Catalysis Communications 58 (2015) 149–153

Contents lists available at ScienceDirect

Catalysis Communications

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

Short Communication

Selective aerobic oxidation of alcohols over Au–Pd/sodium titanate nanotubes

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ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form 9 September 2014
Accepted 10 September 2014
Available online 19 September 2014

Keywords:
Bimetallic Au–Pd catalyst
Sodium titanate nanotubes
TiO_2
Alcohol
Aerobic oxidation

ABSTRACT

The catalytic application of Au–Pd nanoparticles supported on sodium titanate nanotubes (NaTNTs) for liquid-phase aerobic oxidation of alcohols is reported, for the first time. This reaction occurs at 80–120 °C, 1 atm and solvent-/alkali-free conditions yielding the corresponding carbonyls in high selectivity. This catalyst was reusable and found to be more active/selective than the corresponding monometallic Au and Pd catalysts and Au–Pd/TiO_2. Higher dispersion, smaller particle size and higher amount of electron density at gold are the causes for the superior activity of Au–Pd/NaTNT catalyst.

1. Introduction

Selective oxidation of alcohols is a commercially important organic transformation as its products are intermediates in the manufacture of pharmaceuticals, agrochemicals and perfumeries [1]. Conventionally, this reaction is performed with stoichiometric reagents which are expensive and associated with toxicity issues. Considerable focus has been paid to aerobic oxidation over recyclable metal catalysts to make the process green and eco-friendly [2–4]. Among them, gold changed the era of research and development tremendously with the discovery of supported gold nanoparticles (Au NPs) showing interesting catalytic oxidation activity at mild to moderate temperatures and with air as oxidant [5,6]. However, the instability of the catalyst due to the agglomeration of Au NPs at reaction conditions is an issue. Bimetallic Au–Pd showed an improved activity and durability than the monometallic counterparts due to geometric and electronic effects [7]. The choice of support was also found to influence the performance of Au through specific support–metal interactions [7]. The most commonly studied metal oxide support is TiO_2. Of late, a new family of 1D-titanates with nanotube, nanoribbon or nanowire architecture has attracted attention due to their unique physicochemical properties [8]. Among them, titanate nanotubes possess high specific surface area and hollow morphology. They are good ion-exchange materials [9]. They were used as photocatalysts, adsorbents and solid base catalysts [10–12]. Gold supported on titanate nanotubes catalyzes water–gas shift [13] and CO oxidation reactions [14]. We report here, for the first time, the application of Au–Pd/sodium titanate nanotubes (NaTNTs) for the selective oxidation of alcohols under solvent and alkali-free conditions. The influence of reaction conditions and composition of Au and Pd on the oxidation activity and selectivity is studied.

2. Experimental section

2.1. Catalyst preparation

NaTNT was prepared by alkali treatment of anatase titania [9]. NaTNT-supported Au and Au–Pd catalysts were prepared by a deposition–precipitation method using 2 mM aqueous $HAuCl_4 \cdot 3H_2O$ and $Pd(OAc)_2$ as precursor solutions for gold and palladium, respectively, and by maintaining the pH at 7 to 8 (Supplementary data, S1).

2.2. Characterization techniques

Au and Pd contents in the catalysts were determined by an inductively-coupled plasma-optical emission spectrometer (ICP-OES; Spectro Arcos). X-ray powder diffractograms (XRD) were recorded on a PANalytical X'Pert PRO diffractometer (Ni-filtered Cu K_α radiation; $2\theta = 5–80°$). High-resolution transmission electron microscopic (HRTEM) images were measured on a FEI Technai F30 instrument (300 kV field emission gun). Specific surface area (S_{BET}) was determined from N_2 physisorption studies (−196 °C; NOVA 1200 Quanta Chrome). Diffuse reflectance UV–visible (DRUV–vis) spectra were recorded on a

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http://dx.doi.org/10.1016/j.catcom.2014.09.018

Table 1
Composition and textural properties of Au/NaTNT and Au–Pd/NaTNT.

