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An efficient and reusable carbon-supported platinum catalyst for aerobic oxidation of alcohols in water

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Platinum nanoparticles embedded in a hollow porous carbon shell prepared by a photocatalytic reaction acted as a reusable catalyst for the aerobic oxidation of alcohols under atmospheric pressure of oxygen in water.

Oxidation of alcohols into aldehydes, ketones and carboxylic acids is one of the most crucial reactions in the fine chemical and pharmaceutical industries.[1] Stoichiometric quantities of oxidants such as chromates and mineral acids are traditionally employed for these reactions. However, the stoichiometric oxidation process suffers from low atom efficiency and a large amount of waste production, leading to a severe environmental impact.[2] Heterogeneously catalyzed liquid-phase oxidations using molecular oxygen (O_2) as the sole oxidant are an attractive alternative. Among the various catalysts exploited so far,[3] platinum (Pt) supported on activated carbon (Pt/AC) has been studied extensively as a suitable candidate for alcohol oxidation because it works in water under atmospheric pressure of O_2.[4] However, the major drawback of the use of Pt/AC is rapid deactivation due to by-product poisoning and over-oxidation of the Pt catalyst. A common method to minimize these deactivation processes is the introduction of a second metal component such as gold (Au), bismuth (Bi) and lead (Pb).[5] Except for the case of Au addition, however, leaching of these heavy metals is a serious ecological problem for its operation.[6]

Recently, we have fabricated Pt nanoparticles embedded in the porous wall of a hollow carbon shell (*n*Pt@*h*C) by using a titanium(IV) oxide (TiO_2) photocatalytic reaction.[7] The immobilization of Pt nanoparticles inside the framework of porous carbon could prevent particle aggregation, movement and leaching. Due to the specific properties of the *n*Pt@*h*C nanostructure, this material was found to work as an active and reusable catalyst for hydrogenation of various olefins. We therefore decided to investigate the catalytic activity of *n*Pt@*h*C for alcohol oxidation. Herein we report the application of *n*Pt@*h*C to aerobic oxidation in water of various alcohols to prove its efficient promotion of the reaction with high recyclability.

The *n*Pt@*h*C sample was synthesized by a previously reported procedure.[7] To 400 cm^3 of aqueous solution containing 200 mg of phenol and 7.7 μmol of hexachloroplatinic acid (H_2PtCl_6) was added 500 mg anatase TiO_2 powder (Ishihara ST-21, average particle size: 20 nm, BET surface area: 50 m^2g^{-1}). The suspension was photoirradiated under reduced-pressure argon (30 kPa) with a high-pressure Hg lamp for 2.5 h. The brownish powder as-obtained was subjected to carbonization at 973 K for 6 h in vacuum followed by immersion in a 50% hydrofluoric acid (HF) solution for 24 h at room temperature to dissolve the TiO_2 component to give *n*Pt@*h*C (***CAUTION***: *HF solution is very hazardous and corrosive and should be handled with extreme care*.). High-resolution transmission electron microscopy (HRTEM) analysis of *n*Pt@*h*C revealed that the Pt nanoparticles were embedded in the carbon shell and were physically separated from each other by the carbon matrix, and the Pt nanoparticles had a mean diameter of 3.0 nm with a very narrow size distribution (Fig. 1).

Oxidations of 1-phenylethanol were initially carried out using various Pt catalysts under 1 atm of O_2 in water, as shown in Table 1.[8] Among the catalysts examined, the *n*Pt@*h*C catalyst proved to be the most efficient for oxidation of 1-phenylethanol to give the corresponding ketone (entry 1). Commercial Pt/AC samples and a Pt/AC sample prepared by the conventional impregnation–reduction method were found to be less effective: it was found that their activities varied depending on the method for sample preparation or the supplier (entries 2–4). Other Pt catalysts such as Pt supported on alumina (Pt/Al_2O_3), Pt-black, and Pt nanoparticles stabilized with poly(vinylpyrrolidone) (Pt-PVP)[9] gave poor results (entries 5–7). In general, the catalytic activity of Pt/AC catalysts greatly declines after successive catalytic runs (entries 8, 9). On the other hand, after simple extraction by diethyl ether followed by drying at 353 K overnight, the *n*Pt@*h*C catalyst could be readily reused without significant loss of its high level of catalytic activity for at least two successive runs (entries 10, 11). Moreover, TEM observation of *n*Pt@*h*C after these reactions revealed that there is no appreciable change in

