Ferric hydroxide supported gold subnano clusters or quantum dots: enhanced catalytic performance in chemoselective hydrogenation

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An attempt to prepare ferric hydroxide supported Au subnano clusters *via* modified co-precipitation without any calcination was made. High resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have been employed to study the structure and chemical states of these catalysts. No Au species could be observed in the HRTEM image nor from the XRD pattern, suggesting that the sizes of the Au species in and on the ferric hydroxide support were less than or around 1 nm. Chemoselective hydrogenation of aromatic nitro compounds and α,β-unsaturated aldehydes was selected as a probe reaction to examine the catalytic properties of this catalyst. Under the same reaction conditions, such as 100 °C and 1 MPa H_2 in the hydrogenation of aromatic nitro compounds, a 96–99% conversion (except for 4-nitrobenzonitrile) with 99% selectivity was obtained over the ferric hydroxide supported Au catalyst, and the TOF values were 2–6 times higher than that of the corresponding ferric oxide supported catalyst with 3–5 nm size Au particles. For further evaluation of this Au catalyst in the hydrogenation of citral and cinnamaldehyde, selectivity towards unsaturated alcohols was 2–20 times higher than that of the corresponding ferric oxide Au catalyst.

Introduction

In the past decade gold catalysts have aroused increasing interest in the chemistry community,[1–4] and numerous studies have been carried out to expand new reactions catalyzed by supported nano Au, such as the water–gas shift reaction,[5] oxidation of alcohols,[6] epoxidation of propene,[7] direct synthesis of hydrogen peroxide,[8] activation of cyclohexane,[9] *etc.* Our research group also reported that polymer supported gold could be an effective catalyst for carbonylation and CO_2 activation.[10,11]

Among factors proposed to affect the catalytic performance of supported Au catalysts, reducing the dimension of the Au particles was believed to be critical to convert "inert gold " into a highly active catalyst.[12–14] This could be understood from both physical and chemical respects. It is well known that quantum size effects of noble metal particles can be remarkable when the dimensions become comparable with their corresponding Fermi electron wavelength[15,16] (*e.g.* ∼ 0.5 nm for Au and Ag), which could result in changes in physicochemical properties such as optical and luminescent characteristics[17] and catalytic properties[18] in comparison with those of the bulk metal or even those of metal particles > 1 nm in size. Meanwhile, remarkable surface effects together with size effects, which become more evident as decreasing particle size are also aspects proposed to affect the catalytic performance. On the other hand, subnano clusters with several to tens of atoms (the corresponding sizes are usually less than or around 1 nm),[19] possess unique physicochemical properties rather different from a single atom as well as nano clusters with hundreds or thousands of atoms, and are currently attracting considerable attention both in synthesis and application.[19–26] It has been found by Goodman *et al*. that Au clusters with one dimension smaller than three atoms which was related to quantum size effects were most active for low-temperature CO oxidation.[1] In another report of Au particles supported on a zinc oxide surface, no significant adsorption of CO was observed until the Au particles decreased to below 5 nm, and became stronger with the decrease in Au particle size.[14] In our previous study, we also found that ferric hydroxide supported Au catalysts prepared by a co-precipitation method without calcining could possess high performance for selective oxidation of CO in the presence of H_2[27] and the catalytic activity for total CO oxidation is much higher than that of the corresponding catalyst calcined at elevated temperatures. Similar results were also observed by other groups.[28–30] Taking into account the unique properties of ultra-fine metal particles together with the average sizes of Au species in these uncalcined and calcined products being less than 1 nm and 4–20 nm respectively, it can be proposed that the smaller size of Au species (so called Au subnano clusters or quantum dots may be formed) were critical for a superior catalytic performance, although supports may also have a strong impact on the catalytic performance.

Based on this strategy, in this work we report that ferric hydroxide supported Au subnano cluster catalysts could be more effective for the chemoselective hydrogenation of aromatic nitro compounds containing carbonyl, halogen, olefin and ester as well as nitrile groups, and a relatively high selectivity towards unsaturated alcohols was also obtained in a further evaluation of the hydrogenation of α,β-unsaturated aldehydes. Furthermore, this preparation method is time and energy saving, and supported Au catalysts prepared in this way may also be expanded into other reactions with unexpected catalytic performance.

