Fully dispersed Pt entities on nano-Au dramatically enhance the activity of gold for chemoselective hydrogenation catalysis†

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Adding a small amount of fully dispersed Pt entities onto the Au surface in Au/SiO_2 catalyst is found to be an efficient approach to improve the catalytic activity of Au (up to 70-fold) for the hydrogenation of α,β-unsaturated carbonyl compounds, without alternating its selectivity towards C=O or C=C bond hydrogenation.

Chemoselective hydrogenation of α,β-unsaturated carbonyl compounds to their semi-hydrogenated products (*i.e.*, saturated carbonyl compounds from hydrogenation at the C=C bond conjugated with the carbonyl group and unsaturated alcohols from hydrogenation at the C=O bond) is a critical step in organic syntheses of fine chemicals such as fragrances, drugs and others.[1] Supported Au NPs were found to be highly selective towards the hydrogenation of either C=O or C=C bonds in the α,β-unsaturated carbonyl compounds such as cinnamaldehyde,[2,3] acrolein,[4] crotonaldehyde,[5] *etc.*,[6] depending on the size and/or morphology of Au NPs,[2–4] the nature of the support material[2] as well as the reaction conditions.[6] However, the hydrogenation activity of Au NPs was often much lower than those of the platinum-group metals,[5,6] most probably due to an "intrinsic" nobleness of Au for H_2 activation; the dissociative adsorption of H_2 on Au is an activated process and is restricted at the edge and corner sites or at the interface perimeter around Au NPs in contact with oxide support.[7] Such low hydrogenation activity of the Au NPs has been a major obstacle for achieving practical applications.

We have previously employed nearly monodisperse Au NPs to construct Pt-on-Au nanostructures (coded as Pt_m^Au, m refers to the atomic Pt/Au ratio) for electrocatalysts (Pt_m^Au/C) with significantly improved Pt utilization, by chemical deposition of Pt entities/flecks on the Au surface.[8] When the Au NPs were of *ca.* 3.0 nm, the Pt entities were obtained with 90 + % dispersions at $m \leq 0.1$ and showed distinctly high activity for the electrooxidation of methanol as well as formic acid; compared with the commercial Pt/C catalyst, the mass-specific activity of Pt in Pt_m^Au/C was enhanced by up to one order of magnitude for methanol electrooxidation[8] and two orders of magnitude for formic acid electrooxidation.[9] When Au NPs of varying sizes (3–10 nm), but carrying no Pt deposits, were immobilized on SiO_2, they showed high selectivity for the formation of hydrocinnamaldehyde (HCAL) in the hydrogenation of cinnamaldehyde (CAL).[3] We now report that a small amount of fully dispersed Pt entities in SiO_2-immobilized Pt_m^Au catalysts (Pt_m^Au/SiO_2, $m < 0.1$) can enhance up to 70-fold the activity of Au NPs for the chemoselective hydrogenation of α,β-unsaturated carbonyl compounds, without changing the selectivity propensity of Au NPs for the reactions. A possible explanation for this surprising chemistry is presented.

A series of colloidal Pt_m^Au samples was synthesized by reductive deposition of Pt atoms onto nearly mono-disperse PVA-stabilized Au NPs with sizes of 3.0 ± 0.6 nm,[8,9] the atomic Pt/Au ratio was controlled at $m = 0.005$–0.2. The dispersion or percentage exposed of Pt in each Pt_m^Au sample was measured electrochemically according to our previous procedures.[8,9] Immobilization of these colloidal Pt_m^Au with a non-interacting SiO_2 (Degussa, Aerosil 90) support produced the Pt_m^Au/SiO_2 catalysts (Au loading = 1 wt%) for the study of the chemoselective hydrogenation reactions (see ref. 3 and ESI†). The average size of the immobilized Au and Pt_m^Au particles became slightly larger than their colloidal counterparts (TEM images and size distributions of the immobilized Pt_m^Au nanoparticles are presented as Fig. S1 in ESI†), but the features of Au and Pt_m^Au NPs were not changed during the immobilization process.[3,8,9]