Catalyst	Metal content (output, wt.%; ICP-OES)			Textural properties (N_2 physisorption)		
	Au	Pd	Na	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Au(1 wt.%)/NaTNT	0.80	–	6.90	180	0.60	6.0
Au(2 wt.%)/NaTNT	1.54	–	5.31	149	0.47	6.3
Au–Pd(2 wt.%, 3:1)/NaTNT	1.10	0.48	5.10	200	0.70	6.4
Au–Pd(2 wt.%, 1:1)/NaTNT	0.65	0.70	5.20	181	0.64	6.6
Au–Pd(2 wt.%, 1:3)/NaTNT	0.35	1.20	6.60	153	0.55	5.9
Au–Pd(2 wt.%, 1:1)/TiO_2	0.67	0.95	–	23	0.08	7.0

Shimadzu UV-2550 spectrophotometer. X-ray photoelectron spectra (XPS; VG Microtech Multilab ESCA 3000) were acquired with Al K_α radiation. The peak corresponding to carbon 1s (285 eV) was taken as reference.

2.3. Reaction procedure

50 mg of catalyst and 25 mmol of alcohol were charged into a triple-necked, glass, round-bottom flask (25 ml) placed in a temperature-controlled oil bath. The reactor was connected with a water-cooled reflux condenser and an air-filled rubber balloon. Temperature of the reactor was raised to 120 °C and the reaction was conducted for a specific time while stirring the contents. It was then cooled to 25 °C. The reaction mixture was centrifuged and the catalyst was separated out. To 0.5 ml of the liquid portion, 1 ml of mesitylene was added and analyzed by gas chromatography (Varian 3800; CP-8907 — 15 m × 0.25 mm × 0.25 μm column and flame ionization detector). Products were identified by GC–MS (Varian CP-3800; CP-Sil8CB — 30 m × 0.25 mm × 0.25 μm capillary column). In catalyst recycling studies, at the end of each run the reaction mixture was centrifuged and the catalyst was separated. It was then washed with ethanol and water, dried at 110 °C for 12 h and reused in the next recycle without pre-reduction with hydrogen.

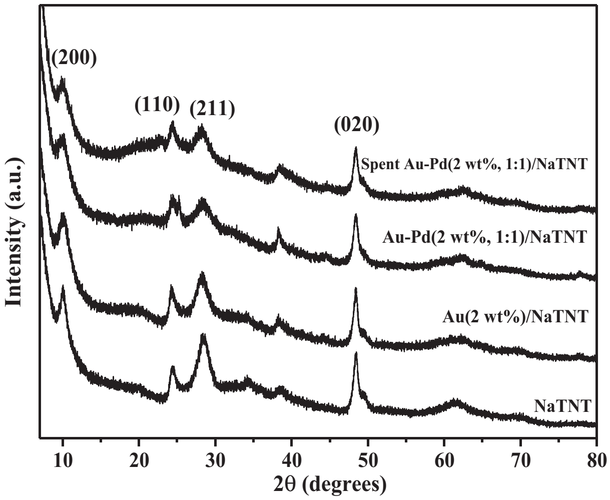

Fig. 1. XRD profiles of NaTNT, Au(2 wt.%)/NaTNT, Au–Pd(2 wt.%, 1:1)/NaTNT and spent Au–Pd(2 wt.%, 1:1)/NaTNT.