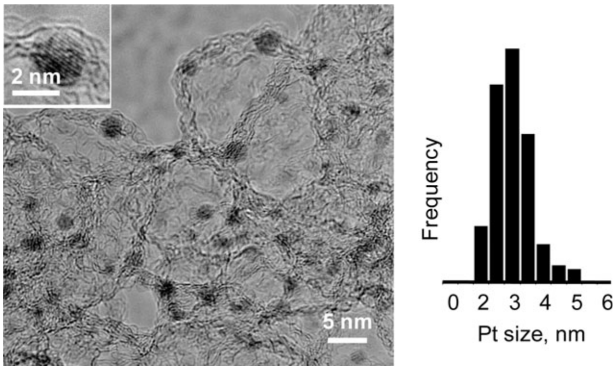

Fig. 1 HRTEM and Pt size distribution of *n*Pt@*h*C.

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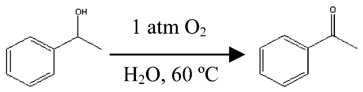
Table 1 Oxidation of 1-phenylethanol using various Pt metal catalysts[a]



Entry	Catalyst	M/S[b] (%)	Conv.[c] (%)	TON[d]
1	*n*Pt@*h*C	0.2	81	405
2	Pt/AC (Wako)	0.2	36	180
3	Pt/AC (N. E.)	0.2	30	150
4	Pt/AC (impreg.)	0.2	20	100
5	Pt-black	0.5	45	90
6	Pt/Al_2O_3	0.2	5	25
7	Pt-PVP	1.0	3	3
8	Pt/AC (Wako)[e]	0.2	10	50
9	Pt/AC (N. E.)[e]	0.2	8	40
10	*n*Pt@*h*C[e]	0.2	76	380
11	*n*Pt@*h*C[f]	0.2	76	380

[a] All the reactions were carried out in water under 1 atm of oxygen at 60 °C for 24 h. [b] Metal/substrate molar ratio. [c] Conversion. [d] Turnover number. [e] After one successive run. [f] After two successive runs.

structure of the catalyst. In addition, because the present system can be operated at a relatively low metal/substrate molar ratio (*ca.* 0.001), TON for Pt of *n*Pt@*h*C is also much larger than that obtained on recently developed resin-supported Pt catalysts.[10] These results indicate the potential ability of *n*Pt@*h*C as a heterogeneous oxidation catalyst.

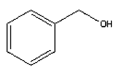
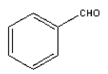
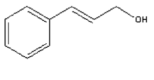
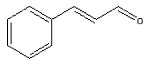
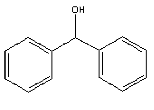
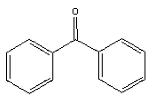
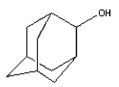
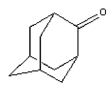
The scope for oxidation using *n*Pt@*h*C is summarized in Table 2. Results obtained for a typical Pt/AC catalyst supplied by Wako are also shown for comparison. The *n*Pt@*h*C catalyst showed high levels of catalytic activity for oxidation of primary alcohols, *i.e.*, benzyl alcohol and cinnamyl alcohol, to yield the corresponding carbonyl compounds (entries 1–4). Although oxidation of a bulky secondary alcohol (benzhydrol) was less efficient compared to the other substrates, the activity level of *n*Pt@*h*C was still higher than that of Pt/AC (entries 5, 6). Interestingly, aerobic oxidation of 2-adamantanol, a sterically hindered non-activated alicyclic alcohol, also proceeded smoothly on the *n*Pt@*h*C catalyst (entries 7, 8). To the best of our knowledge, oxidation of 2-adamantanol has only been performed using supported Ru and homogeneous complexes of Pd and Fe in organic solvents,[11] and oxidation using *n*Pt@*h*C is therefore the first example of Pt-catalyzed efficient oxidation of 2-adamantanol in water.