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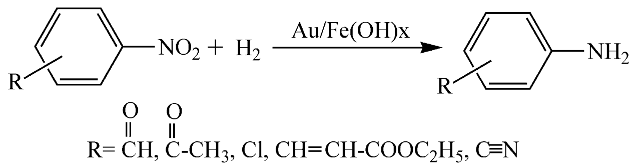
Selective hydrogenation of substrates with a range of functional groups represents an important process in the manufacture of fine chemicals, such as dyes, cosmetics, pharmaceuticals, *etc.*[31–33] Specific examples include the chemoselective hydrogeneation of nitro componds and hydrogenation of α,β-unsaturated aldehydes to the corresponding allylic alcohols. Aromatic amines, especially in the presence of other functional groups are important industrial intermediates for a variety of specific and fine chemicals.[34] Catalytic hydrogenation of nitro compounds is a classic route to afford the corresponding aromatic amines. The reduction of simple nitro compounds is readily carried out with various commercial catalysts, but the selective reduction of the nitro group with H_2 in the presence of other reducible groups is more challenging. Very recently, Corma and Serna[35] reported that gold supported on TiO_2 or Fe_2O_3 catalyzed the chemoselective hydrogenation of nitroarenes, suggesting that properly prepared oxide supported Au could be a versatile catalyst for various reactions with excellent catalytic performance. In this work, we report that Au subnano clusters supported on ferric hydroxide exhibited enhanced catalytic performance in the hydrogenation of nitro compounds (Scheme 1).



Scheme 1 Selective hydrogenation of aromatic nitro compounds.

Experimental

Catalyst preparation

A series of ferric hydroxide or oxide supported catalysts with different Au loadings (1.0–1.1 wt%) were prepared by co-precipitation. Dilute aqueous solutions of $HAuCl_4·4H_2O$ (0.1 g ml^{-1}) and $Fe(NO_3)_3·9H_2O$ (1 mol l^{-1}) were mixed uniformly, then added drop-wise into aqueous Na_2CO_3 solution (1 mol l^{-1}) with vigorous stirring at 20 °C until the pH of the solution was adjusted to 8.0–8.5. After 2 h stirring and 2.5 h aging, the resulting precipitate was filtered off and washed with distilled water, and dried at room temperature (*ca.* 15–20 °C) for 24 h. Then, the resulting ferric hydroxide supported Au was treated in two different ways: (i) dried at 110 °C for 0.5 h (denoted as $Au/Fe(OH)_x$) or (ii) calcined at 400 °C for 2 h (denoted as Au/Fe_2O_3-4). For the propose of comparison, 2.6 wt% $Au/Co(OH)_x$ as well as blank $Fe(OH)_x$ were prepared in this manner, dried at 110 °C for 0.5 h without being calcined at higher temperatures. 4.4 wt% Au/Fe_2O_3 bought from the World Gold Council (denoted as Au/Fe_2O_3-WGC) and Raney-Ni prepared with reference to an earlier report[36] were also employed. All reagents used in this procedure are analytical grade and were used without further purification.

Sample characterization

BET surface areas (S_{BET}) were obtained by physisorption of N_2 at 77 K using a Micromeritics ASAP 2010. It must be mentioned that the $Au/Fe(OH)_x$ catalyst samples were outgassed to 0.1 Pa at 100 °C so as to ensure that no changes occurred in the support structure. The other catalysts, Au/Fe_2O_3-4 and Au/Fe_2O_3-WGC, were outgassed to 0.1 Pa at 200 °C.

Au loadings in the catalyst samples were measured using atomic absorption spectroscopy (AA240, Varian). High resolution transmission electron microscopic (HRTEM) investigations were carried out using a JEOL JEM-2010 electron microscope. The Au catalyst powder was suspended in toluene using ultrasonic dispersion for 5–10 min and then the resulting solution was dropped onto a holey-carbon film supported by a 300 mesh copper grid.

