_x$	C=O	С–О	O=N
CTF <sub>DCB</sub> [eV]	398.41	400.16	402.71	-	-	532.0	
[%]	44.4	49.7	5.9	-	-	100	
Pd/CTF <sub>DCB</sub> [eV]	398.50	400.15	402.71	-	-	532.43	535.51
[%]	27.9	56.2	15.9	-	-	88.7	11.3
CTF <sub>DCP</sub>	398.17	399.99	401.82	404.71	530.51	532.33	535.85
[%]	44.3	41.5	10.3	3.9	39.5	54.0	6.5
Pd/CTF <sub>DCP</sub> [eV]	398.42	400.92	-	404.49	530.99	532.60	535.22
[%]	88.4	9.9	-	1.7	23.9	58.5	10.3
$C_3N_4$ [eV]	398.58	400.61	-	404.11	-	531.45	
[%]	78	18.4	-	3.6	-	100	
$Pd/C_3N_4$ [eV]	398.69	400.78	-	404.60	-	531.8	533.80
[%]	92.5	6.4	-	1.1	-	67.0	25.1

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synthesis some of the  $C_3N$  sites are hydrolyzed to make active sites with which the Pd can associate. In addition, by comparing C/N/O distribution before and after Pd deposition, we noted that in the case of  $CTF_{DCP}$  there was an increase in N (from 14 to 30%), whereas in the case of  $C_3N_4$ there was a decrease (from 57 to 28%). This could mean that in the case of  $C_3N_4$ , the N sites bound Pd NPs, thereby preventing the migration of Pd over the  $C_3N$  sites. Thus an important difference between Pd/CTF<sub>DCP</sub> and Pd/C<sub>3</sub>N<sub>4</sub> is the adsorption site of the Pd NPs that could heavily modify the electronic structure of Pd NPs.

### Conclusion

We have demonstrated the effect of nitrogen heteroatoms on the catalytic liquid-phase oxidation of alcohols. As a base level catalytic activity, we took one of the Pd particles grown on carbon supports without nitrogen heteroatoms. Similarly sized Pd particles on carbon-based supports in which nitrogen heteroatoms are incorporated show an increase in activity (up to converted mol  $(mol Pd)^{-1}h^{-1} =$ 14131  $h^{-1}$  with 57% nitrogen). This increase in activity varies linearly with nitrogen content of the support. The accepted mechanism of the reaction could correlate the improved catalytic activity to the enhanced basicity of the support. However, the basic properties of Pd on CTF<sub>DCP</sub> and C<sub>3</sub>N<sub>4</sub> were comparable. A determining factor appeared to be the Pd coordination site: the most active catalyst seemed to be the one in which a more relevant coordination of Pd on N groups was revealed. This in turn led to a linear correspondence of the increased catalytic activity with the amount of N groups. Such a correlation with nitrogen and activity introduces a new way to tune the activity of supported metal particles through the introduction of molecules that contain nitrogen functionality.

#### **Experimental Section**

CTFs were synthesized as reported elsewhere.<sup>[11]</sup> Carbon nitride (C<sub>3</sub>N<sub>4</sub>) powder was prepared by the thermal polymerization of cyanamide (99%, Aldrich) at 550°C in an alumina crucible for 4 h in air according to the procedure reported elsewhere.<sup>[13,21-23]</sup> After preparation, the  $C_3N_4$  was yellow and showed a graphite-like structure ( $2\theta = 13.3$  and  $27.5^{\circ}$ ) with an interplanar spacing of approximately 0.33 nm. The average grain size was estimated to be 7 nm (Debye-Sherrer equation).<sup>[24]</sup> Palladium nanoparticles were deposited onto the C-N polymeric supports through the sol immobilization technique generated by NaBH4 reduction of Na2[PdCl4] salt in the presence of a protective agent (polyvinyl alcohol, PVA).<sup>[25]</sup> The three catalysts prepared in this study are labeled Pd/CTF<sub>DCB</sub>, Pd/CTF<sub>DCP</sub>, and Pd/C3N4. The total Pd loading was 1 wt %. Inductively coupled plasma (ICP) analyses were performed with a Jobin Yvon JV24 instrument to verify the quantitative metal loading on the support by checking the residual metal in the filtrate. Carbon, hydrogen, and nitrogen analysis for CTF support was performed with a Vario Micro setup. Carbon, hydrogen, and nitrogen analysis for C3N4 was performed by Gailbrath Laboratories, Knoxville, Tennessee, USA.