The chemoselective hydrogenation of CAL is a well studied "standard" reaction among the hydrogenation of α,β-unsaturated carbonyl compounds.[2,3,6,10] As schemed in Table 1, the hydrogenation at the C=C bond produces HCAL, an important intermediate for the syntheses of pharmaceuticals for the treatment of HIV,[11] while hydrogenation at the C=O bond produces cinnamyl alcohol (COL), a pharmaceutical intermediate for the syntheses of cinnarizine, naftifine, toremifene, *etc*. Summarized in Table 1 are the catalytic data of the Pt_m^Au/SiO_2 catalysts ($0 < m \leq 0.2$) for the hydrogenation of CAL. The Au NPs carrying no Pt (*i.e.*, Au/SiO_2 or Pt_m^Au/SiO_2 of $m = 0$) produced a low CAL conversion (11%) in a reaction period as long as 12 h. When the same Au NPs were loaded with a very small amount of Pt ($m = 0.005$), however, a dramatically higher CAL conversion (20%) was achieved in a reaction period of only 4 h. Increasing the amount of Pt up to $m = 0.2$ in the Pt_m^Au/SiO_2 catalyst resulted in continued shortening of the reaction period for achieving the CAL conversion between 11–20%. For instance, a reaction period of 15 min was found long enough to produce a CAL conversion of 15% over the $Pt_{0.05}$^Au/SiO_2 catalyst; the CAL conversion increased up to 23, 33, 44 and 63% when the reaction period was prolonged, respectively, to 0.5, 1.0, 2.0, and 4.0 h over this catalyst of $m = 0.05$ (see Table S1 of ESI†).

To make a rigorous comparison of the Au activity in these Pt_m^Au/SiO_2 catalysts, the mass specific activity of Au (MAS_{Au}, the CAL consumption rate by mol h^{-1} g_{Au}^{-1}) was calculated using the reaction data at CAL conversion levels

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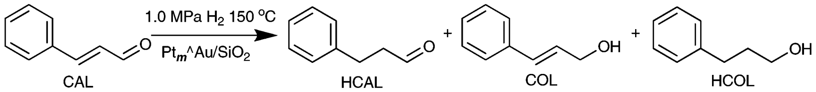
Table 1 Selective hydrogenation of cinnamaldehyde at 150 °C under 1.0 MPa H_2 (CAL/Au (molar) = 1600; stirring speed: 900 rpm)



Catalyst	Pt dispersion (%)	Rxn. time/min	CAL conv. (%)	Sel. (%) HCAL	COL	HCOL	MSA_{Au}/mol h^{-1} g_{Au}^{-1}	$TOF_{Pt}{}^{a}/s^{-1}$
SiO_2	—	240	0	—	—	—	—	—
Au/SiO_2	—	720	11	73	23	4	0.07 (1)[b]	—
$Pt_{0.005}$^Au/SiO_2	>99	240	20	77	15	8	0.40 (6)	4.42
$Pt_{0.01}$^Au/SiO_2	>99	120	19	79	17	4	0.76 (11)	4.42
$Pt_{0.05}$^Au/SiO_2	>99	15	15	72	19	9	4.77 (68)	5.24
$Pt_{0.1}$^Au/SiO_2	90.4	15	16	71	21	8	5.09 (73)	3.11
$Pt_{0.2}$^Au/SiO_2	62.1	15	15	75	19	6	4.77 (68)	2.12
5 wt% Pt/SiO_2	25.0	120	14	84	13	4	—	0.13

[a] Obtained by assuming that the exposed Pt atoms were solely responsible for the catalyst activity. [b] Data in the parentheses give the numbers relative to the Au/SiO_2 catalyst.

between 11–20% (obtained by adjusting the length of the reaction period). The MSA_{Au}, number listed in the column second to the last in Table 1, increased remarkably with m for all Pt_m^Au/SiO_2 catalysts such that the MSA_{Au} for $Pt_{0.05}$^Au/SiO_2 and $Pt_{0.1}$^Au/SiO_2 was enhanced by a factor of 68 and 73, respectively. It should be emphasized that this dramatic enhancement of the Au activity was achieved without modifying the selectivity of Au/SiO_2 for HCAL. This point is well demonstrated in Fig. 1, which correlates the product selectivity with the conversion level of CAL using all of the reaction data over every Pt_m^Au/SiO_2 catalyst (Table S1 in ESI†). The selectivity for HCAL was kept at the levels of 70–80%‡ over a wide range of CAL conversion, while the fully hydrogenated product (HCOL) increased slightly with increasing CAL conversion, at the expense of COL.