X-Ray diffraction (XRD) measurements for the structure determination were carried out on a Siemens D/max-RB powder X-ray diffractometer. Diffraction patterns were recorded with Cu-Kα radiation (40 mA, 40 kV) over a 2θ-range of 10° to 75° and a position-sentient detector using a step size of 0.01° and a step time of 0.15 s.

The X-ray photoelectron (XPS) spectroscopy analyses were performed with a VG ESCALAB 210 instrument. Mg-Kα radiation at a pass energy of 150 eV at an energy scale calibrated *versus* the C 1s peak at 284.6 eV arising from adventitious carbon were used. The surface composition of the samples was determined from the peak areas of the corresponding lines using a Shirley-type background and empirical cross section factors for XPS. The sample powders were mounted on double-sides adhesive tape. The pressure in the analysis chamber was in the range of 10^{-9} torr during data collection and the sample was maintained at such a low pressure for 24 h without heating before being analyzed.

^1H NMR and ^{13}C NMR spectra were recored on an INOVA-400 MHz NMR spectrometer, and the chemical shifts were reported in parts per millon (ppm, δ). Qualitative analyses were also conducted with a HP 6890/5973 GC-MS with chemstation containing a NIST mass spectral database.

Catalytic performance testing

Catalytic experiments of chemoselective hydrogenation of nitro compounds were carried out in a 90 ml autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, 0.2 g substrate and 4 ml tetrahydrofuran (ethanol for 2-chloronitrobenzene, distilled before use) as solvent were placed into the autoclave together with 0.1 g catalyst. After being sealed, the reactors were flushed three times with 4 MPa hydrogen and then pressurized at 1 or 2.5 MPa. Finally, each autoclave was heated to the required temperature (90–150 °C) and a slight increase in pressure was observed. No further hydrogen was added to the autoclaves during the experiment.

Selective hydrogenations of α,β-unsaturated aldehydes were carried out in a 90 ml autoclave equipped with magnetic stirring. A mixture of 4 ml alcohol as solvent, 0.2 g substrate, 0.085 g 1-butanol or 1-octanol serves as internal standard and 0.1 g as-prepared catalyst were successfully charged into the autoclave. After being flushed two times with 4 MPa hydrogen, the reaction mixtures were pressured at 2 MPa and heated to 65–100 °C for different substrates.

Quantitative analyses were conducted with a HP 6820 GC equipped with a FID detector. The GC yields were obtained using an internal standard method.

Table 1 Basic physicochemical properties of the supported Au catalysts

Catalysts	Au loading/wt%	Support	BET surface area/m^2 g^{-1}	Mean pore diameter/Å
Au/Fe(OH)$_x$	1.0	Fe(OH)$_x$	243.3	32.7
Au/Fe$_2$O$_3$-4	1.1	α-Fe$_2$O$_3$	20.1	106.6
Au/Fe$_0$O$_3$-WGC	4.4	α-Fe$_2$O$_3$	39.0	109.1

Results and discussion

Typical data such as Au loadings, BET surface areas, *etc.* are summarized in Table 1.

It is observed that Au/Fe(OH)$_x$ possesses a relatively higher BET surface area of 243.3 m^2 g^{-1}, while after being calcined at 400 °C the BET surface area decreased greatly to 20.1 m^2 g^{-1} which is comparable to that of Au/Fe$_2$O$_3$-WGC, 39.0 m^2 g^{-1}. Au loadings were increased slightly after being calcined at elevated temperature and this should be related to losing the adsorbed water and the transformation of ferric hydroxide into ferric oxide, although the same quantity of gold precursors were initially used. Meanwhile, calcination significantly enlarged the mean pore diameters of Au/Fe(OH)$_x$, from 32.7 Å to 106.6 Å after being calcined at 400 °C.

In order to get explicit details of Au particle size, 1.0 wt% Au/Fe(OH)$_x$ and 1.1 wt% Au/Fe$_2$O$_3$-4 were examined with HRTEM, Fig. 1. Au species were invisible over 1.0 wt% Au/Fe(OH)$_x$, suggesting that the Au species were highly dispersed into or on Fe(OH)$_x$, or more precisely, Au species in or on the Fe(OH)$_x$ were subnano clusters containing a few Au atoms, and no structural changes between 1.0 wt% Au/Fe(OH)$_x$ and pure Fe(OH)$_x$ (not shown here) could be discerned. However, after being calcined at 400 °C, Au species of 3–5 nm in size were clearly visible and aggregation of the supports was directly observed.

