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Unique catalysis of gold nanoparticles in the chemoselective hydrogenolysis with H_2: cooperative effect between small gold nanoparticles and a basic support†

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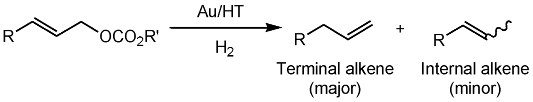
Gold nanoparticles on hydrotalcite act as a heterogeneous catalyst for the chemoselective hydrogenolysis of various allylic carbonates to the corresponding terminal alkenes using H_2 as a clean reductant. The combination of gold nanoparticles and basic supports elicited significantly unique and selective catalysis in the hydrogenolysis.

For heterogeneous catalysts, the size of the metal nanoparticles (NPs) and the interactions between the active metal species and the support greatly influence the catalytic activity.[1] In this context, considerable effort has been devoted to controlling the size of metal nanoparticles, screening supports, and altering the composition of the supports to achieve high catalytic performance. Recently, small Au NPs on appropriate supports have been revealed to show significantly unique catalytic abilities compared to other supported metal NPs, not only in oxidation reactions, but also in reduction reactions.[2,3] For example, atomically precise $Au_{25}(SR)_{18}$ nanoparticles on Fe_2O_3 and TiO_2 catalyze the selective hydrogenation of α,β-unsaturated carbonyl compounds to allylic alcohols through the coordination of carbonyl oxygen to the vacant site of Au nanoparticles,[3b] and Au/TiO_2 can selectively hydrogenate substituted nitroaromatics to the corresponding anilines where the favored adsorption of the nitro group on the TiO_2 surface leads to the high chemoselectivity.[2a] We have also found that Au NPs supported on hydrotalcite (Au/HT) and on hydroxyapatite (Au/HAP) showed high catalytic activities towards the chemoselective reductions of epoxides[4–6] and amides[7] to the corresponding alkenes and amines, respectively, and the activities and chemoselectivities of the Au NPs were much higher than those of other metal NPs.

Hydrogenolysis of allylic heterosubstituents to alkenes is important in organic chemistry because it allows the preparation of various alkenes and the use of an allyl group as a protective group for alcohols, carboxylic acids and amines.[8,9] To date, allylic heterosubstituents have been transformed into the corresponding *internal* alkenes through hydrogenolysis using Pd/C with H_2,[9a,10] $RhCl(PPh_3)_3$ with *N*-propyl-1,4-dihydronicotinamide,[11] and $Pd(PPh_3)_4$ with silanes,[12] potassium boron hydride,[13] or metal hydrides.[14] On the other hand, catalytic systems for the production of the corresponding *terminal* alkenes from allylic heterosubstituents are rare; only Pd–phosphine complexes with formates or SmI_2 as a reductant have been reported.[15] These Pd complex systems, however, suffer from the requirement of additional phosphines and amines, the use of stoichiometric amounts of hazardous reductants, and a tedious workup for the separation and reuse of the catalysts. Therefore, the development of a green catalytic system for the hydrogenolysis of allylic heterosubstituents to *terminal* alkenes using heterogeneous catalysts with H_2 as a clean reductant is a challenging issue.

Herein, we report that hydrotalcite-supported Au NPs (Au/HT) efficiently catalyze the hydrogenolysis of allylic carbonates to the corresponding *terminal* alkenes with H_2 as an ideally green reductant (Scheme 1). The chemoselectivity is significantly superior to those of other metal NPs. To the best of our knowledge, this report is the first example of the selective hydrogenolysis of allylic carbonates to *terminal* alkenes with H_2.