3. Results and discussion

3.1. Catalyst characterization

Na/Ti mole ratio of NaTNT determined by ICP-OES (0.65) was nearly the same as the theoretical value (0.67) for $Na_2Ti_3O_7$. For supported metal catalysts, depending on their composition, 65–80% of input Au and 70–96% of Pd remained in their final composition (Table 1). XRD showed typical peaks at 10.1, 24.3, 28.4 and 48.5° corresponding to reflections from (200), (110), (211) and (020) planes, respectively, of NaTNT with $Na_2Ti_3O_7$ composition (JCPDS files: 31-1329 and 41-0192; Fig. 1). The peak at 10.1° is a signature for the nanotube morphology [15]. Metal deposition didn't alter the support structure. No additional peaks due to metals (JCPDS files: 04-0784 and 05-068) were detected for Au/NaTNT and Au–Pd/NaTNT indicating that Au and Pd particles were, perhaps, below the X-ray detection limit. HRTEM (Fig. 2) confirmed the tubular morphology with outer and inner diameters being 9.8 and 4.8 nm, respectively (Supplementary data, S2). It pointed out the complete conversion of TiO_2 into $Na_2Ti_3O_7$. Pd reduced the average particle size of Au from 2.3 nm (Au(2 wt.%)/NaTNT) to 1.2 nm (Au–Pd(2 wt.%, 1:1)/NaTNT) (Supplementary data, S3). Metal particles were evenly distributed on the surface of NaTNT in Au–Pd(2 wt.%,

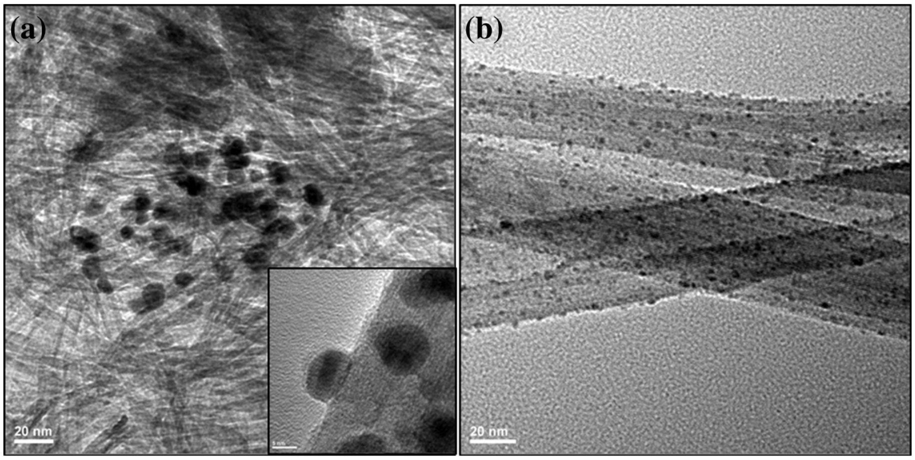

Fig. 2. HRTEM images: (a) Au(2 wt.%)/NaTNT and (b) Au–Pd(2 wt.%, 1:1)/NaTNT.

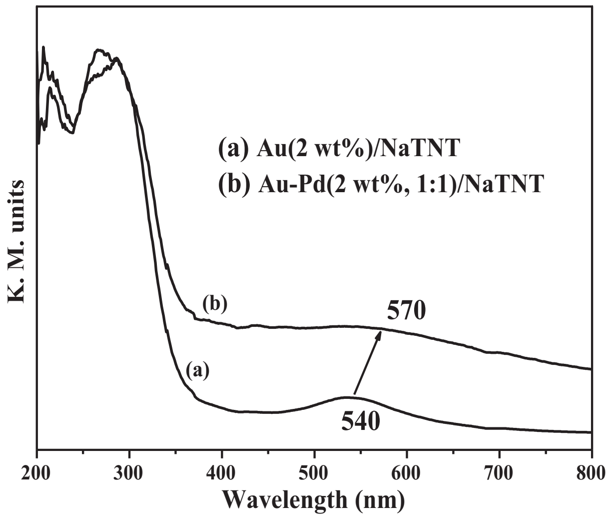

Fig. 3. DRUV–vis spectra: (a) Au(2 wt.%)/NaTNT and (b) Au–Pd(2 wt.%, 1:1)/NaTNT.

