Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Experimental details

1) *Preparation of the catalytic materials*

1, 3, 5-trisubstituted benzene spacer (**1**; 1, 3, 5-tris[(3-methylimidazolio)methyl]-2,4,6-trimethylbenzene tribromide) was synthesized through a well-established method [1, 2, 3]. The ligand **1** (1.0 mmol, 0.645g) was dissolved in 10 ml deionized water. $Na[AuCl_4]$ (0.02mmol) was dissolved in 1.0 ml deionized water and added into the solution of **1**. Yellow precipitates were formed. NH_2NH_2 (0.022 mmol in 1.0 ml H_2O) was added into the above mixture by a microinjector under sonication. A purple solution of Au nanoparticles was obtained. $H_5PV_2Mo_{10}O_{40}$ (1.0 mmol, 1.74 g) in 5.0 ml deionized water was added into the solution of Au nanoparticles and 1. The floccule solids were collected by centrifugation and washed by deionized water for five times. The solids were further washed with ethanol and diethyl ether and dried under N_2 flow. The resulting catalyst was stored in nitrogen atmosphere.

2) Activity testing

To a 100-ml Schlenk tube were added 10ml deionized water, 1.0 mmol substrate, 10 mg catalyst (approximately 1.0 mol% of the substrate). The reaction mixtures were stirred in open air at the given reaction temperature for 3.0 h. After the reaction, the mixtures were destroyed by ultrasonic treatment. The catalyst was separated by centrifugation and recovered by water washing and directly recycled to the next reaction batch. The liquid phase was determined by GC. GC was carried out over GC-2014 (SHIMADZU) with high temperature capillary column (MXT-1, 30m, 0.25mm ID) and FID detector.

3) *Materials characterization*

Transmission electron microscopy (TEM) was performed on a JEOL 2010 TEM operated at an accelerating voltage of 200 kV. The Au and Mo concentrations in the aqueous solution after the reaction were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) by using Perkin Elmer Optima 5300 dv.

Reference

[1] P. J. Cragg, in *A Practical Guide to Supramolecular Chemistry*, John Wiley & Sons Ltd, Chichester, 2005, pp30-34.
[2] K. Sate, S. Arap, T. Yamagishi, *Tetrahedron Lett.* 1999, **40**, 5219-5222.
[3] J. Howarth, N. A. Al-Hashimy, *Tetrahedron Lett.* 2001, **42**, 5777–5779.

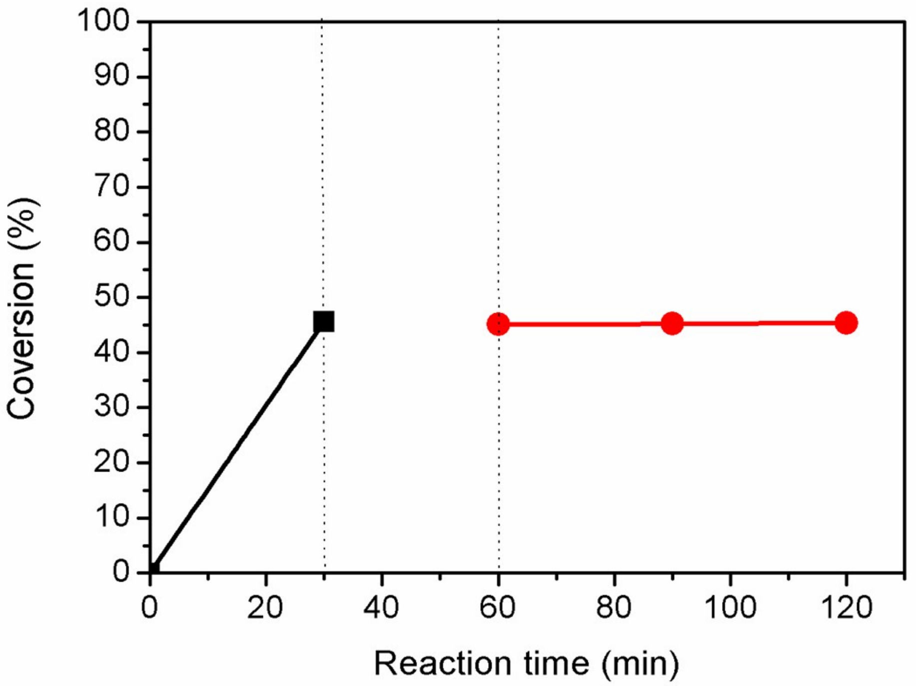

Fig. S1 Hot filtration test of Au NPs/1/POM catalyst for benzyl alcohol oxidation. Reaction conditions: 10ml deionized water, 1.0 mmol benzyl alcohol, 10 mg catalyst (approximately 1.0 mol% of the substrate), stirred in open air, reaction temperature: 75℃.