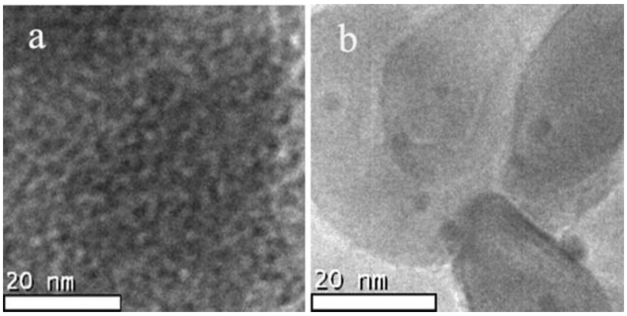


Fig. 1 HRTEM images of supported gold catalysts: (a) 1.0 wt% Au/Fe (OH)$_x$, (b) 1.1 wt% Au/Fe$_2$O$_3$-4.

Structural characteristics of the catalysts have also been investigated by X-ray diffraction (XRD). Fig. 2a showed no evident characteristic diffraction peaks of Au, indicating that the Au species in Au/Fe(OH)$_x$ were ultra-highly dispersed, which was consistent with the HRTEM image. Besides, it could also be seen that ferric hydroxide in this low-temperature prepared catalyst was amorphous. These results are in agreement with our previous findings.[37] After being calcined at 400 °C, XRD patterns showed significante changes in Au/Fe$_2$O$_3$-4, Fig. 2b. It showed a well-resolved reflection pattern which was attributed to hematite with the main diffraction peaks at 24.2, 33.2, 35.6, 49.5 and 54.1 (2θ/°). Moreover, the characteristic diffraction pattern of metallic gold at 38.2 and 44.4 (2θ/°) was noted. It can be concluded that, after calcination at 400 °C, formation of α-Fe$_2$O$_3$ crystallites was evident and Au crystallites could also be detected, which suggested that calcination at elevated temperatures would cause Au species aggregation.

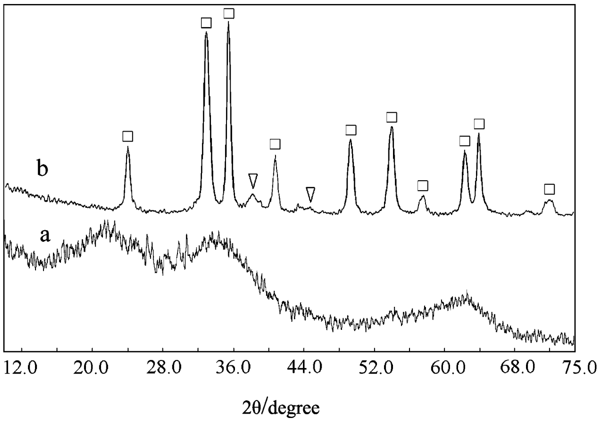


Fig. 2 X-Ray diffraction patterns for supported Au catalysts: (a) 1.0 wt% Au/Fe (OH)$_x$, (b) 1.1 wt% Au/Fe$_2$O$_3$-4. (□) hematite; (▽) metallic gold.

To gain insight into the chemical states of the Au species, the as-prepared catalysts were also characterized by X-ray photoelectron (XPS) spectroscopy (Fig. 3). It could be seen that the chemical state of the surface Au species on Au/Fe(OH)$_x$ was, as expected, a mixture of Au$^+$ (B.E. 4f$_{7/2}$ = 86.0 eV) and metal Au (B.E. 4f$_{7/2}$ = 83.8 eV), and the corresponding atom ratio Au$^+$/Au was 0.33. However, after being calcined at 400 °C, the Au species changed

