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Description				



Selective Aerobic Oxidation of 1,3-Propanediol to 3-Hydroxypropanoic Acid using Hydrotalcite Supported Bimetallic Gold Nanoparticle Catalyst in Water

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Abstract. Selective oxidation of 1,3-propanediol (1,3-PD) to 3-hydroxypropanoic acid (3-HPA), an important industrial building block, was successfully achieved using hydrotalcite-supported bimetallic Au nanoparticle catalysts in water at 343 K under aerobic and base-free conditions. The highest yield of 42% with 73% selectivity towards 3-HPA was afforded by 1wt% $Au_{0.8}Pd_{0.7}-PVP/HT$ catalyst.

Keywords. Selective aerobic oxidation, 1,3-Propandiol, 3-Hydroxypropanoic acid, AuPd bimetallic catalyst.

INTRODUCTION

3-Hydroxypropanoic acid (3-HPA) is classified as ω-hydroxyl-aliphatic carboxylic acid and a bifunctional, three carbon organic compound which has been identified as a potent new generation chemical intermediate. It occupies third position in the classification of the main strategic building blocks obtained from biological resources [1]. Due to its bifunctionality, it can be converted into a number of high value chemicals (*e.g.* acrylic acid, poly-3-HPA, propiolactone, polyesters etc.) [2], these are employed in the production of adhesives, fibers, and resins by simple chemical transformations. It can further undergo selective oxidation of 3-HPA to give malonic acid (MA) and its derivatives which together represent an important market.

Despite major research efforts, 3-HPA is still a rare and costly chemical commercialized as an aqueous solution by few suppliers. 3-HPA has been synthesized via biological routes from 3-hydroxypropanaldehyde, glucose, and glycerol [3, 4]. Allyl alcohol can serve 3-HPA via selective oxidation and hydration reaction [5, 6]. Synthesis of 3-HPA is also reported in patent literatures from β -propiolactone [7], 3-hydroxypropanaldehyde [8], and vinyl acetate [9]. Another patent shows that acrylic acid can undergo hydration reaction to give 3-HPA in water [10]. Behr et al. showed an interesting pathway for the synthesis of 3-HPA from 1,3-propanediol (1,3-PD), an aliphatic diol, by selective oxidation over Pt and Pd based bi- and tri- metallic catalysts using a large quantity of NaOH and high O₂ pressures [11]. Such a "non green" chemical route, results in the formation of products as sodium salts which

requires excess energy consumption to obtain 3-HPA in Na-free form. There is therefore a need to develop a new green strategy for the production of 3-HPA. This paper addresses the production of 3-HPA by selective aerobic oxidation of 1,3-PD. 1,3-PD is obtained from glycerol [12] which is produced as a by-product during biodiesel production [13], thereby making it an ideal substrate for the synthesis of 3-HPA.

Supported gold based bimetallic nanoparticles (NPs) catalysts have been used for the selective aerobic oxidation of alcohols [6, 14-19]. The recent studies commonly used polymer capped highly dispersed bimetallic NPs catalysts like AuPd-PVA/TiO₂ (PVA: Polyvinyl alcohol) [15], AuPt-PVA/MgO [16], and AuPd-PVA/C [17, 18]. A common feature employed for the liquid phase aerobic oxidation of alcohols using Au catalyst involves the need for bases such as NaOH and K₂CO₃ to activate the alcohols. From the view point of green chemistry, it is therefore desirable to develop bifunctional catalysts combining NPs with solid base supports. It has been demonstrated that hydrotalcite-supported bimetallic AuPd NPs (AuPd-PVP/HT (PVP: polyvinylpyrrolidone)) are active for aerobic oxidations of aromatic alcohols without external base additives in toluene solvent [19], suggesting synergy between AuPd NPs and basic sites of the HT.

As a novel application of the AuPd-PVP/HT catalysts, we hereby wish to report the base-free and aerobic oxidation of 1,3-PD toward 3-HPA in water catalyzed by heterogeneous and reusable AuPd-PVP/HT under mild reaction conditions. Generally, oxidation of aliphatic primary alcohols is difficult rather than that of aromatic alcohols [20]. Recently, Ide and Davis reported the oxidation of 1,3-PD over Pt/carbon catalyst to afford 3-HPA with 11% yield (20% conversion) under 10 bar O₂ in the presence of acetic acid at 343 K [21]. This paper describes the highest 3-HPA yield of 42% (58% conversion) under an atmospheric O₂ pressure in water at 343 K and determines apparent activation energy by kinetic approach to ascertain the influence of Pd atom on the oxidation of 1,3-PD, which were not reported in our previous paper [19].