Table S1 Typical catalytic aerobic oxidation of alcohols

Entry	Catalysts and Reaction Conditions	Typical Substrates	Target compound yield (%)	References
1	Homogeneous catalyst 2 mol% $Mn(NO_3)_2$, 2mol% $Co(NO_3)_2$, 10mol% TEMPO, acetic acid, 40℃,1atm O_2	 n-$C_6H_{13}CH_2OH$ n-$C_7H_{15}CH(CH_3)OH$ $PhCH_2OH$ $PhCH(CH_3)OH$ $PhCH{=}HCH_2OH$	Aldehyde or ketone 97(6h) 100(5h) 98(10h) 98(6h) 99(3h)	Cecchetto, A., Fontana, F., Minisci, F., and Recupero, F. (2001) Tetrahedron Lett., 42, 6651.
2	Homogeneous catalyst 1 mol% $H_5PV_2Mo_{10}O_{40}$, 3mol% TEMPO, acetone, 100℃, 2atm O_2	n-$C_7H_{15}CH_2OH$ n-$C_6H_{13}CH(CH_3)OH$ $PhCH_2OH$ cis-$C_3H_7CH{=}CHCH_2OH$	98(18h) 96(18h) 100(6h) 100(10h)	Daniel, R.B., Alsters, P., and Neumann, R. (2001) J. Org. Chem., 66, 8650.
3	Homogeneous catalyst [Cu(MeCN)4]X (5 mol%), bpy (5 mol%), TEMPO (5 mol%), NMI (10 mol%), CH_3CN, air, 25℃	$PhCH_2OH$	Conversion and aldehyde selectivity >95 (<99) (3h)	J. M. Hoover and S. S. Stahl, J. Am. Chem. Soc., 2011, 133, 16901.
4	Homogeneous catalyst $RuCl_2(PPh_3)_3$ (0.5 mol%) TEMPO (1.5 mol%), PhCl, O_2–N_2 (8:92 v/v) 10 bar, 100℃	$PhCH_2OH$	Conversion and aldehyde selectivity >99 (>99) (2.5h)	A. Dijksman, A. Marino-Gonzalez, J. Am. Chem. Soc., 2001, 123, 6826.
5	Homogeneous catalyst Pd(OAc)2 (3 mol%), TEA (6 mol%), 3 A MS, THF–toluene , O_2, 25℃	$PhCH_2OH$	Conversion and aldehyde selectivity 84 (>99) (12h)	M. J. Schultz, C. C. Park and M. S. Sigman, Chem. Commun., 2002, 3034.
6	Homogeneous catalyst $(HQ)_2V(O)(OiPr)$ (2 mol%), NEt_3 (10 mol%, DCE , Air, 60℃	$PhCH_2OH$	Conversion and aldehyde selectivity 82(>99) (24h)	S. K. Hanson, R. Wu and L. A. P. Silks, Org. Lett., 2011, 13, 1908.
7	Heterogeneous catalyst		Conversion and aldehyde selectivity	K. Yamaguchi, K. Mori, J.