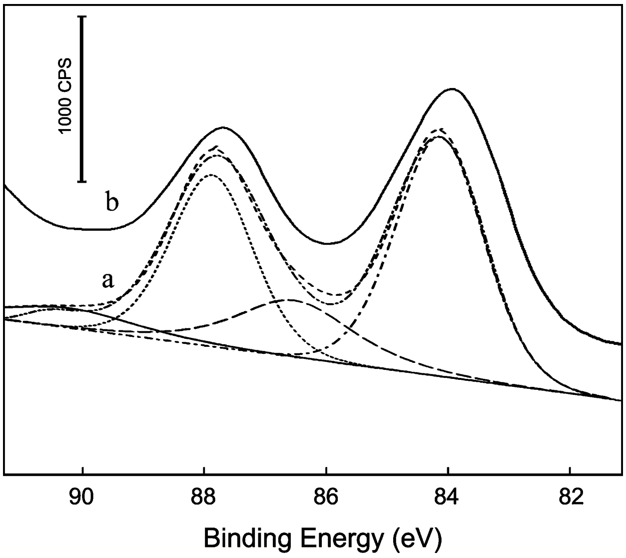


Fig. 3 XPS spectra of supported Au catalysts: (a) 1.0 wt% Au/Fe (OH)$_x$, (b) 1.1 wt% Au/Fe$_2$O$_3$-4.

to mainly to metal Au (B.E. $4f_{7/2} = 83.7$ eV), which was almost identical to the Au/Fe_2O_3-WGC (B.E. $4f_{7/2} = 83.6$ eV).

Chemoselective hydrogenation of nitro compounds

Catalytic performances of the as-prepared ferric hydroxide supported Au catalysts as well as other catalysts treated in traditional manners were tested. Firstly, hydrogenation of 4-nitrobenzaldehyde was tested, Table 2. Pure $Fe(OH)_x$ gave only lower activity, but after incorporation of Au into the $Fe(OH)_x$, the hydrogenation activity increased greatly and 96% conversion with selectivity of 99% could be achieved over 1.0 wt% Au/$Fe(OH)_x$. Conversions decreased sharply over 1.1 wt% Au/Fe_2O_3-4 and moderately over 4.4 wt% Au/Fe_2O_3-WGC, though with comparable selectivity for 4-aminobenzaldehyde. When the amount of 4.4 wt% Au/Fe_2O_3-WGC charged was increased to 0.25 g, >99% conversion with selectivity of 98% was obtained. This result was consistent with an earlier report.[12] Trace amounts of (4-aminophenyl)methanol, 4-aminotoluene and *p*-nitrotoluene were detected as by-products over 1.0 wt% Au/$Fe(OH)_x$, while the main by-products resulting from Au/Fe_2O_3-4 and Au/Fe_2O_3-WGC were 4-aminotoluene (12% and 0.6% respectively) and *p*-nitrotoluene (4.7% and 0.3% respectively), indicating those catalysts calcined at elevated temperatures have similar selectivity. In the case of blank $Fe(OH)_x$, 51.8% 4-aminotoluene and 38.2% *p*-nitrotoluene were also detected. From the composition of byproducts, it can be speculated that hydrogenation of 4-nitrobenzaldehyde over nano Au began at the nitro group, then a small amount of carbonyl hydrogenation occurred, and *p*-nitrotoluene may have resulted from active sites on the support. It is worth noting that the TOF value over 1.0 wt% Au/$Fe(OH)_x$ reached 251, which, though relatively low, is still six times higher than that of 4.4 wt% Au/Fe_2O_3-WGC. As for 2.6 wt% Au/$Co(OH)_x$, inferior catalytic performance both in activity and selectivity was obtained in comparison with 1.0 wt% Au/$Fe(OH)_x$, indicating that the support also plays an important role in catalytic activity. In the case of Raney-Ni, 19% (4-aminophenyl)methanol and 16.3% complete hydrogenation by-product, 4-aminotoluene, were detected, indicating a poor selectivity for the desired amine.