EXPERIMENTAL

Chemicals

Hydrogen tetrachloroaurate tetrahydrate (HAuCl₄•4H₂O, 99% purity), Palladium chloride (PdCl₂, 99% purity), 25% Ammonia solution (NH₃ aq.), potassium chloride (KCl), Ethylene glycol (EG) and sodium carbonate decahydrate (Na₂CO₃•10H₂O) were supplied by Wako Pure Chemical Ind. Ltd. 1,3-Propanediol (98% pure, further purified by distillation before use, 1,3-PD) and 3-hydroxypropanoic acid (30% in water, 3-HPA) were purchased from Tokyo chemical Ind. Ltd. Co. Polyvinylpyrrolidone (PVP, Mw= 58,000) and Mg-Al hydrotalcite (HT, Mg/Al= 5.03) was purchased from Acros Organics Co. and Tomita Pharmaceutical Co. Ltd., respectively.

Catalyst Preparation

Monometallic bare Au/HT catalyst was prepared by the deposition-precipitation method using NH₃ aq. [22], followed by calcinations at 473 K. In brief, HT (1 g) was added to an aqueous solution of HAuCl₄ (1.2 mM, 40 ml) with a vigorous stirring, and the pH of the solution was adjusted to 10 by addition of NH₃ aq. solution. The obtained solution was vigorously stirred for 6 h followed by 30 min reflux at 373 K. The resulting solid was filtered, washed thoroughly with water, and dried at 473 K for 12 h. Finally, the ruby-colored solid catalyst was obtained.

Bimetallic 1wt% Au_xPd_y NPs protected by PVP agents were prepared by the polyol reduction method with EG under reflux condition followed by the addition of HT according to the previous report [19]. For instance, the preparation of Au_{0.8}Pd_{0.2}-PVP/HT (0.8wt% Au, 0.2wt% Pd) was as follows: An mixed aqueous solution (50 ml) of PdCl₂ (0.0188 mmol), KCl (0.1 g) and HAuCl₄•4H₂O (0.0406 mmol) was refluxed in the presence of PVP (0.58 g) and EG (50 ml) for 2 h, thereafter, HT (1.0 g) was added to the formed colloidal dispersion to stabilize the formed Au_{0.8}Pd_{0.2}-PVP NPs onto the surface of HT with an additional stirring for 1 h. The obtained catalyst was filtered, washed, and dried in vacuum overnight. The Pd content was varied in the range of 0 to 100%, and the total amount of both metals in the colloidal dispersion (x + y) was kept as 1wt%. The X-ray diffraction measurements confirmed the crystal structure of both Au/HT and Au_{0.8}Pd_{0.2}-PVP/HT to be identical to the parent HT (Figure 1(a)). The total amount of metal loading was determined to be 1.01wt% in Au/HT and 1.06wt% in Au_{0.8}Pd_{0.2}-PVP/HT analyzed by ICP-AES, respectively. Absence of surface plasmon resonance corresponding to Au NPs (480-580 nm) in the UV-vis spectra of all Au_xPd_y-PVP NPs suggested Au-Pd alloy formation in Au_xPd_y-PVP NPs dispersed solutions (Figure 1(b)). TEM

