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Pt, Pd and Au nanoparticles supported on a DNA–MMT hybrid: efficient catalysts for highly selective oxidation of primary alcohols to aldehydes, acids and esters†

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Novel DNA–MMT hybrid supported metal nanoparticle catalysts, such as Pt/DNA–MMT, Pd/DNA–MMT, Au/DNA–MMT, were prepared for application in highly selective aerobic oxidation of primary alcohols to aldehydes, acids and esters, respectively. Taking advantage of the water-soluble reversibility of these catalysts, all the transformations could be performed smoothly in water and reuse of the catalysts has also been accomplished by a very simple phase separation process.

The selective oxidation of alcohols has been considered as one of the most fundamental transformations in organic chemistry, both for laboratory research and industrial manufacturing. Traditionally, such transformation has been performed with stoichiometric inorganic oxidants and notably chromium reagents, accompanied with a large amount of waste.[1] From the viewpoints of atom economy and environmental concern, more and more attention has been directed toward the aerobic oxidation of alcohols catalyzed by reusable heterogeneous catalysts using molecular oxygen as the oxidant.[2] Recently, heterogeneous catalysts for selective oxidation of secondary alcohols to ketones have been widely developed.[3] But selective oxidation of primary alcohols to the corresponding aldehydes is difficult because primary alcohols often suffer from overoxidation to generate acids. Esterification is also one of the most fundamentally important reactions in organic synthesis. The traditional esterification usually requires synthesis of carboxylic acids or activated carboxylic acid derivatives such as acid anhydrides or acid chlorides.[4] So the selective aerobic oxidation of alcohols to esters is more attractive and challenging for organic synthesis and green chemistry. Although the direct transformation of alcohols to esters by dehydrogenation of alcohols has been developed,[5] the direct oxidative esterification from alcohols using molecular oxygen is rare.[6]

Recently organic–inorganic hybrids, maintaining mechanical properties of both organic and inorganic materials, have received much attention.[7] Montmorillonite (MMT), which is a type of naturally occurring clay, has been used as a host material in the preparation of composites and has potential applications in catalysis, separation, and the optical and electrical fields.[8] And the natural DNA has been applied successfully as the template of metal nanoparticles by our group for organic reactions.[9] Taking advantage of the easy availability and good water dispersibility of MMT and DNA, we chose Na–MMT and fish sperm DNA as the starting materials to synthesize the hybrid. Herein, we describe the highly selective oxidation of primary alcohols to the corresponding carbonyl compounds, such as aldehydes, acids and esters under mild conditions in water, catalyzed by novel DNA and MMT hybrid (DNA–MMT) supported metal nanoparticle catalysts (metal/DNA–MMT).

First of all, a hybrid of DNA–MMT was successfully prepared. After preparation of the hybrid, the different catalysts Pt/DNA–MMT, Pd/DNA–MMT, Au/DNA–MMT were synthesized according to the method reported previously by our group (see experimental details in the ESI†). These metal/DNA–MMT catalysts exhibited stability in air with good reversible solubility in water and ethanol. When the catalysts were characterized (see the ESI† for the detailed analyses), we employed them directly in selective aerobic oxidation of benzyl alcohol (**1a**) in water at room temperature with $LiOH\cdot H_2O$ as a base (Table 1, entries 1–3). To our delight, the Pd/DNA–MMT catalyst showed high catalytic activity for oxidation of benzyl alcohol (**1a**) to benzoic acid (**3a**) with an excellent yield of 99%. Although the catalytic activities of Pt/DNA–MMT and Au–DNA–MMT were not very high under these conditions, Pt/DNA–MMT and Au/DNA–MMT could oxidize **1a** to benzaldehyde (**2a**) and benzyl benzoate (**4a**), respectively, with high selectivity. After simple optimization, when the temperature was 60 °C and potassium phosphate was used as the base, Pt/DNA–MMT could selectively oxidize **1a** to **2a** with a good yield of 86% (Table 1, entry 6). The yield of **4a** improved to 95% when Au/DNA–MMT was employed as the catalyst under the optimal conditions (Table 1, entry 9). Moreover, the comparison of these metal/DNA–MMT catalysts with the reported metal/DNA