Hydrogenation of aromatic nitro compounds with carbonyl, chlorine, alkene and nitrile groups over these catalysts was also investigated. Propably due to electron-accepting effects, *p*-nitroacetophenone, 2-chloronitrobenzene and ethyl-4-nitrocinnamate could be selectively hydrogenated under more mild reaction conditions as compared with the hydrogenation of 4-nitrobenzaldehyde. As can be seen, >99% conversions with high selectivities were obtained in hydrogenation of the substrates over 1.0 wt% Au/$Fe(OH)_x$. The main by-products resulting from 1.0 wt% Au/$Fe(OH)_x$ in the hydrogenation of *p*-nitroacetophenone were 4-ethylbenzenamine and 4-vinylbenzenamine, while 0.1% and 14% 4-ethylbenzenamine as the only byproduct were detected over Au/Fe_2O_3-4 and Au/Fe_2O_3-WGC respectively. As for ethyl-4-nitrocinnamate, the reduction of the nitro group without further hydrogenation of the alkene and ester carbonyl can also be successfully reached. Catalytic hydrogenation of 2-chloronitrobenzene to afford the corresponding chloroaniline is an important procedure affording intermediates for fine chemical use, such as pharmaceuticals, dyes, herbicides and pesticides.[38] Investigations have been carried out over Pt,[39,40] Ag[41]

Table 2 Comparison of the catalytic performances for chemoselective hydrogenation of aromatic nitro-compounds

Substrates	Catalysts	Au loadings/wt%	$T/°C$	Pressure/MPa	Reaction time/h	Conversion (%)	Selectivity (%)	TOF/h^{-1}
4-Nitrobenzaldehyde	$Fe(OH)_x$	—	100	1	1	3	10	—
	Au/$Fe(OH)_x$	1.0	100	1	1	96	99	251
	Au/Fe_2O_3-4	1.1	100	1	1	40	83	95
	Au/Fe_2O_3-WGC	4.4	100	1	1	70	98	42
	Au/$Co(OH)_x$	2.6	100	1	1	42	75	42
	Raney-Ni	—	100	1	1	99	63	0.7
p-Nitroacetophenone	Au/$Fe(OH)_x$	1.0	95	1	0.75	>99	99	318
	Au/Fe_2O_3-4	1.1	95	1	0.75	52	86	150
	Au/Fe_2O_3-WGC	4.4	95	1	0.75	57	99	41
2-Chloronitrobenzene	Au/$Fe(OH)_x$	1.0	90	1	0.75	>99	99	334
	Au/Fe_2O_3-4	1.1	90	1	0.75	24	80	73
	Au/Fe_2O_3-WGC	4.4	90	1	0.75	65	88	49
Ethyl-4-nitrocinnamate	Au/$Fe(OH)_x$	1.0	100	1	0.75	>99	99	238
	Au/Fe_2O_3-4	1.1	100	1	0.75	18	99	39
	Au/Fe_2O_3-WGC	4.4	100	1	0.75	40	99	22
4-Nitrobenzonitrile	Au/$Fe(OH)_x$	1.0	150	2.5	2	48	99	68
	Au/Fe_2O_3-4	1.1	150	2.5	2	7	99	9
	Au/Fe_2O_3-WGC	4.4	150	2.5	2	25	99	8

and Au[42,43] catalysts in order to avoid the accompanying pollution resulting from the use of acid agents in stoichiometric reducing reactions, or from the use of toxic and unsafe hydrogenation agents, such as hydrazine. Nevertheless, undesired hydrodechlorination reactions are usually observed over those metal catalysts.[38,39,44] In our case, >99% conversion with no dechlorination reaction was successfully achieved under a low hydrogen pressure and reaction temperature, while distinct decreases in conversion over 1.1 wt% Au/Fe_2O_3-4 and 4.4 wt% Au/Fe_2O_3-WGC were obtained. The only by-product in this reaction was *N*-ethyl-chloroaniline and its proportion increased with the calcination temperature the catalysts been treated at, from 0.5% for Au/$Fe(OH)_x$ to 20% for Au/Fe_2O_3-4. It is worth noting that it has been reported that the by-product *N*-ethyl-chloroaniline could not be further hydrogenated to the desired product by increasing the reaction time.[42] In the case of 4-nitrobenzonitrile, when the reaction was carried out at 100 °C for 2 h, only 15% of conversion was obtained. It increased to 48% upon raising the reaction temperature to 150 °C, indicating the harsh reaction conditions required for substrates with nitrile groups, which were inconsistent with another report.[35] Characterizations of the main products are given below.