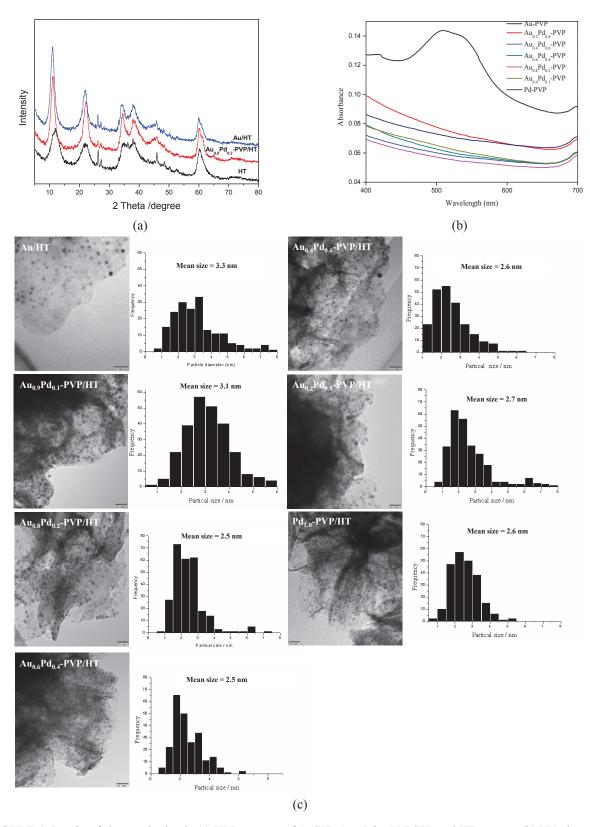


FIGURE 1. Results of characterization in (a) XRD patterns of Au/HT, $Au_{0.8}Pd_{0.2}$ -PVP/HT, and HT support, (b) UV-vis spectra of Au_xPd_y NPs dispersed solution with various Au:Pd weight ratios, and (c) TEM images of monometallic and bimetallic Au catalysts.

images indicated that the synthesized NPs were well-dispersed and stabilized onto the HT support in various x/y cases (Figure 1(c)).

Catalyst Characterization

The morphology of both monometallic and bimetallic Au catalyst was analyzed by transmission electron microscopy (TEM; Hitachi H-7100) operating at 100 kV. Powdered X-ray diffraction patterns were obtained with a Rigaku Smartlab X-ray diffractometer using Cu K α radiation (λ = 0.154 nm) accelerated at 40 kV and 20 mA. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was obtained using Shimadzu ICPS-7000 ver.2 to estimate the real concentration of Au and Pd in Au/HT monometallic and Au_xPd_y-PVP/HT bimetallic catalysts. The Ultraviolet and visible (UV-vis) spectra were measured by a Perkin-Elmer Lambda35 spectrometer at room temperature with a light path length of 1 cm.

Aerobic oxidation of 1,3-propanediol

The oxidation of 1,3-PD was carried out in a 30 ml Schlenk flask attached to a reflux condenser. In a general procedure, 0.1 g catalyst in 7.5 ml water was added to the Schlenk flask, and purged with O_2 flow before reaction under stirring (500 rpm) followed by the addition of 1 mmol of 1,3-PD. Subsequently, the reaction mixture was stirred at desired temperature for a given reaction time under O_2 flow (10 ml min⁻¹) at atmospheric pressure. After that, the reaction mixture was diluted by adding 7.5 ml water, the resulting mixture was centrifuged and filtered using a Milex-LG 0.20 μ m syringe filter, and the products were analyzed by HPLC (WATERS 600 PUMP) equipped with a refractive index detector. A Shodex RSpak KC-811 column was used in aqueous 0.1wt% H_3PO_4 as the eluent at a flow rate of 1.0 ml min⁻¹ at 323 K.

The catalyst was separated, washed with 15 ml of a 10% Na₂CO₃ aqueous solution followed by washing with 30 ml of water, and dried in vacuum overnight at room temperature before reuse.

RESESULTS AND DISCUSSION

Aerobic oxidation of 1,3-PD to 3-HPA was carried out using 1wt% Au_xPd_y -PVP/HT catalysts with varying Au:Pd weight ratios (x: y). The results are summarized in Table 1 (entries 3-10). The bimetallic Au_0 $_8$ Pd $_0$ $_2$ -PVP/HT

TABLE 1. Comparison of catalytic activities of hydrotalcite supported Au_xPd_v NPs for aerobic oxidation of 1,3-PD.^a

HO OH
$$\frac{\text{Catalyst, O}_2}{343 \text{ K, } 12 \text{ h}}$$
 HO OH OH OH OH OH OH AA