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† Electronic supplementary information (ESI) available: Experimental details, characterization of catalysts and characterization of products. See DOI: 10.1039/c3cc41545g

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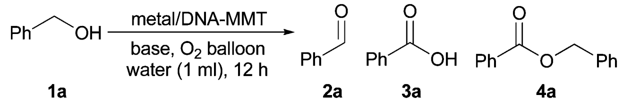
Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Base (equiv.)	Yield[b] (%)		
			2a	3a	4a
1[c]	*Pt/DNA–MMT*	*LiOH·H_2O (1.5)*	*<1*	*99*	*n.d.*
2[c]	Pt/DNA–MMT	LiOH·H_2O (1.5)	33	12	n.d.
3[c]	Au/DNA–MMT	LiOH·H_2O (1.5)	15	5	38
4[d]	Pt/DNA–MMT	LiOH·H_2O (1.5)	60	38	n.d.
5[d]	Pt/DNA–MMT	$K_3PO_4\cdot 3H_2O$ (1.5)	70	26	n.d.
6[d]	*Pt/DNA–MMT*	*$K_3PO_4\cdot 3H_2O$ (0.05)*	*86*	*7*	*n.d.*
7[e]	Au/DNA–MMT	LiOH·H_2O (1.5)	20	30	46
8[e]	Au/DNA–MMT	Cs_2CO_3 (1.5)	11	9	75
9[e]	*Au/DNA–MMT*	*Cs_2CO_3 (0.75)*	*3*	*<1*	*95*

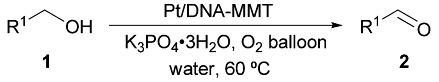
[a] Reaction conditions: **1a** (0.50 mmol), metal/DNA–MMT (Pt: 1.5 mol%, Pd: 1.7 mol%, Au: 2.9 mol%). [b] Determined by GC-MS with an internal standard. [c] 25 °C. [d] 60 °C. [e] 50 °C.

catalysts showed that metal/DNA–MMT catalysts had higher catalytic activity (see Table S1, ESI†).

With the optimized conditions in hand, the selective oxidation of various alcohols to the corresponding aldehydes was studied (Table 2). Table 2 shows that substituents on the aromatic ring hardly affected the reactivity and all the alcohols could afford the products in good to excellent yields. And the retrieved catalysts could be reused without a significant loss of their high catalytic performance (Tables 2–4, entry 1).

Subsequently, the scope of the alcohols in the reaction catalyzed by Pd/DNA–MMT was extended under the optimal conditions (Table 3). The reactions with alcohols bearing electron-withdrawing groups (entries 2–5) and electron-donating substituents (entries 6–8) proceeded smoothly to give the desired products in excellent yields. When strong electron-withdrawing groups were used, the reaction temperature needed to be elevated (entries 9 and 10). Moreover, heterobenzylic alcohol was also a good reaction substrate (entries 11 and 12).

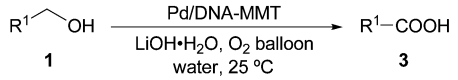
Table 2 Selective oxidation of alcohols to aldehydes[a]



Entry	R^1	Product	Yield[b] (%)
1	Ph	**2a**	86(80[c])
2	4-F-Ph	**2b**	78
3	3-F-Ph	**2c**	75
4	4-Cl-Ph	**2d**	96
5	3-Cl-Ph	**2e**	87
6	4-Me-Ph	**2f**	74
7	3-MeO-Ph	**2g**	90
8	4-MeO-Ph	**2h**	98

[a] Reaction conditions: **1** (0.50 mmol) in 1 mL of H_2O, Pt/DNA–MMT (Pt: 1.5 mol%), $K_3PO_4\cdot 3H_2O$ (0.05 equiv.), 60 °C, O_2 balloon, 12 h. [b] Determined by GC-MS using diphenyl as an internal standard. [c] Reuse of the catalyst at the third round.