4-Aminobenzaldehyde: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 1H), 7.65 (d, $J = 6.60$ Hz, 2H), 6.64 (d, $J = 6.59$ Hz, 2H), 4.60 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 152.6, 132.2, 127.0, 113.9; MS *m*/*z*: 122 (M^+ + 1, 5%), 106 (M^+ − 15, 100%).

1-(4-Aminophenyl)ethanone: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, $J = 6.69$ Hz, 2H), 6.63 (d, $J = 6.74$ Hz, 2H), 4.16 (bs, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 151.1, 130.8, 127.7, 113.6, 26.1; MS *m*/*z*: 135 (M^+, 48%), 120 (M^+ − 15, 100%).

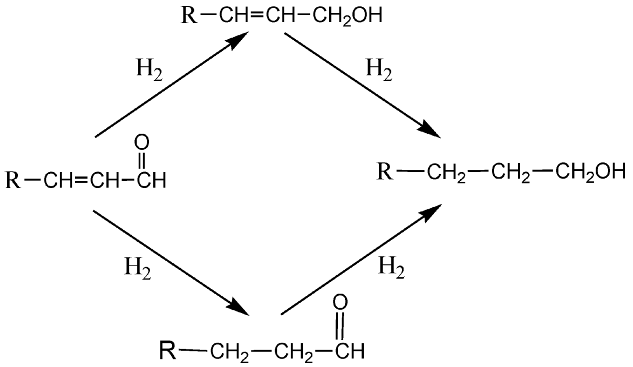
2-Chlorobenzenamine: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60–7.30 (m, 4H, C_6H_4), 3.7 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.9, 129.4, 127.6, 119.3, 119.0, 115.8; MS *m*/*z*: 127 (M^+, 100%), 92 (M^+ − 35, 20%).

Ethyl 3-(4-aminophenyl)acrylate: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 16.1 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 6.61 (d, $J = 8.1$ Hz, 2H), 6.19 (d, $J = 16.0$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.90 (br, 2H), 1.32 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 148.6, 144.8, 140.5, 129.8, 128.6, 124.1, 122.5, 113.7, 61.0, 60.1; MS *m*/*z*: 191 (M^+, 71%), 146 (M^+ − 45, 100%).

Hydrogenation of α,β-unsaturated aldehydes

Selective hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols attracts much interest in heterogeneous catalyt research owing to its importance in the fine chemical, pharmaceutical and cosmetic industries.[31,32,45] However, from the aspect of thermodynamics, hydrogenation of the C=C bond is favoured over the C=O group (stronger negative free reaction enthalpy of 35 kJ mol^{-1}). Besides, for kinetic reasons, the C=C bond is more reactive than the bond of the C=O group. Consequently, these conjugated functional groups are particularly difficult to hydrogenate to the corresponding unsaturated alcohols, and the saturated aldehyde or saturated alcohol are often the exclusive reaction products. A simple illustration is shown in Scheme 2.

Selective hydrogenation of C=O in α,β-unsaturated aldehydes has only been achieved in a number of cases, for example with heterogeneous Pt, Ag, Co and Ru catalysts.[46–52] In recent years, it has been found that supported Au catalysts exhibited potential application in controlling the intermolecular selectivity in the hydrogenation of α,β-unsaturated aldehydes,[53–54] and a number of studies have been carried out.[55–62] In this work, we further evaluated the catalytic properties of ferric hydroxide supported Au catalyst in the hydrogenation of acrolein, citral and cinnamaldehyde.



Scheme 2 Transformation of the α,β-unsaturated aldehydes.