1:1)/NaTNT (Fig. 2(b)); only the lattice fringes corresponding to (111) plane of Au with an interplanar distance of 0.24 nm [16] were detected indicating that it is the most exposed plane (Supplementary data, S2). Pd is expected to form a monolayer on the surface of Au at certain concentrations and thereby control the size of Au particles. Also based on electrode potentials, Pd leads to the reduction of Au which in turn hinders the growth of the nanoparticle. These materials were mesoporous showing type IV nitrogen-isotherms with H2-hysteresis loop (Supplementary data, S4). S_{BET} of the catalysts was in the range of 149–200 m^2/g and pore diameter was between 5.9 and 7.0 nm.

Au(2 wt.%)/NaTNT showed a characteristic localized surface plasmon resonance at 540 nm (Fig. 3). In the case of Au–Pd(2 wt.%, 1:1)/NaTNT, this band broadened and shifted to 570 nm because of changes in the band structure of Au in the presence of Pd forming bimetallic nanocomposite and reduction in Au particle size (Fig. 3). Au–Pd(2 wt.%, 1:1)/TiO_2 showed XPS lines at 83.4 and 87.1 eV arising from the core levels of Au $4f_{7/2}$ and $4f_{5/2}$, respectively (Fig. 4). Metallic gold shows $4f_{7/2}$ line at 84.0 eV [17]. For Au–Pd(2 wt.%, 1:1)/NaTNT, these spectral lines were weak and appeared at still lower BE values (82.8 and 86.5 eV, respectively). While weak intensity is indicative of the location of Au inside the nanotubes of NaTNT, their position at lower BE suggests a higher amount of electron density ($Au^{\delta-}$) as a consequence of electron transfer from NaTNT to Au. Reduction in particle size is an alternative reason for a lower BE value of Au on NaTNT compared to that on TiO_2. The lines for Pd^0 in Au–Pd(2 wt.%, 1:1)/TiO_2 appeared at 335.4 ($3d_{5/2}$) and 340.7 eV ($3d_{3/2}$) and in Au–Pd(2 wt.%, 1:1)/NaTNT at 335.3 and 340.4 eV, respectively.

3.2. Catalytic activity

Au/NaTNT and Au–Pd/NaTNT catalyzed the oxidation of benzyl alcohol with aerial oxygen at 120 °C under solvent- and alkali-free conditions (Table 2). Benzaldehyde is the major product (70.2–98.5 wt.% selectivity) with benzoic acid, benzyl benzoate, benzene and toluene as minor products. While benzaldehyde and benzoic acid formed via oxidation reaction, benzene occurred by decarbonylation and toluene by the disproportionation of benzyl alcohol [18]. Benzyl benzoate is produced by the esterification of benzoic acid with benzyl alcohol [12]. At our experimental conditions (air = 1 atm, reaction temperature = 120 °C, reaction time = 10 h), benzyl alcohol conversion was very little (1.5 wt.%) in the absence of a metal catalyst. The supported gold [Au(1 wt.%)/NaTNT] catalyzed this reaction yielding benzyl alcohol conversion of 15.2 wt.% and benzaldehyde selectivity of 98.5 wt.%. This value is comparable to the reports by others using erstwhile supports [19,20]. With increasing Au content from 1 to 2 wt.%, the conversion of benzyl alcohol doubled (from 15.2 to 30.0 wt.%) but the selectivity for benzaldehyde decreased (from 98.5 to 94.3 wt.%); the selectivity for benzyl benzoate and benzene + toluene increased from 1.5 to 4 wt.% and 0 to 1.7 wt.%, respectively (Table 2; run nos. 1 and 2). Upon promotion with Pd, the conversion of benzyl alcohol raised from 15.2 to 63.0 wt.% and TOF increased from 187 to 318 h^{-1}; benzaldehyde selectivity decreased from 98.5 to 82.7% as more and more benzaldehyde converted to benzoic acid and benzyl benzoate (compare run nos. 1 and 4). The presence of Pd also enhanced the selectivity of undesired products, although its overall content was low — benzene (from 0 to 6.4 wt.%) and toluene (from 0 to 1.1 wt.%). The activity of Au–Pd/NaTNT (TOF = 318 h^{-1} based on total metal content and 516 h^{-1} based on surface metal atoms) was superior to Au–Pd/TiO_2 (TOF = 240 h^{-1} based on total metal content and 470 h^{-1} based on surface metal atoms). Selectivity for benzaldehyde was lower and toluene formation was higher on the latter (compare run nos. 4 and 6).