The hydrogenolysis of cinnamyl methyl carbonate (**1**) using various supported Au NPs of similar particle sizes[16] was carried out in toluene under an atmospheric pressure of H_2 (Table 1). Au/HT exhibited the highest activity, affording the corresponding terminal alkene 3-phenylpropene (**2**) and the internal alkene β-methyl styrene (**3**) in 98% selectivity (**2** : **3** = 10 : 1), as well as small amounts of the alkane by-products 3-phenylpropane (PP) and methyl 3-phenylpropyl carbonate (PC) (entry 1). The basic MgO support also showed high selectivity for **2**, but the yield of **2** was much lower than that obtained with Au/HT (entry 8). Weakly basic supports such as CeO_2 and Al_2O_3 resulted in moderate yields of **2** with lower selectivities (entries 6 and 7). The non-basic supports TiO_2 and SiO_2 showed extremely low activities in this transformation (entries 9 and 10). No reaction occurred when unsupported



Scheme 1

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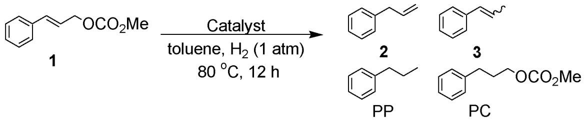
Table 1 Hydrogenolysis of **1** using various catalysts with H_2[a]



Entry	Catalyst	*d* (nm)	Conv.[b] (%)	Sel.[b] (%)			
				2 and **3**	**2** : **3**	PP	PC
1	Au/HT	2.7	> 99	98	10 : 1	< 1	< 1
2[c]	Au/HT	2.7	> 99	> 99	10 : 1	0	0
3[c,d]	Au/HT	2.7	> 99	> 99	10 : 1	0	0
4[c,e]	Au/HT	2.7	99	> 99	10 : 1	0	0
5[c,f]	Au/HT	2.7	98	> 99	10 : 1	0	0
6	Au/CeO_2	3.8	78	62	8 : 1	3	35
7	Au/Al_2O_3	3.6	86	46	7 : 1	12	42
8	Au/MgO	3.1	32	97	9 : 1	1	2
9	Au/TiO_2	3.7	23	49	8 : 1	8	43
10	Au/SiO_2	14	< 1	—		—	—
11	Au NPs[g]	3.5	0	—		—	—
12[h]	Pd/HT		> 99	0		10	90
13[h]	Pd/C[i]		> 99	0		16	84
14[h]	Pt/HT		> 99	0		6	94
15	Rh/HT		17	0		15	85
16	Ru/HT		2	0		—	—
17	Ag/HT		1	0		—	—
18	Cu/HT		< 1	—		—	—
19	Au/HT	5.8	87	93	9 : 1	2	4
20	Au/HT	7.9	78	82	8 : 1	4	13
21	Au/HT	11	60	61	7 : 1	8	31
22	Au/HT	20	31	43	7 : 1	15	42

[a] Reaction conditions: catalyst (M: 2.3 mol%), toluene (5 mL), **1** (0.2 mmol). [b] Determined by GC using an internal standard technique. [c] 60 °C, 16 h. [d] 60 °C, 48 h. [e] Reuse 1. [f] Reuse 2. [g] Prepared according to ref. 17. [h] 1 h. [i] Obtained from Sigma Aldrich.

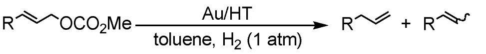
Au NPs were used and aggregation of the Au particles was observed (entry 11).[17] The above results clearly demonstrate that basic supports are necessary for the selective formation of **2** from **1**. Notably, lowering the reaction temperature to 60 °C increased the selectivity for the alkenes to over 99%, while suppressing the hydrogenation of the C=C bond of both **1** and **2** (entry 2). Moreover, the C=C bonds of the alkene products were completely intact, even after prolonged heating following the complete consumption of **1** (entry 3). To confirm whether the Au/HT-catalyzed hydrogenolysis occurs on the solid surface of Au/HT, Au/HT was removed by filtration from the reaction mixture at 40% conversion of **1**. Continuous treatment of the resulting filtrate under similar reaction conditions did not afford any products (see Fig. S3, ESI†). In addition, inductively coupled plasma (ICP) analysis showed the absence of Au species in the filtrate (detection limit of 0.1 ppm), revealing that no leaching occurred during the reaction. These results confirm that the hydrogenolysis proceeds on the Au NPs immobilized on the HT. The recovered Au/HT catalyst was reusable for a subsequent reaction without any pretreatment; Au/HT exhibited a high catalytic activity and selectivity in the reuse experiments without loss of its efficiency (entries 4 and 5).