The results obtained for the hydrogenation of these α,β-unsaturated aldehydes on gold supported catalysts are reported in Table 3. As can be seen, in the case of acrolein, no allyl alcohol was obtained on Au/$Fe(OH)_x$, Au/Fe_2O_3-4 and Au/Fe_2O_3-WGC catalysts under the present reaction conditions, and propanal became the main product in all these cases. This may be caused by the high hydrogen coverage which was reported to be harmful to the chemoselectivity towards unsaturated alcohols.[63] As for the hydrogenation of citral, the main products obtained on Au/$Fe(OH)_x$ were unsaturated alcohols (geraniol and nerol, *E* and *Z* forms of 3,7-dimethyl-2,6-octadienol, respectively), derived from the hydrogenation of the *E* and *Z* isomers of citral. Citronellal (3,7-dimethyl-6-octenal) derived from the hydrogenation of C=C adjacent to C=O in citral and citronellol (3,7-dimethyl-6-octenol) were the other products. On Au/Fe_2O_3-4 catalyst, citronellal became the main product accompanied by an obvious decrease in the proportion of unsaturated alcohols, from 63% to 25%. As for Au/Fe_2O_3-WGC, a similar hydrogenation product distribution was obtained. The catalytic activity of Au/Fe_2O_3-4 is slightly increased as compared with Au/$Fe(OH)_x$, which may be caused by the increase in Au particle size as reported by Claus *et al.*[64] However, it is worth noting that the unsaturated alcohols, geraniol and nerol, are the main products of Au/$Fe(OH)_x$, indicating the high selectivity of this catalyst towards the hydrogenation of the C=O bond.

In the hydrogenation of cinnamaldehyde (*E*-3-phenylpropenal), Au/$Fe(OH)_x$ exhibited a relatively high selectivity of 82% towards the cinnamic alcohol (*E*-3-phenylprop-2-enol). As for Au/Fe_2O_3-4 and Au/Fe_2O_3-WGC catalysts with 3–5 nm size Au particles, hydrogenation of cinnamaldehyde led mainly to the formation of saturated aldehyde, and the selectivity to cinnamic alcohol was relatively low, 4% and 13% respectively. It seems that selectivities toward the formation of unsaturated alcohol can be, at least to a certain degree, correlated with the morphological properties of gold, particularly the Au particle size.

Table 3 Comparison of the catalytic performances for chemoselective hydrogenation of α,β-unsaturated aldehydes

Substrates	Catalysts	Au loadings/wt%	T/°C	Reaction time/h	Conversion (%)	Selectivity (%)			
						Saturated aldehyde[a]	Saturated alcohol[b]	Unsaturated alcohol[c]	Others[d]
Acrolein	Au/Fe(OH)$_x$	1.0	65	3	89	76	1	—	23
	Au/Fe$_2$O$_3$-4	1.1	65	3	67	75	—	—	25
	Au/Fe$_2$O$_3$-WGC	4.4	65	3	73	70	—	—	23
Citral	Au/Fe(OH)$_x$	1.0	100	11	93	24	12	63	1
	Au/Fe$_2$O$_3$-4	1.1	100	11	98	41	30	25	4
	Au/Fe$_2$O$_3$-WGC	4.4	100	11	88	24	13	61	2
Cinnamaldehyde	Au/Fe(OH)$_x$	1.0	100	12	86	11	6	82	1
	Au/Fe$_2$O$_3$-4	1.1	100	12	98	71	19	4	6
	Au/Fe$_2$O$_3$-WGC	4.4	100	12	81	72	5	13	10

[a] Saturated aldehyde: propanal for acrolein, citronellal for citral and hydrocinnamaldehyde for cinnamaldehyde. [b] Saturated alcohol: 1-propanol for acrolein, citronellol for citral and 3-phenylpropanol for cinnamaldehyde. [c] Unsaturated alcohol: allyl alcohol for acrolein, geraniol and nerol for citral and cinnamic alcohol for cinnamaldehyde. [d] Others: acrylic acid and formyldihydropyran for acrolein, 1,1-diethoxy-3,7-dimethylocta-2,6-diene and ethyl-3,7-dimethyloct-6-enoate for citral and 1-(3,3-diethoxypropyl)benzene for cinnamaldehyde.

Conclusions

It was found for the first time that ferric hydroxide supported Au catalysts could exhibit enhanced activity and selectivity in the chemoselective hydrogenation of aromatic nitro compounds. While after calcining at elevated temperatures and with aggregation of Au species (although the size only increased to 3–5 nm) Au/Fe$_2$O$_3$-4 exhibited an inferior catalytic performance. Though the detailed mechanism is not clear at this stage, it is proposed that Au subnano clusters play an important role in the enhanced catalytic performance, though the supports may also make a contribution. This catalyst preparation strategy may be extended to other reactions with satisfactory results.

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