As discussed in our previous report,[7] the Pt catalyst in *n*Pt@*h*C is embedded in the carbon matrix which contains well-developed micropore and mesopore systems. These pores provide three-dimensional hydrophobic channels and spaces where efficient mass transfer and preferential adsorption of the reaction substrate take place efficiently. These unique properties of *n*Pt@*h*C, therefore, result in a high concentration of the substrate around the Pt catalyst, leading to the efficient catalytic function compared to the conventional Pt/AC sample. Moreover, the special location of the Pt catalyst in the present *n*Pt@*h*C sample, *i.e.*, entrapment in the porous carbon matrix, also effectively prevents its agglomeration during reactions. This unique characteristic is likely to contribute its noticeable reusability unlike Pt/AC. Further studies on mechanistic details and possible extension to other organic syntheses are currently underway.

In conclusion, we have proved that *n*Pt@*h*C has high potential as a heterogeneous oxidation catalyst. Owing to the requirement of only a small amount of Pt to induce reactions in water under 1 atm of O_2, it is expected that this composite can be used for synthesis of a wide range of useful chemicals from alcohols.

Dr Takao Sakata and Prof. Hirotaro Mori (Osaka University) are gratefully acknowledged for their help in TEM measurements. Y. H. Ng is grateful for the scholarship from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 19028042, "Chemistry of Concerto Catalysis") from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Table 2 Oxidation of various alcohols using *n*Pt@*h*C and Pt/AC[a]

Entry	Catalyst	Substrate	Product	M/S[b] (%)	Conversion (%)	Selectivity[c] (%)	TON[d]
1	*n*Pt@*h*C			0.1	90	51	900
2	Pt/AC			0.1	89	49	890
3	*n*Pt@*h*C			0.1	99	75	990
4	Pt/AC			0.1	69	95	690
5	*n*Pt@*h*C			0.2	42	—[e]	210
6	Pt/AC			0.2	16	—[e]	80
7	*n*Pt@*h*C			0.2	72	—[e]	360
8	Pt/AC			0.2	21	—[e]	105

[a] All the reactions were carried out in water under atmospheric oxygen at 60 °C for 24 hours. Pt/AC was supplied by Wako Pure Chemical. [b] Metal/substrate molar ratio. [c] The remain is carboxylic acid of the corresponding alcohols. [d] Turnover number. [e] Ketone is the sole product.