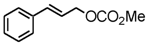
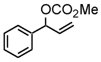
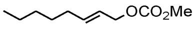
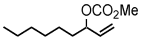
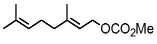
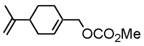
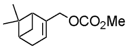
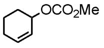
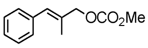
Next, various metal NPs supported on HT were examined in the hydrogenolysis of **1** under similar reaction conditions (entries 12, 14–18). When Pd/HT, Pt/HT and Rh/HT were used in place of Au/HT, the undesired hydrogenation of **1** occurred to give alkanes, and no alkene products were obtained (entries 12, 14 and 18). Other metal NPs on HT, such as Ru/HT, Ag/HT and Cu/HT, barely worked as catalysts (entries 16–18). The use of Pd/C[18] under the present conditions resulted in the formation of undesired alkanes (entry 13). These phenomena reveal that Au NPs have unique and high catalytic activity for the hydrogenolysis of allylic carbonates to alkenes with H_2.

The size effect of the Au NPs was then investigated. The hydrogenolysis of **1** with H_2 using a series of Au/HTs with different particle sizes was carried out (entries 1, 19–22).[19] Interestingly, the selectivity, as well as the yield of **2**, increased with a decrease in the size of the Au NPs. Larger Au NPs showed a lower selectivity for **2** due to hydrogenation of the C=C bonds of both **1** and **2**. These results suggest, therefore, that immobilization of small Au NPs on HT is essential for the selective hydrogenolysis of **1** to the terminal alkene **2**. The high chemoselectivity of Au/HT with small Au NPs in the hydrogenolysis of allylic carbonates to terminal alkenes was observed with other substrates (Table 2). Both aliphatic and alicyclic allylic carbonates, such as geranyl methyl carbonate, methyl perillyl carbonate and methyl mirtenyl carbonate, were selectively transformed into the corresponding terminal alkenes (entries 5–7).

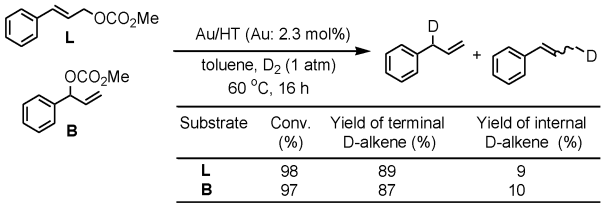
To investigate the reaction mechanism for the Au/HT-catalyzed hydrogenolysis, several control experiments were carried out. Both the linear allylic carbonate *trans*-cinnamyl methyl carbonate (**L**) and the branched allylic carbonate 1-phenyl-prop-2-enyl methyl carbonate (**B**) were treated with Au/HT under a H_2 atmosphere to afford the terminal alkene 3-phenylpropene with similar selectivity (Table 2, entries 1 and 2). The use of D_2 instead of H_2 in the Au/HT-catalyzed hydrogenolysis of both **L** and **B** provided 3-(D)-3-phenylpropene as a major product (Scheme 2). No hydrogenation, isomerization or H–D exchange reaction occurred when treating (H)-3-phenylpropene with D_2 in the presence of Au/HT. These results suggest that Au/HT-catalyzed hydrogenolysis may mainly proceed *via* a π-allyl

Table 2 Au/HT-catalyzed hydrogenolysis of allylic carbonates with H_2[a]



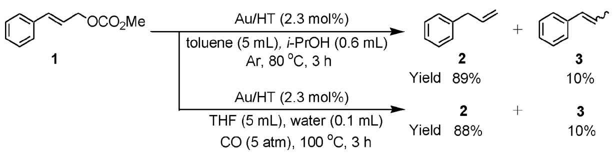
Entry	Substrate	Temp. (°C)	Time (h)	Conv.[b] (%)	Sel.[b] (%)	Terminal : internal
1		60	16	> 99	> 99	10 : 1
2		60	16	> 99	> 99	9 : 1
3		100	12	93	99	6 : 1
4		100	12	91	99	6 : 1
5		100	12	90	94	6 : 1
6		90	20	90	95	4 : 1
7		100	16	92	99	6 : 1
8		100	12	83	> 99	—
9		80	24	94	> 99	10 : 1

[a] Reaction conditions: Au/HT (Au: 2.3 mol%), toluene (5 mL), substrate (0.2 mmol). [b] Determined by GC using an internal standard technique.