Entry	Catalyst	Conv. /%	Yield (Sel.) /%		Particle size ^b /nm	Metal amount ^c /mmol g ⁻¹		TON
			3-НРА	MA	-	Au	Pd	_
1	Au/HT	36	30 (83)	6 (17)	3.3	0.0513	0	59
2^d		26	24 (93)	2 (7)				95
3	$Au_{1.0}$ -PVP/HT	1	0 (0)	0(0)	Agglomerates	0.0432	0	0
4	$Au_{0.9}Pd_{0.1}\text{-PVP/HT}$	45	30 (67)	3 (7)	3.1	0.0551	0.0141	43
5	$Au_{0.8}Pd_{0.2}\text{-PVP/HT}$	58	42 (73)	10 (17)	2.5	0.0396	0.0216	69
6^d		37	32 (86)	5 (14)				105
7	$Au_{0.6}Pd_{0.4}\text{-PVP/HT}$	67	32 (48)	18 (27)	2.5	0.0301	0.042	44
8	$Au_{0.4}Pd_{0.6}\text{-PVP/HT}$	76	20 (26)	24 (32)	2.6	0.0270	0.093	19
9	$Au_{0.2}Pd_{0.8}\text{-PVP/HT}$	61	18 (30)	14 (23)	2.7	0.0127	0.122	14
10	$Pd_{1.0}$ -PVP/HT	17	15 (88)	0 (0)	2.6	0	0.156	10

^aReaction conditions: 1,3-PD (1.0 mmol), H₂O (7.5 ml), 1wt% Catalyst (0.1 g, ^d0.05 g), O₂ flow (10 ml min⁻¹), 343 K, 12 h, ^bDetermined by TEM measurements about 270 NPs for each sample (See Figure 1(c)). ^cEstimated by ICP-AES analysis.

3-HPA: 3-hydroxypropanoic acid, MA: malonic acid, Au_{0.8}Pd_{0.2}-PVP/HT: 0.8wt% Au and 0.2wt% Pd composed the catalyst.

showed the highest catalytic activity among the various Au_xPd_y -PVP/HTs (entries 5) whereas $Au_{1.0}$ -PVP/HT showed no activity (entry 3). The monometallic $Pd_{1.0}$ -PVP/HT catalyst was moderately active (entry 10). An increase in the amount of Pd content from 0.1wt% to 0.6wt% resulted in an increase of 1,3-PD conversion, leading to decrease in the yield and selectivity for 3-HPA by overoxidation to MA (entries 4, 5, 7, 8).

It is interesting to note that the yield of 3-HPA reached 42% over bimetallic $Au_{0.8}Pd_{0.2}$ -PVP/HT catalyst with a small decrease in selectivity from 83% to 73% and an increase in conversion from 36% to 58% when compared with monometallic bare Au-supported HT (Au/HT) (entries 1 and 5). It has been shown that the catalytic performance of Au NPs has been enhanced markedly by alloying with a second metal [16-19]. The turnover number per total metal (TON) for the oxidation of 1,3-PD using bimetallic $Au_{0.8}Pd_{0.2}$ -PVP/HT (0.05 g) was calculated to be 105 at 343 K for 12 h with 32% yield and 86% selectivity (entry 6).

Time profiles for the oxidation reaction of 1,3-PD over the Au/HT and Au_{0.8}Pd_{0.2}-PVP/HT catalysts at 343 K are plotted in Figure 3(a). With an increased reaction time, the 1,3-PD conversion increased and the selectivity of 3-HPA gradually decreased due to further oxidation of the primary hydroxyl group of 3-HPA to MA. The highest yield (42%) with 73% selectivity of 3-HPA and 58% conversion of 1,3-PD was achieved after 12 h of the reaction over Au_{0.8}Pd_{0.2}-PVP/HT catalyst. It was also observed that the Au_{0.8}Pd_{0.2}-PVP/HT exhibited a higher activity than that of Au/HT in all steps. In other word, the reaction rate on bimetallic Au_{0.8}Pd_{0.2}-PVP/HT catalyst was faster than monometallic Au/HT catalyst for aerobic oxidation of 1,3-PD.