	RuHAP, Toluene , Air, 80℃	$PhCH_2OH$	100 (95) (3h)	Am. Chem. Soc., 2000, 122, 7144.
8	Heterogeneous catalyst $Ru(OH)_x/Fe_3O_4$ (3.8 mol% Ru), Toluene, O_2, 105℃	$PhCH_2OH$	Conversion and aldehyde selectivity >99 (99) (1 h)	M. Kotani, T. Koike, Green Chem., 2006, 8, 735.
9	Heterogeneous catalyst Polyaniline-supported $VO(acac)_2$ (2.3 mol% V), Toluene, O_2, 100℃	$PhCH_2OH$	Conversion and aldehyde selectivity 98 (>99) (9 h)	S. R. Reddy, D. Da Tetrahedron Lett., 2004, 45, 3561.
10	Heterogeneous catalyst PdHAP-0 (0.2 mol%) , Trifluorotoluene, O_2, 90℃	$PhCH_2OH$	Conversion and aldehyde selectivity >99 (>99) (1 h)	K. Mori, T. Hara, T. Mizugaki, J. Am. Chem. Soc., 2004, 126, 10657.
11	Heterogeneous catalyst Pd/MgO (1 mol%), Trifluorotoluene, O_2, 70–80℃	$PhCH_2OH$	Conversion and aldehyde selectivity 100(>92) (20 h)	U. R. Pillai, Green Chem., 2004, 6, 161.
12	Heterogeneous catalyst Silica-supported Pd (3 mol% Pd), Toluene, O_2, 90℃	$PhCH_2OH$	Conversion and aldehyde selectivity 100 (>99) (2.5 h)	D. Choudhary, S. Paul, Green Chem., 2006, 8, 479.
13	Heterogeneous catalyst Pd@SBA-15 (0.4 mol%), K_2CO_3 (1 equiv.), Air, Toluene, 80℃	$PhCH_2OH$	Conversion and aldehyde selectivity >99(>99) (5.5 h)	B. Karimi, S. Abedi, Angew. Chem. Int. Ed., 2006, 45, 4776.
14	Heterogeneous catalyst AuCNT (0.2 mol%); NaOH (3 equiv.) , Air, THF, 25℃	$PhCH_2OH$	Conversion and aldehyde selectivity 100(>99) (12 h)	R. Kumar, E. Gravel, A. Hagege, H. Li, Nanoscale, 2013, 5, 6491.
15	Heterogeneous catalyst Au (2.7 wt%)/1%; CuO/3% MCM41, O_2, Toluene, 80℃	$PhCH_2OH$	Conversion and aldehyde selectivity 73(94) (20 h)	H. Wang, W. Fan, Y. He, J. Wang, J. Catal., 2013, 299, 10.

Table S2 Summary of specific influencing factors of alcohol oxidation over Au catalysts

Solvent-free oxidation of alcohols over Au catalysts
(D. I. Enache, D.W. Knight and G. J. Hutchings, Catal. Lett., 2005, 103, 43.)

Sample Name	Preparation Method	Alcohol Type	Conversion/%	1-Octanal Selectivity/%
0.7 wt% Au/SiO_2	Co-precipitation	1-octanol	0	–
5 wt% Au/Fe2O_3	Co-precipitation	1-octanol	1.5	55.9
2 wt% Au/CeO_2	Co-precipitation	1-octanol	0.57	100
2 wt% Au/TiO_2	Impregnation	1-octanol	0	–
2 wt% Au/C	Impregnation	1-octanol	0	–

Reaction conditions: 40 ml alcohol, 0.2 g catalyst, 1500 rpm, 100 °C, $pO_2 = 0.2$ MPa, 3 h reaction.

Sample Name	Preparation Method	Alcohol Type	Conversion/ %	Benzaldehyde Selectivity/%
0.7 wt% Au/SiO_2	co-precipitation	Benzyl alcohol	1.9	100
5 wt% Au/Fe_2O_3	co-precipitation	Benzyl alcohol	7.1	87.6
2 wt% Au/CeO_2	co-precipitation	Benzyl alcohol	3.4	100
2 wt% Au/TiO_2	impregnation	Benzyl alcohol	0.65	100
2 wt% Au/C	impregnation	Benzyl alcohol	2.3	90.4

Reaction conditions: 40 ml alcohol, 0.2 g catalyst, 1500 rpm, 100 °C, $pO_2 = 2$ bar, 3 hr reaction.

Base effect of 1-octanol oxidation over Au catalyst
(L. Prati, A. Villa, C. Campione and P. Spontoni, Top. Catal., 2007, 22, 319.)

Catalyst	Conversion/%	1-Octanal Selectivity/%	TOF/h^{-1}
In the absence of base			
1% Au/C	0	0	0
1% Pd/C	2	70	8
1% Pt/C	2	>99	10
1% Au–Pd/C	17	70	15
1% Au–Pt/C	20	75	22
Catalyst	Conversion/%	Octanoate selectivity/%	TOF/h^{-1}
In the presence of base (NaOH/octanol = 4)			
1% Au/C	23	96	58
1% Pd/C	2	97	8
1% Pt/C	4	90	10
1% Au–Pd/C	93	98	413
1% Au–Pt/C	62	78	210

Catalyst	Conversion/%	Selectivity/%			TOF/h^{-1}
		2-Octenal	3-Octene-1-ol	Octanal	
1% Au/C	0	0	0	0	0
1% Pd/C	3	0	0	0	24
1% Pt/C	1	0	0	0	5
1% Pd–Au/C	97	20	58	20	552
1% Pt–Au/C	8	10	90	0	39

Reaction conditions: substrate/metal = 1000, pO_2 = 3 atm, T = 50 °C, reaction time = 2 h.