The reactions were carried out in a thermostatted glass reactor (30 mL) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 mL) that contained oxygen at 2 atm. The oxygen

uptake was followed by a mass flow controller connected to a PC through an A/D board. The oxidation experiments were carried out in the presence of a solvent (0.0463 mol substrate, substrate/metal=5000 (mol/mol), benzyl alcohol/cyclohexane: 50:50 (vol%), 80°C,  $pO_2=2$  atm). Periodically samples were removed from the reactor for analysis. Nitrogen sorption analyses were carried out with an Autosorb-1 instrument after evacuating the samples at 150°C overnight. The surface areas were determined by applying the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.25. The pore volume was calculated at a relative pressure of 0.99. Nonlocal density functional theory pore-size distribution was determined by using the carbon/slit–cy-lindrical pore model.

X-ray photoelectron spectroscopy (XPS) data were collected with a PHI 3056 spectrometer with an Al anode source operated at 15 kV and an applied power of 350 W. Samples were manually pressed between two pieces of indium foil; the piece of In foil with the sample on it was then mounted onto the sample holder with a piece of carbon tape (Nisshin E.M. Co., Ltd.). Adventitious carbon was used to calibrate the binding energy shifts of the sample (C1s=284.8 eV).<sup>[26]</sup> High-resolution data was collected at a pass energy of 5.85 eV with 0.05 eV step sizes and a minimum of 200 scans to improve the signal-to-noise ratio; lower-resolution survey scans were collected at a pass energy of 93.5 eV with 0.5 eV step sizes and a minimum of 25 scans. Transmission electron microscopy (TEM) data were collected on the Pd/C3N4 catalysts with a Hitachi HF3300 TEM/STEM equipped with a cold field-emission gun and operated at 300 kV. TEM images were collected for Pd/CTF<sub>DCB</sub> and Pd/ CTF<sub>DCP</sub> with a FEI Tecnai G<sup>2</sup> 20 S-TWIN CM200 LaB6 electron microscope operating at 200 kV. The powder samples of the catalysts were directly mounted onto copper grids covered with a carbon film.

Thermogravimetric analyses (TGA) were performed with a Perkin– Elmer TGA7 using a heating rate of 10 °C min<sup>-1</sup> from 50 to 500 °C.

Adsorption of CO<sub>2</sub> was followed in situ in the attenuated total reflection mode (ATR-IR) with a Vector 22 spectrometer (Bruker Optics) equipped with a commercial ATR mirror unit and a liquid-nitrogencooled MCT detector. A thin film was produced on a ZnSe internal reflection element (IRE, 45°,  $50 \times 20 \times 2$  mm; Crystran) by drying in air an aqueous suspension that contained 10 mg of the sample. After mounting the sample in a homemade cell, pure CO<sub>2</sub> (50 mL min<sup>-1</sup>) was allowed to flow through the cell while ATR-IR spectra were measured by co-adding 200 scans at 4 cm<sup>-1</sup> resolution for 1 h. Then the cell was purged with Ar and desorption was followed for 30 min.

Adsorption of O<sub>2</sub> was performed with a Thermo Electron Corporation TPD/R/O 1100 catalytic surface analyzer. The sample was treated with a hydrogen flow at 100°C for 1 h, then H<sub>2</sub> was removed by an Ar flow at 100°C. The sample was cooled at room temperature. Oxygen chemisorptions were performed by pulsing O<sub>2</sub> (50 mLmin<sup>-1</sup>) at room temperature.

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