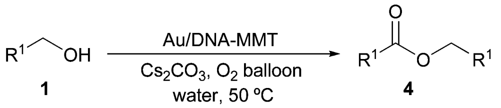
Table 3 Selective oxidation of alcohols to carboxylic acid[a]



Entry	R^1	Product	Yield[b] (%)
1	Ph	**3a**	98 (89[c])
2	4-F-Ph	**3b**	94
3	3-F-Ph	**3c**	93
4	4-Cl-Ph	**3d**	90
5	3-Cl-Ph	**3e**	85
6	4-Me-Ph	**3f**	95
7	3-Me-Ph	**3g**	88
8	4-MeO-Ph	**3h**	83
9[d]	4-NO_2-Ph	**3i**	76
10[e]	4-CF_3-Ph	**3j**	83
11	2-Thienyl	**3k**	76
12	2-Furyl	**3l**	75

[a] Reaction conditions: **1** (0.50 mmol) in 1 ml of H_2O, Pd/DNA–MMT (Pd: 1.7 mol%), LiOH·H_2O (1.5 equiv.), 25 °C, O_2 balloon, 12 h. [b] Isolated yield. [c] Reuse of the catalyst at the fifth round. [d] 50 °C. [e] 80 °C.

Table 4 Selective oxidation of alcohols to esters by self-esterification[a]



Entry	R^1	Product	Yield[b] (%)
1	Ph	**4a**	94 (81[c])
2	4-F-Ph	**4b**	71
3	4-Cl-Ph	**4c**	74
4	4-Br-Ph	**4d**	85
5	2-Br-Ph	**4e**	54
6	4-Me-Ph	**4f**	73
7	3-Me-Ph	**4g**	70
8	4-MeO-Ph	**4h**	61
9	4-NO_2-Ph	**4i**	51
10	2-NO_2-Ph	**4j**	—
11[d]	2-Naphthyl	**4k**	67

[a] Reaction conditions: **1** (0.50 mmol) in 1 ml of H_2O, Au/DNA–MMT (Au: 2.9 mol%), Cs_2CO_3 (0.75 equiv.), 50 °C, O_2 balloon, 12 h. [b] Isolated yield. [c] Reuse of the catalyst at the fifth round. [d] 20 h.

As for Au/DNA–MMT, the direct catalytic transformation of different alcohols to esters was also studied (Table 4). The electronic effect of the aromatic substitution of the alcohols had little influence on the reaction and a series of functional groups including fluoro, chloro, bromo, methyl, methoxy and nitro were well tolerated to give the desired products in moderate to good yields (entries 2–4 and 6–9). However, the steric effect of the substituents had a great influence on the reaction. The yield of 4-bromobenzyl alcohol was apparently higher than that of 2-bromobenzyl alcohol (entries 4 and 5) and **4j** could not be obtained when the nitro group was at the *ortho*-position of the benzene ring (entry 10). The reaction of the large steric hindrance substrate also proceeded smoothly upon increasing the reaction time (entry 11).

To get insight into the mechanism of the selective oxidation of alcohols, some control experiments were performed (Scheme 1). Firstly, the selective oxidation of alcohols to acids was studied. Benzoic acid was not observed and only a small amount of benzaldehyde was obtained in the absence of water. It was noted that water was crucial for this oxidation of alcohols. Moreover, cross-esterification was performed with *o*-nitrobenzyl alcohol and various benzyl alcohols, affording the corresponding esters in moderate to good yields. The reaction of *o*-nitrobenzyl alcohol