Substrate	Conv. (%)	Yield of terminal D-alkene (%)	Yield of internal D-alkene (%)
L	98	89	9
B	97	87	10

Scheme 2



Scheme 3

intermediate generated from an allylic carbonate. In our previous studies on the deoxygenation of epoxides, it was found that the polar hydrogen species Au-hydride and H^+ were formed through cooperative effects between the Au NPs and the basic sites of HT when using 2-propanol or CO/H_2O, as well as H_2 as the reductant.[4,5] When 2-propanol or CO/H_2O was employed instead of H_2, hydrogenolysis of **1** also occurred to provide **2** and **3** with similar selectivity, which suggests the generation of Au-hydride and H^+ as active species in these reactions (Scheme 3).

Bearing in mind that the Au/HT-catalyzed hydrogenolysis of allylic carbonates may involve the generation of Au-hydride and H^+ species and the formation of π-allyl intermediates, the following reaction path is proposed. First, heterolytic dissociation of H_2 occurs at the interface between the Au NPs and the basic sites of HT to give Au-hydride and H^+ on the HT surface.[6] The H^+ species generated on the HT reacts with the allylic carbonate to form a π-allyl Au intermediate, followed by attack of the hydride to afford the corresponding alkene (see Fig. S4, ESI†). Hydride transfer to the more substituted C3-side of the π-allyl intermediate in the present Au/HT-H_2 system is not similar to the previously reported hydrogenolysis using $Pd(PPh_3)_4$ with metal hydride affording the internal alkenes *via* the attack of Pd-hydride on the less substituted C1-side.[12–14,20] This phenomenon is also different from the γ-attack of H^+ on η^1-allyl gold species giving the corresponding alkenes.[21]

In conclusion, Au/HT catalyzes the highly chemoselective hydrogenolysis of allylic carbonates to the corresponding terminal alkenes with H_2 without C=C bond hydrogenation of the substrates or products. The Au NPs exhibited significantly different selectivity from those of other metal NPs. The polar hydrogen species Au-hydride and H^+ are formed through the heterolytic cleavage of H_2 at the interface between the Au NPs and the HT surface, which may react with the allylic carbonates to selectively afford terminal alkenes *via* the formation of π-allyl intermediates. The effect of small Au NPs on the highly selective hydrogenation of the C–O bond can be explained by the increasing interfacial area between the Au NPs and the HT which enables the exclusive formation of Au-hydride and H^+. The present study highlights the importance of the combination of small gold nanoparticles and a basic support for achieving high chemoselectivity.

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Notes and references

1 (*a*) Y. Zhang, X. Cui, F. Shi and Y. Deng, *Chem. Rev.*, 2012, **112**, 2467; (*b*) A. Villa, M. Schiavoni and L. Prati, *Catal. Sci. Technol.*, 2012, **2**, 673; (*c*) T. Tsukuda, H. Tsunoyama and H. Sakurai, *Chem.–Asian J.*, 2011, **6**, 736.

2 (*a*) M. Boronat, P. Concepción, A. Corma, S. Gonzalez, F. Illas and P. Serna, *J. Am. Chem. Soc.*, 2007, **129**, 16230; (*b*) A. Corma and P. Serna, *Science*, 2006, **313**, 332.

3 (*a*) M.-M. Wang, L. He, Y.-M. Liu, Y. Cao, H.-Y. He and K.-N. Fan, *Green Chem.*, 2011, **13**, 602; (*b*) Y. Zhu, H. Qian, B. A. Drake and R. Jin, *Angew. Chem., Int. Ed.*, 2010, **49**, 1295; (*c*) P. Claus, H. Hofmeister and C. Mohr, *Gold Bull.*, 2004, **37**, 181.