The composition of Au–Pd affected benzyl alcohol conversion and benzaldehyde selectivity. A composition with 1:1 wt/wt of Au and Pd

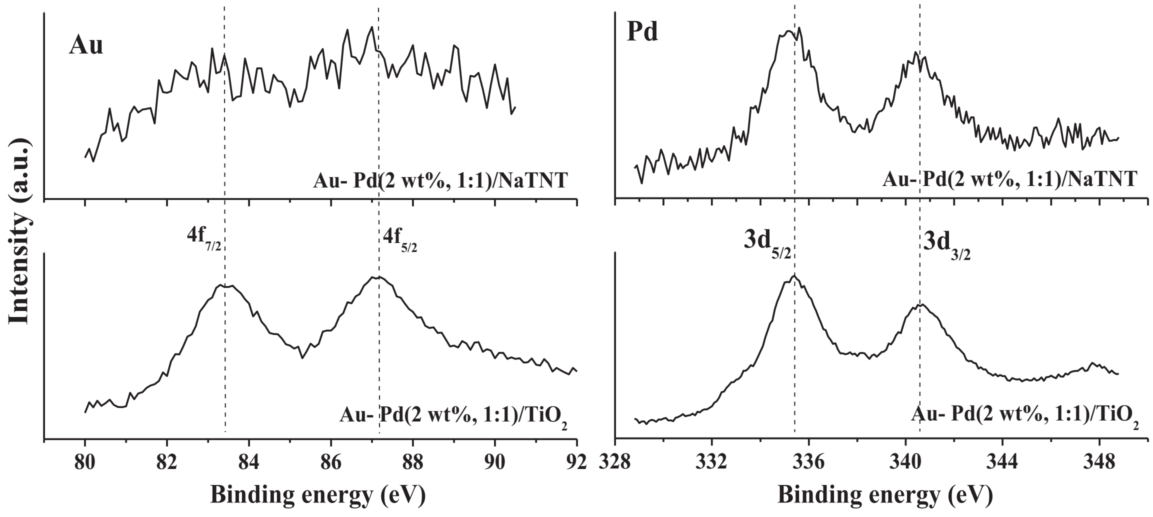

Fig. 4. XPS of Au–Pd(2 wt.%, 1:1)/TiO_2 and Au–Pd(2 wt.%, 1:1)/NaTNT.

Table 2
Catalytic activity data for the aerial oxidation of benzyl alcohol over NaTNT- and TiO_2-supported Au and Au–Pd catalysts.[a]

Run no.	Catalyst	Conversion (wt.%)	TOF (h^{-1})	Product selectivity (wt.%)				
				Benzaldehyde	Benzoic acid	Benzyl benzoate	Benzene	Toluene
1	Au(1 wt.%)/NaTNT	15.2	187 (264)	98.5	0	1.5	0	0
2	Au(2 wt.%)/NaTNT	30.0	192 (283)	94.3	0	4.0	1.2	0.5
3	Au–Pd(2 wt.%, 3:1)/NaTNT	50.5	250 (419)	81.6	0.8	11.1	5.9	0.6
4	Au–Pd(2 wt.%, 1:1)/NaTNT	63.0	318 (516)	82.7	0.6	9.2	6.4	1.1
5	Au–Pd(2 wt.%, 1:3)/NaTNT	53.9	206	70.2	1.0	20.1	7.2	1.5
6	Au–Pd(2 wt.%, 1:1)/TiO_2	57.0	240 (470)	75.6	5.7	2.6	1.1	15
7	Pd(2 wt.%)/NaTNT	50.2	205	78.8	2.2	10.7	5.3	3.0