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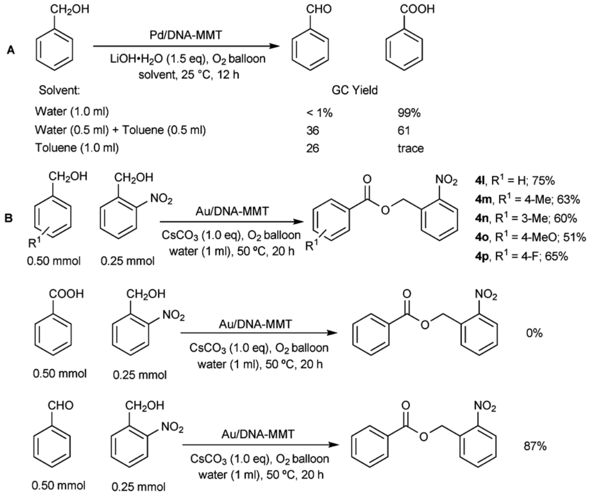
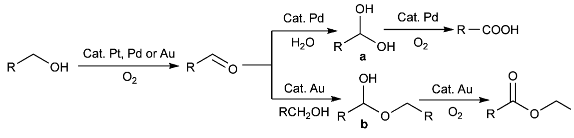


Scheme 1 Control experiments for the reaction mechanism.



Scheme 2 Plausible reaction mechanism.

with benzaldehyde can be carried out smoothly to obtain the ester with a good yield (87%) whereas the reaction of *o*-nitrobenzyl alcohol with benzoic acid did not work. These results indicated that the aldehyde rather than the carboxylic acid should be the intermediate of this transformation.

In terms of these experimental results and previous reports,[5b,6,9b] the possible mechanism is depicted in Scheme 2. First of all, the alcohol is oxidized to the aldehyde under the catalysis of Pt/DNA–MMT, Pd/DNA–MMT or Au/DNA–MMT. Then the aldehyde is selectively converted to the diol (**a**) by hydration and **a** was rapidly oxidized to the product of acid under the catalysis of Pd/DNA–MMT, which is the first pathway. The other pathway is that the alcohol attacks the aldehyde to generate the hemiacetal (**b**) and the product of ester is obtained by oxidation of **b** in the presence of Au/DNA–MMT.

In conclusion, we have developed novel Pt, Pd and Au nanoparticle catalysts supported on a hybrid of natural DNA and MMT, which show higher activity and selectivity for oxidation of primary alcohols than DNA-templated nanoparticles. Depending on these catalytic systems, highly efficient formation of the corresponding aldehydes, carboxylic acids and esters is achieved. Both oxidative self-esterification as well as cross-esterification of various alcohols can be performed smoothly. Although bimetallic nanoparticles as efficient catalysts for selective oxidation of primary alcohols to the aldehydes, carboxylic acids and esters have been reported,[6e] to the best of our knowledge, this is the first example of these transformations catalyzed by monometallic nanoparticles. Taking advantage of the water-soluble reversibility of these catalysts, all the transformations proceed well in water under mild conditions and the catalysts can be recovered and reused by a simple phase separation process. Detailed mechanistic studies and other applications of these catalysts in organic reactions are in progress.

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Notes and references

1 (*a*) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weeden, *J. Chem. Soc.*, 1946, 39; (*b*) G. Cainelli and G. Cardillo, *Chromium oxidation in organic chemistry*, Springer, Berlin, 1984.

2 (*a*) G. ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636; (*b*) Y. Uozumi and R. Nakao, *Angew. Chem., Int. Ed.*, 2003, **42**, 194; (*c*) K. Mori, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 10657; (*d*) T. Malat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037; (*e*) H. Tsunoyama, H. Sakurai, Y. Negishi and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 9374; (*f*) Y. H. Ng, S. Ikeda, T. Harada, Y. Morita and M. Matsumura, *Chem. Commun.*, 2008, 3181.

3 (*a*) H. Miyamura, R. Matsubara, Y. Miyazaki and S. Kobayashi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4151; (*b*) J. Zheng, S. Y. Lin, X. H. Zhu, B. W. Jiang, Z. Yang and Z. Y. Pan, *Chem. Commun.*, 2012, **48**, 6235; (*c*) D. Tsukakmoto, Y. Shiraishi, Y. Sugano, S. Lchikawa, S. Tanaka and T. Hirai, *J. Am. Chem. Soc.*, 2012, **134**, 6309; (*d*) C. Shang and Z.-P. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 9938; (*e*) B. KaRimi and F. K. Esfahani, *Adv. Synth. Catal.*, 2012, **354**, 1319; (*f*) A. Buonerba, C. Cuomo, S. O. Sánchez, P. Canton and A. Grassi, *Chem.–Eur. J.*, 2012, **18**, 709; (*g*) Z. S. Hou, N. Theyssen, A. Brinkmann and W. Leitner, *Angew. Chem., Int. Ed.*, 2005, **44**, 1346.