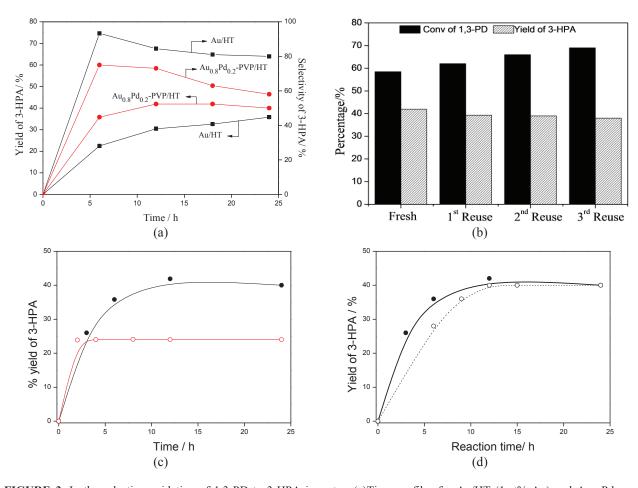


FIGURE 3. In the selective oxidation of 1,3-PD to 3-HPA in water, (a)Time profiles for Au/HT (1wt% Au) and Au_{0.8}Pd_{0.2}-PVP/HT (0.8wt% Au and 0.2wt% Pd), and (b) Recyclability of 1wt% Au_{0.8}Pd_{0.2}-PVP/HT catalyst. Time courses of 1wt% Au_{0.8}Pd_{0.2}-PVP/HT (closed circle) were also plotted with different two cases: (c) the catalyst was removed at 2 h (open circle) or (d) in the presence of TEMPO (15 mg) (open circle). Reaction conditions: 1,3-PD (1 mmol), catalyst (0.1 g), water (7.5 ml), 343 K, O₂ flow (10 ml min⁻¹).

The reusability of the $Au_{0.8}Pd_{0.2}$ -PVP/HT catalyst was tested and was found to be reusable up to three times without significant loss in its catalytic activity and selectivity (Figure 3(b)). There was few observable change in the particle size of $Au_{0.8}Pd_{0.2}$ alloy around at 2.5 nm after the reaction whereas the Au/HT showed a slight increase in the mean particle size from 3.3 nm to 3.5 nm.

The possibility of catalyst leaching was ruled out by carrying out successive reactions after removal of solid $Au_{0.8}Pd_{0.2}$ -PVP/HT catalysts from the solution. Further continuation of the reaction after catalyst removal resulted in no significant increase in the yield of 3-HPA (Figure 3(c)). These results indicate that the present oxidation reactions of 1,3-PD are truly heterogeneous.

In order to understand the reaction pathway over the Au_{0.8}Pd_{0.2}-PVP/HT catalyst, an investigation using a radical scavenger, TEMPO, (2,2,6,6-tetramethyl piperidin-1-yl)oxidanyl, was performed. In the reaction using Au_{0.8}Pd_{0.2}-PVP/HT, TEMPO (0.1 mmol) moderately influenced the oxidation rate of 1,3-PD with no significant change in 3-HPA yields after 12 h (Figure 3(d)). This indicates that the dominant reaction mechanism does not involve the formation of a carbon centered free radical, in which case the yield of 3-HPA would have decreased in the presence of TEMPO at the end of the reaction. This is in agreement with our report of aerobic oxidation of alcohols over AuPd-PVP/HT catalyst [19].

The comparison of the reaction results for Au/HT and Au_xPd_y-PVP/HT suggests that Pd content in the Au_xPd_y-PVP/HTs has a strong influence on the catalytic activity. It has been observed that the difference in ionization potentials of Au and Pd causes the electron transfer from Pd to Au thereby creating partial negative charges on Au and partial positive charges on Pd in PVP stabilized Au-Pd bimetallic catalysts [19]. Au L₃-edge X-ray adsorption near-edge structure (XANES) features of Au_xPd_y-PVP/HTs are shown in Figure 4. Lower intensities in Au_xPd_y-PVP/HTs than Au-PVP/HT and Au foil in the white-line (WL) area, which attributed to the possibility for electron transition from 2p to 5d state in Au atoms in the sample, indicated that the Au_xPd_y-PVP/HTs possessed much negativity in 5d state of Au atoms than Au_{1.0}-PVP/HT and Au foil. Thus, these indicated that Au atoms in bimetallic samples increased electronic charges in 5d state in compare with Au foil and Au_{1.0}-PVP/HT. The evolution of these partial charges may stabilize the transition state which could explain the higher activity of Au_xPd_y-PVP/HT catalyst than Au/HT in the aerobic oxidation of 1,3-PD to 3-HPA.

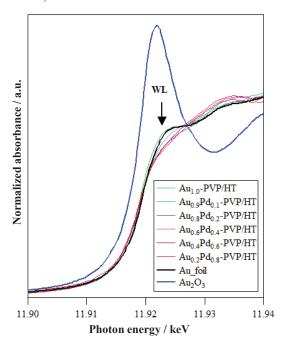


FIGURE 4. Au L₃-edge XANES features of Au_xPd_y-PVP/HTs with references of Au foil and Au₂O₃.