[a] Reaction conditions: Catalyst = 50 mg, benzyl alcohol = 25 mmol, p(air) = 1 atm, reaction temperature = 120 °C, and reaction time = 10 h, Turnover frequency (TOF) = moles of benzyl alcohol converted per mole of total metal in the catalyst (ICP-OES) per hour. TOF values in parentheses are those calculated based on mole of benzyl alcohol converted per mole of surface metal atoms (estimated from TEM) per hour.

was found to be highly active and selective. Such enhancement in catalytic activity is already known for Au–Pd on other supports [19,20]. Higher activity of the present catalyst is due to the uniform dispersion and smaller size of metal particles (1.2 instead of 2.3 nm; HRTEM) as well as synergistic electronic effects between the metal and support. Au atoms draw electron density away from Pd and NaTNT. Enache et al. [21] and Chen et al. [22] have also made such observation in related systems. The smaller the particle size, the higher would be the availability of surface active sites and interactions with the support which then can lead to a higher activity of the catalysts.

Benzyl alcohol conversion over Au–Pd(2 wt.%, 1:1)/TiO_2 and Au–Pd(2 wt.%, 1:1)/NaTNT increased with increasing reaction time (Supplementary data, S5). However, benzaldehyde selectivity decreased at higher conversion levels due to the consecutive reaction of ester formation. At similar conversion levels, Au–Pd(2 wt.%, 1:1)/NaTNT showed a higher selectivity for benzaldehyde than Au(2 wt.%)/NaTNT and Au–Pd(2 wt.%, 1:1)/TiO_2 (Fig. 5). TOF at the end of 1 h over TiO_2- and NaTNT-supported Au–Pd(2 wt.%, 1:1) was 964 and 1635 h^{-1} (based on total metal content), respectively. Metal particles on TiO_2 have an average diameter of 1.5 nm while those on NaTNT are of 1.2 nm (Supplementary data, S6). The difference in metal particle sizes is the possible cause for difference in the catalytic activity of these two systems. This reaction occurred even at a temperature as low as 80 °C over Au–Pd(2 wt.%, 1:1) catalyst and benzyl alcohol conversion of 50.0% and benzaldehyde selectivity of 93% were obtained (Supplementary data, S7). With a view to optimize the temperature, reactions were conducted at 80, 100 and 120 °C. Benzyl alcohol conversion increased with increasing reaction temperature, but a loss in selectivity for benzaldehyde was observed at higher temperatures (Supplementary data, S6). Upon reuse, Au–Pd(2 wt.%, 1:1)/NaTNT showed a marginal loss (by 5 wt.%) in benzyl alcohol conversion but no further loss in the activity was detected in subsequent recycles (Supplementary data, S8). The structure of the catalyst was intact even after the 5th recycle (XRD, Fig. 1). ICP-OES analysis revealed a marginal loss in the metal content (500 ppm for Au and 200 ppm for Pd). Zhang and co-workers [23,24] reported the application of silica-supported Au–Cu and Au–Ag alloy nanoparticles for the selective oxidation of alcohols at 80 °C. Benzyl alcohol conversion of 96% and benzaldehyde selectivity of >99% were obtained. But 50 times higher amount of the catalyst compared to that used in the present study was employed to achieve the reported conversion. Moreover, the catalyst needed reduction in between the recycles to maintain the conversion, which is not the case with the catalysts of the present study. The activity of Pd(2 wt.%)/NaTNT was higher (50.2 wt.%, TOF = 205 h^{-1}) than that of Au(2 wt.%)/NaTNT (30.0 wt.%; TOF = 192 h^{-1} based on total metal content). However, the selectivity for aldehyde on the former was lower (78.8 wt.%) than on the latter (94.3 wt.%). Bimetallic Au–Pd/NaTNT showed an enhanced activity (63.0 wt.%; TOF = 318 h^{-1}) than either of the monometallic catalysts. It was proposed [25,16] that in the case of Pd the rate determining step is the transfer of H-atom from the β-carbon of the adsorbed alkoxide forming the aldehyde and a Pd-hydride species. For Au, it is the H-abstraction by an Au-superoxide species. Since Au draws electron density from Pd, it can activate molecular oxygen more easily than without Pd, forming a superoxide like active oxygen species which in turn initiates the reaction. At the same time, the electron depleted Pd (in the presence of Au) easily eliminates hydride species from the β-carbon of alkoxide. Thus, the co-presence of Pd with Au facilitates the oxidation rate. The scope of Au–Pd(2 wt.%, 1:1)/NaTNT for a range of structurally different alcohols was investigated (Table 3). The structure and substituent have