Notes and references

1. T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037; T. Mallat and A. Baiker, *Catal. Today*, 1994, **19**, 247; N. Kakiuchi, Y. Maeda, T. Nishimura and S. Uemura, *J. Org. Chem.*, 2001, **66**, 6620; T. Nishimura, N. Kakiuchi, M. Inoue and S. Uemura, *Chem. Commun.*, 2000, 1245; G. T. Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636; A. Abad, C. Almela, A. Corma and H. Garcia, *Chem. Commun.*, 2006, 3178; H. Tsunoyama, H. Sakurai, Y. Negishi and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 9374; M. Nechab, C. Einhorn and J. Einhorn, *Chem. Commun.*, 2004, 1500; T. Matsushita, K. Ebitani and K. Kaneda, *Chem. Commun.*, 1999, 265; K. Yamaguchi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2002, **41**, 4538.
2. W. J. Mijs and C. R. H. de Jonge, *Organic Synthesis by Oxidation with Metal Compounds*, Plenum Press, New York, 1986; B. M. Trost and I. Fleming, *Comprehensive Organic Synthesis*, Pergamon Press, Oxford, 1991; G. Cainelli and G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer-Verlag, Berlin, 1984.
3. Z. Opre, D. Ferri, F. Krumeich, T. Mallat and A. Baiker, *J. Catal.*, 2006, **241**, 287; N. Zheng and G. D. Stucky, *Chem. Commun.*, 2007, 3862; A. Abad, P. Concepcion, A. Corma and H. Garcia, *Angew. Chem., Int. Ed.*, 2005, **44**, 4066; A. Biffis, S. Cunial, P. Spontoni and L. Prati, *J. Catal.*, 2007, **251**, 1; Y. Uozumi and R. Nakao, *Angew. Chem. Int. Ed.*, 2003, **42**, 194; K. Yamaguchi and N. Mizuno, *Chem.–Eur. J.*, 2003, **9**, 4353; K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2002, **124**, 11572.
4. C. Donze, P. Korovchenko, P. Gallezot and M. Besson, *Appl. Catal. B*, 2007, **70**, 621; P. Korovchenko, C. Donze, P. Gallezot and M. Besson, *Catal. Today*, 2007, **121**, 13; C. Bronnimann, Z. Bodnar, R. Aeschimann, T. Mallat and A. Baiker, *J. Catal.*, 1996, **161**, 720; T. Mallat, C. Bronnimann and A. Baiker, *Appl. Catal. A: General*, 1997, **149**, 103.
5. H. H. C. M. Pinxt, B. F. M. Kuster and G. B. Marin, *Appl. Catal. A: General*, 2000, **191**, 45; T. Mallat, Z. Bodnar, P. Hug and A. Baiker, *J. Catal.*, 1995, **153**, 131; P. Gallezot, *Catal. Today*, 1997, **37**, 405; N. Dimitratos, A. Villa, D. Wang, F. Porta, D. Su and L. Prati, *J. Catal.*, 2006, **244**, 113; R. Oi and S. Takenaka, *Chem. Lett.*, 1988, 115; A. Deffernez, S. Hermans and M. Devillers, *Appl. Catal. A: General*, 2005, **282**, 303; C. Keresszegi, T. Mallat, J. Grunwaldt and A. Baiker, *J. Catal.*, 2004, **225**, 138.
6. F. Alardin, B. Delmon, P. Ruiz and M. Devillers, *Catal. Today*, 2000, **61**, 255; S. Hermans and M. Devillers, *Catal. Lett.*, 2005, **99**, 55; M. Besson and P. Gallezot, *Catal. Today*, 2000, **57**, 127.
7. Y. H. Ng, S. Ikeda, T. Harada, S. Higashida, T. Sakata, H. Mori and M. Matsumura, *Adv. Mater.*, 2007, **19**, 597; Y. H. Ng, S. Ikeda, T. Harada, S. Park, T. Sakata, H. Mori and M. Matsumura, *Chem. Mater.*, 2008, **20**, 1154.
8. A general procedure for oxidation of 1-phenylethanol is as follows: into a reaction vessel equipped with a reflux condenser and balloon were placed the *n*Pt@*h*C (4.7 mg, Pt: 0.5 μmol), 1-phenylethanol (0.25 mmol), and water (2.5 cm^3). Then the mixture was heated at 333 K for 24 h under an atmospheric pressure of O_2 with vigorous stirring. After the reaction, the solution was transferred into a sample tube and extracted with diethyl ether. A portion of the diethyl ether solution was withdrawn and subjected to GC analysis.
9. Polyvinylpyrrolidone-stabilized Pt (Pt-PVP) was synthesized as follows: PVP (66 mg) was added to a solution of hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$; 0.03 mmol, 15.5 mg) in water (5 ml) and ethanol (45 ml) and the mixture was heated under reflux for 3 h.
10. Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, *Angew. Chem., Int. Ed.*, 2007, **46**, 704; T. Wang, C. Xiao, L. Yan, L. Xu, J. Luo, H. Shou, Y. Kou and H. Liu, *Chem. Commun.*, 2007, 4375; A. Biffis and L. Minati, *J. Catal.*, 2005, **236**, 405.
11. S. E. Martin and D. F. Suarez, *Tetrahedron Lett.*, 2002, **43**, 4475; B. Zhan and A. Thompson, *Tetrahedron*, 2004, **60**, 2817; K. Yamaguchi and N. Mizuno, *New J. Chem.*, 2002, **26**, 972; M. J. Schultz, S. S. Hamilton, D. R. Jensen and M. S. Sigman, *J. Org. Chem.*, 2005, **70**, 3343.

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