As it would be expected, the reference 5 wt% Pt/SiO_2 (STREM, d_{Pt} = *ca.* 4 nm) catalyst appeared more active than Au/SiO_2 with no Pt and showed some higher selectivity for HCAL. The numbers in the last column of Table 1 show the turn-over frequency data of CAL over Pt (TOF_{Pt}), obtained by assuming that the exposed Pt atoms were solely responsible for the catalyst activity using the CAL hydrogenation data in Table 1 (CAL conversion 11–20%). Compared with that for the reference Pt/SiO_2, the TOF_{Pt} for every Pt_m^Au/SiO_2 catalyst was surprisingly higher. For the Pt in the Pt_m^Au/SiO_2 catalysts, the fully dispersed Pt (99+% dispersion at $m \leq 0.05$) showed very similar TOF_{Pt} numbers (4.4–5.2 s^{-1}) that were significantly higher than the Pt with lower dispersions (Pt_m^Au/SiO_2 at $m \geq 0.1$). This explains why the MSA_{Au} for the $Pt_{0.1}$^Au/SiO_2 and $Pt_{0.2}$^Au/SiO_2 catalysts cannot be much higher than that for $Pt_{0.05}$^Au/SiO_2, though, on the basis of $Pt_{0.05}$^Au/SiO_2, the overall amount of Pt was doubled in $Pt_{0.1}$^Au/SiO_2 and redoubled in $Pt_{0.2}$^Au/SiO_2. This discussion identifies that the fully dispersed Pt entities showed the highest efficiency for the activity enhancement of their underlying Au NPs in Pt_m^Au/SiO_2 catalysts.

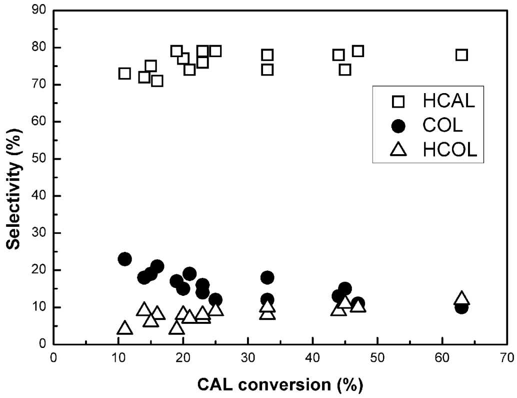
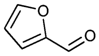
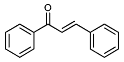
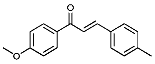


Fig. 1 Selectivity–conversion curve for CAL hydrogenation over Pt_m^Au/SiO_2 catalysts at 150 °C.

The two catalysts Au/SiO_2 and $Pt_{0.05}$^Au/SiO_2 were also compared for the hydrogenation of several other α,β-unsaturated carbonyl compounds, including heterocyclic aldehyde (furfural) and aromatic ketones (chalcone and 4′-methoxy-4-methylchalcone). As shown in Table 2, the Au/SiO_2 catalyst without Pt was hardly active for these reactions but showed very specific selectivity (>99%) for the hydrogenation at the C=O bond of furfural and the C=C bond of the ketones. The activity became one order of magnitude higher (10–20 fold) with the presence of the fully dispersed Pt entities (*i.e.*, over $Pt_{0.05}$^Au/SiO_2) while the specific product selectivity remained unchanged (see Table S2 of ESI†). These results demonstrate again that the fully dispersed Pt entities enhanced the activity of their underlying Au NPs without disturbing the selectivity propensity of the hydrogenation catalysis by Au NPs. Therefore, hydrogenation both at the C=C and C=O bonds can be dramatically accelerated by the presence of the Pt entities. To be noted, the product of the furfural hydrogenation in this study, furfuryl alcohol, is an important starting molecule for the manufacture of resins,[12] the addition of a very small amount of Pt entities (m = 0.05) improved its productivity by 10-fold, which would have important implication for application development.