Based on the above results, we propose a reaction mechanism involving the formation of an alkoxide intermediate (Figure 5). Firstly, O_2 molecule is activated on Au^{δ} to form AuO^{-} peroxo and/or AuO_2^{-} superoxo species [23, 24]. Dissociative adsorption of 1,3-PD on AuPd sites forms AuPd-alkoxide species. This step is promoted by basic sites on hydrotalcite surface [19, 22]. The Au oxo species then abstract the hydrogen on the α -

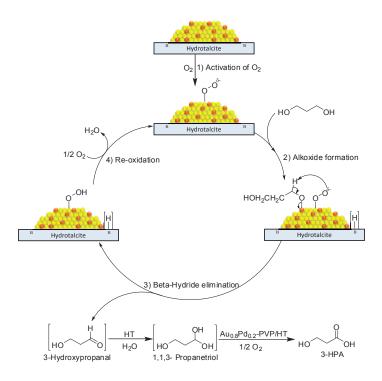


FIGURE 5. Proposed mechanism for aerobic oxidation of 1, 3-PD to 3-HPA using the 1wt% Au_{0.8}Pd_{0.2}-PVP/HT catalyst.

carbon leading to β -hydride elimination to give carbonyl compound (which subsequently, *in situ* is converted into 3-HPA) and Au-hydroperoxide species. Reaction of O_2 with the Au-hydroperoxide forms H_2O and regenerates active Au species to complete the catalytic cycle.

The O_2 flow rate (10-50 ml min⁻¹) did not influence the oxidation rate of 1,3-PD, indicating that the O_2 activation steps are fast. Therefore, the rate-determining step is proposed to be the β -hydride elimination step [19, 22, 25-27]. The rate constant k were determined at various temperatures assuming a first-order kinetics with respect to 1,3-PD

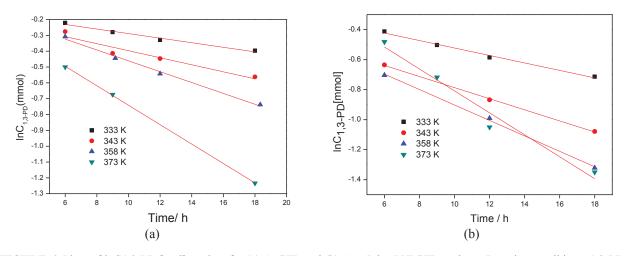


FIGURE 6. Plots of lnC1,3-PD [mol] vs time for (a) Au/HT, and (b) Au_{0.8}Pd_{0.2}-PVP/HT catalysts. Reaction conditions: 1,3-PD (1 mmol), 1wt% catalyst (0.1 g), water (7.5 ml), O₂ flow (10 ml min⁻¹).

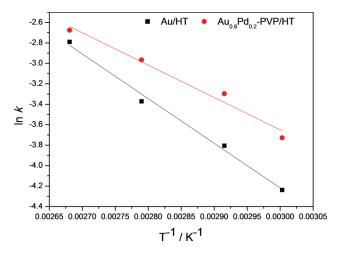


FIGURE 7. Arrhenius plots for the oxidation of 1,3-PD over Au/HT and Au_{0.8}Pd_{0.2}-PVP/HT catalysts.

amount (Figure 6(a) and (b)). The Arrhenius plots (Figure 7) show that the activation energies for the Au/HT and the $Au_{0.8}Pd_{0.2}$ -PVP/HT are 37.1 and 26.1 kJ mol⁻¹, respectively. This indicates that the synergy between Au and Pd atoms in nanoparticles may facilitate the slow β -hydride elimination step.

CONCLUSIONS

We showed that 1wt% Au_{0.8}Pd_{0.2}-PVP/HT catalyst prepared by a polyol reduction method is more active than 1wt% bare Au/HT prepared by a deposition-precipitation method for the selective oxidation of 1,3-PD to 3-HPA. Alloying Au with Pd has been shown to increase the yield of 3-HPA with high conversion of 1,3-PD. We found that the Au_{0.8}Pd_{0.2}-PVP/HT catalyst decreases activation energy in the rate-determination step for the aerobic oxidation of 1,3-PD and it leads nice activity in comparison with bare Au/HT catalyst. Finally, it was found that our Au_{0.8}Pd_{0.2}-PVP/HT catalyst is able to oxidize not only aromatic alcohols in toluene but also aliphatic 1,3-PD in water solvent.