4 (*a*) J. Iqbal and R. R. Srivastava, *J. Org. Chem.*, 1992, **57**, 2001; (*b*) J. Otera, *Chem. Rev.*, 1993, **93**, 1449; (*c*) K. Ishihara, M. Kubota, H. Kurihara and H. Yamatoto, *J. Am. Chem. Soc.*, 1995, **117**, 4413; (*d*) G. W. Breton, *J. Org. Chem.*, 1997, **62**, 8952.

5 (*a*) J. Zhang, E. Balaraman, G. Leitus and D. Milstein, *Organometallics*, 2011, **30**, 5716; (*b*) C. Gunanathan, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2009, **131**, 3146; (*c*) S. Musa, L. Shaposhnikov, S. Cohen and D. Gelman, *Angew. Chem., Int. Ed.*, 2011, **50**, 3533.

6 (*a*) F.-Z. Su, J. Ni, H. Sun, Y. Cao, H.-Y. He and K.-N. Fan, *Chem.–Eur. J.*, 2008, **14**, 7131; (*b*) R. L. Oliveira, P. K. Kiyohara and L. M. Rossi, *Green Chem.*, 2009, **11**, 1366; (*c*) T. Ishida, M. Nagaoka, T. Akita and M. Haruta, *Chem.–Eur. J.*, 2008, **14**, 8456; (*d*) S. Gowrisankar, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 5139; (*e*) K. Kaizuka, H. Miyamura and S. Kabayashi, *J. Am. Chem. Soc.*, 2010, **132**, 15096; (*f*) S. Arita, T. Koike, Y. Kayaki and T. Ikariya, *Chem.–Asian. J.*, 2008, **3**, 1479.

7 (*a*) Y. S. Choi, K. H. Wang, M. Z. Xu and I. J. Chung, *Chem. Mater.*, 2002, **14**, 2936; (*b*) A. Dolbecq, E. Dumas, C. R. Mayer and P. Mialane, *Chem. Rev.*, 2010, **110**, 6009; (*c*) V. M. Agranovich, Yu. N. Gartstein and M. Litinskaya, *Chem. Rev.*, 2011, **111**, 5179; (*d*) M. P. Shores, B. M. Bartlett and D. G. Nocera, *J. Am. Chem. Soc.*, 2005, **127**, 17986.

8 (*a*) T. J. Pinnavaia, *Science*, 1983, **220**, 365; (*b*) B. M. Choudary, M. L. Kantam, K. V. S. Ranganath and K. K. Rao, *Angew. Chem., Int. Ed.*, 2005, **44**, 322; (*c*) B. Veisz, Z. Király, L. Tóth and B. Pécz, *Chem. Mater.*, 2002, **14**, 2882; (*d*) L. X. Shao and M. Shi, *Adv. Synth. Catal.*, 2003, **345**, 963; (*e*) S. D. Miao, Z. M. Liu, B. X. Han, J. Huang, Z. Y. Sun, J. L. Zhang and T. Jiang, *Angew. Chem., Int. Ed.*, 2006, **45**, 266.

9 (*a*) Y. Wang, G. H. Ouyang, J. T. Zhang and Z. Y. Wang, *Chem. Commun.*, 2010, **46**, 7912; (*b*) Y. Wang, D. P. Zhu, L. Tang, S. J. Wang and Z. Y. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1; (*c*) L. Tang, H. Y. Sun, Y. F. Li, Z. G. Zha and Z. Y. Wang, *Green chem.*, 2012, **14**, 3423.