It should be noted that the Pt entities on Au NPs did not improve the catalytic activity of Au NPs in the Pt_m^Au/SiO_2 catalysts during the transfer-hydrogenation of CAL using benzyl alcohol as the H-donor (see Table S3 of ESI†). Thus, a change of the H-source from molecular H_2 to benzyl alcohol significantly "suppressed" the catalytic activity of Pt_m^Au/SiO_2 catalysts. Interestingly, the selectivity for COL was as high as 63% over Au/SiO_2 but it decreased to *ca.* 30% over the Pt_m^Au/SiO_2 catalysts (m = 0.005–0.2) in the transfer

Table 2 Catalytic hydrogenation of α,β-unsaturated carbonyl compounds at 150 °C under 1.0 MPa H_2 (stirring speed: 900 rpm)

			Sel.[b] (%)	
Substrate	Catalyst	Conv.[a] (%)	C=C	C=O
	Au/SiO_2	1	—	>99
	$Pt_{0.05}$^Au/SiO_2	10	—	>99
	Au/SiO_2	3	>99	—
	$Pt_{0.05}$^Au/SiO_2	20	>99	—
	Au/SiO_2	3	>99	—
	$Pt_{0.05}$^Au/SiO_2	62	>99	—

[a] For the reaction of furfural, substrate/Au (molar) = 1600, rxn. time = 240 min; for the reaction of chalcones, substrate/Au (molar) = 1000, rxn. time = 60 min. [b] C=C: product of C=C bond hydrogenation; C=O: product of C=O bond hydrogenation.

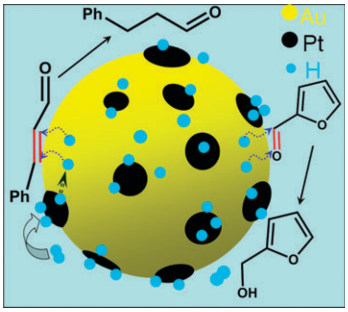


Fig. 2 Pt promotion of the hydrogenation catalysis of Au NPs.

hydrogenation reaction, which is in contrast to the case when high pressure H_2 was the H-source (Table 1). These differences in the reactions over Pt_m^Au/SiO_2 using H_2 and benzyl alcohol as the H-source are further evidence in favor of the fact that the promoted H_2 activation by the Pt sites is the main cause for the dramatic activity enhancement of Au NPs in the conventional chemoselective hydrogenation reactions (Tables 1 and 2).

Therefore, the activity enhancement of Au NPs by the deposition of Pt entities for the chemoselective hydrogenation of α,β-unsaturated carbonyl compounds could be explained by a synergic effect of Pt and Au (Fig. 2). It seems reasonable that the Pt sites were responsible for the dissociative activation of H_2 molecules while the Au sites for the adsorption-activation of the substrate molecules. The activated H atoms would then migrate by spill over toward nearby Au sites for a fast reaction with the adsorbed substrate. The dramatic enhancement of the Au activity by the fully dispersed Pt entities would suggest that the overall reaction rate was determined by the activation of H_2 or supply of H atoms. On the other hand, the well maintained selectivity propensity of the Au NPs in the hydrogenation reactions, regardless of Pt in the Pt_m^Au/SiO_2 catalyst, would indicate that such chemoselective hydrogenation selectivity was governed by the adsorption mode of the substrate molecules on the Au surface.

Recycling of the $Pt_{0.05}$^Au/SiO_2 catalyst for CAL hydrogenation was also attempted. After the reaction, the reacted catalyst was separated, washed with toluene, dried under vacuum and then reused for the same reaction. The CAL conversion and product selectivity data obtained over this recovered catalyst were found similar to those over the fresh one, proving that the catalyst was reusable.

In summary, a small amount of fully dispersed Pt entities loaded on Au NPs resulted in dramatic activity enhancement of the Au NPs (up to 70-fold) for the chemoselective hydrogenation of α,β-unsaturated carbonyl compounds, without changing the selectivity propensity of Au NPs for the reactions. A synergic effect between Pt and Au in the Pt_m^Au/SiO_2 catalysts is proposed to explain this observation, in which the Pt sites function to activate the H_2 molecules while the Au sites serve to activate the unsaturated substrate molecules by chemisorption.

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Notes and references

‡ The selectivity for HCAL was 92% at 150 °C using a home made reactor in our earlier work.[3] This difference could arise from system-associated errors in the H_2 pressure and reaction temperature. The Parr reactor employed in this study is equipped with a well-calibrated pressure gauge (±1 psi) and reports the temperature with a thermal couple inside a Hastelloy autoclave reactor, while in the earlier work[3] the temperature was recorded by a thermocouple in the heating unit outside a stainless autoclave reactor and the error for H_2 pressure could be ±30 psi.

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