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REFERENCES

 T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, A. Manheim, D. Elliot, L. Lasure, S. Jones, M. Gerber, K. Ibsen, L. Lumberg and S. Kelley, *Top value added chemicals from biomass, Volume I: Results*

- of Screening for Potential Candidates from Sugars and Synthesis Gas (the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy laboratory (NREL), August 2004)
- 2. C. D. Pina, E. Falletta and M. Rossi, Green Chem 13, 1624-1632 (2011).
- 3. X. Jiang, X. Meng and M. Xian, Appl. Microbiol Biotechnol 82, 995-1003 (2009).
- 4. J. E. Jo, S. M. Raj, C. Rathnasingh, E. Selvakumar, W. C. Jung and S. Park, Appl Microbiol Biotechnol 81, 51-60 (2008).
- 5. C. D. Pina, E. Falletta and M. Rossi, ChemSusChem 2, 57-58 (2009).
- 6. E. Falletta, C. D. Pina, M. Rossi, Q. He, C. J. Kiely and G. J. Hutchings, Faraday Discuss 152, 367-379 (2011).
- 7. J. H. Hugh and T. Kingsport, U.S. Patent Appl. Pub. No. US2466419 A (1949).
- 8. T. Haas, C. Brossmer, M. Meier, D. Arntz and A. Freund, Europe Patent Appl. Pub. No. EP0819670 A2 (1998).
- 9. G. R. Eastham, A. J. Rucklidge and D. C. Hamilton, U.S. Patent Appl. Pub. No. US 2006/0128985 A1 (2006).
- 10. X. Meng, T. Abraham and P. Tsobanakiss, U.S. Patent Appl. Pub. No. US 2007/0015936 A1 (2007).
- 11. A. Behr, A. Botulinski, F. J. Carduck and M. Schneider, U.S. Patent Appl. Pub. No. US5321156A (1994).
- 12. Y. Nakagawa, Y. Shinmi, S. Koso and K. Tomishige, J. Catal. 272, 191-194 (2010).
- 13. G. A. Krause, Soil 36, 648-651 (2008).
- 14. T. Kotionova, C. Lee, P. J. Miedziak, N. F. Dummer, D. J. Willock, A. F. Carley, D. J. Morgan, D. W. Knight, S. H. Taylor and G. J. Hutchings, Catal. Lett. 142, 1114-1120 (2012).
- 15. D. I. Enache, J. K. Edward, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, Science **311**, 362-365 (2006).
- G. L. Brett, Q. He, C. Hammond, P. J. Miedziak, N. Dimitratos, M. Sankar, A. A. Herzing, M. Conte, J. A. Lopez-Sanchez, C. J. Kiely, D. W. Knight, S. H. Taylor and G. J. Hutchings, Angew. Chem. Int. Ed. 50, 10136-10139 (2011).
- 17. N. Dimitratos, J. A. Lopez-Sanchez, S. Meenakshisub-daram, J. M. Anthonykutty, G. Brett, A. F. Carley, S. H. Taylor and G. J. Hutchings, Green. Chem. 11, 1209-1216 (2009).
- 18. A. Villa, C. Campione and L. Prati, Catal. Lett. 115, 133-136 (2007).
- 19. S. Nishimura, Y. Yakita, M. Katayama, K. Higashimine and K. Ebitani, Catal. Sci. Technol. 3, 351-359 (2013).
- 20. For example, see; S. E. Davis, M. S. Ide and R. J. Davis, Green Chem. 15, 17-45 (2013) as a recent review.
- 21. M. S. Ide and R. J. Davis, J. Catal. 308, 50-59 (2013).
- 22. N. G. Gupta, S. Nishimura, A. Takagaki and K. Ebitani, Green. Chem. 13, 824-827 (2011).
- 23. M. Okumura, Y. Kitagawa, T. Kawakami and M. Haruta, Chem. Phys. Lett. 459, 133-136 (2008).
- 24. H. Tsunoyama, N. Ichikuni, H. Sakurai and T. Tsukuda, J. Am. Chem. Soc. 131, 7086-7093 (2009).
- 25. K. Ebitani, K. Motokura, T. Mizugaki and K. Kaneda, Angew. Chem. Int. Ed. 117, 3489-3492 (2005).
- 26. A. Abad, A. Corma and H. Garcia, Chem. Eur. J. 14, 212-222 (2008).
- 27. K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, J. Am. Chem. Soc. 122, 7144-7145 (2000).