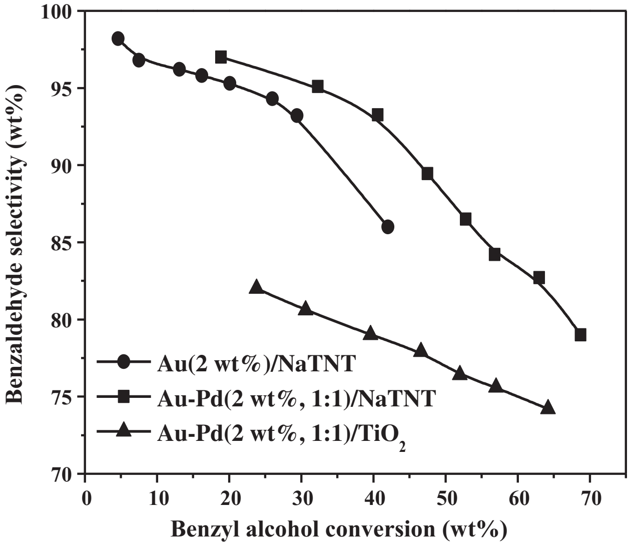

Fig. 5. Oxidation of benzyl alcohol over supported Au and Au–Pd NPs: Conversion versus selectivity plot.

Table 3
Aerobic oxidation alcohols over Au–Pd(2 wt.%, 1:1)/NaTNT catalyst.[a]

Run no.	Alcohol	Alcohol conversion (wt.%)	Aldehyde/ketone selectivity (wt.%)
1	3-Methoxybenzyl alcohol	53.7	84.3
2	4-Methoxybenzyl alcohol	41.5	85.0
3	4-Methy benzyl alcohol	40.0	86.0
4	4-Chlorobenzyl alcohol	10.0	82.0
5	4-Nitrobenzyl alcohol	10.0	89.0
6	1-Phenylethanol	84.0	86.0
7	2-Phenylethanol	10.0	100
8	Cinnamyl alcohol	60.5	75.5
9	Crotyl alcohol	75.6	70.0
10	Furfuryl alcohol	18.8	65.0
11	Cyclohexanol	11.5	100

[a] Reaction conditions: Same as in Table 2.

a marked effect on alcohol conversion. Our future publication will address a detailed study of the electronic and steric effects on the reaction.

4. Conclusions

Catalytic application of Au–Pd/NaTNT for the selective aerial oxidation of alcohols was studied. The activity of this catalyst was found to be higher than Au/NaTNT, Pd/NaTNT and Au–Pd/TiO_2. Physicochemical studies revealed that the particles of Au were smaller and uniformly dispersed on the support in the presence of Pd. Au atoms on NaTNT in the presence of Pd were richer in electron density and thereby enhanced the activation of molecular oxygen enabling a higher oxidation activity. A range of 1° and 2°-alcohols were converted into corresponding carbonyl compounds.

Acknowledgment

D.N. acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi for the Research Fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.09.018. These data include MOL files and InChiKeys of the most important compounds described in this article.

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