4 T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2010, **49**, 5545.

5 T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem.–Eur. J.*, 2010, **16**, 11818.

6 A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2011, **50**, 2986.

7 Y. Mikami, A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem.–Eur. J.*, 2010, **17**, 1768.

8 J. Tsuji and T. Mandai, *Synthesis*, 1996, 1.

9 (*a*) N. K. Garg, D. D. Caspi and B. M. Stoltz, *J. Am. Chem. Soc.*, 2004, **126**, 9552; (*b*) R. J. Cvetovich, D. H. Kelly, L. M. DiMichele, R. F. Shuman and E. J. J. Grabowski, *J. Org. Chem.*, 1994, **59**, 7704.

10 D. D. Caspi, N. K. Garg and B. M. Stoltz, *Org. Lett.*, 2005, **7**, 2513.

11 K. Nakamura, A. Ohno and S. Oka, *Tetrahedron Lett.*, 1983, **24**, 3335.

12 E. Keinan and N. Greenspoon, *J. Org. Chem.*, 1983, **48**, 3545.

13 R. O. Hutchins, K. Learn and R. P. Fulton, *Tetrahedron Lett.*, 1980, **21**, 27.

14 (*a*) O. Dangles, F. Guibe and G. Balavoine, *J. Org. Chem.*, 1987, **52**, 4984; (*b*) E. Keinan and N. Greenspoon, *Tetrahedron Lett.*, 1982, **23**, 241; (*c*) H. Matsushita and E. Negishi, *J. Org. Chem.*, 1982, **47**, 4161; (*d*) R. O. Hutchins and K. Learn, *J. Org. Chem.*, 1982, **47**, 4382; (*e*) F. Guibe and Y. S. M'Leux, *Tetrahedron Lett.*, 1981, **22**, 3591.

15 (*a*) A. Yoshida, T. Hanamoto, J. Inanaga and K. Mikami, *Tetrahedron Lett.*, 1998, **39**, 1777; (*b*) T. Hayashi, H. Iwamura, M. Naito, Y. Matsumoto and Y. Uozumi, *J. Am. Chem. Soc.*, 1994, **116**, 775; (*c*) T. Mandai, T. Matsumoto, M. Kawada and J. Tsuji, *J. Org. Chem.*, 1992, **57**, 6090; (*d*) M. Oshima, I. Shimizu, A. Yamamoto and F. Ozawa, *Organometallics*, 1991, **10**, 1221; (*e*) J. Tsuji, I. Shimizu and I. Minami, *Chem. Lett.*, 1984, 1017; (*f*) J. Tsuji, T. Yamakawa, M. Kaito and T. Mandai, *Tetrahedron Lett.*, 1978, **18**, 2075; (*g*) H. Hey and H. J. Arpe, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 928.

16 T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Green Chem.*, 2009, **11**, 793.

17 N. R. Jana, L. Gearheart and C. J. Murphy, *Langmuir*, 2001, **17**, 6782.

18 It has been reported that commercially available Pd/C was effective in the hydrogenolysis of cyclic allylic carbonate (ref. 10) as well as various protective groups. See: (*a*) L. Jobron and O. Hindsgaul, *J. Am. Chem. Soc.*, 1999, **121**, 5835; (*b*) E. A. Papageorgiou, M. J. Gaunt, J. Yu and J. B. Spencer, *Org. Lett.*, 2000, **2**, 1049.

19 Au/HTs with different particle sizes were prepared by changing the Au content. See ref. 6 for the preparation of Au/HTs.

20 Hydride transfer to the more substituted C3-side of the π-allyl intermediate is observed in the Pd complex with formates. See ref. 8 and 15.

21 (*a*) S. Komiya and S. Ozaki, *Chem. Lett.*, 1988, 1431; (*b*) T. Sone, S. Ozaki, N. C. Kasuga, A. Fukuoka and S. Komiya, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1523.