Green Chemistry

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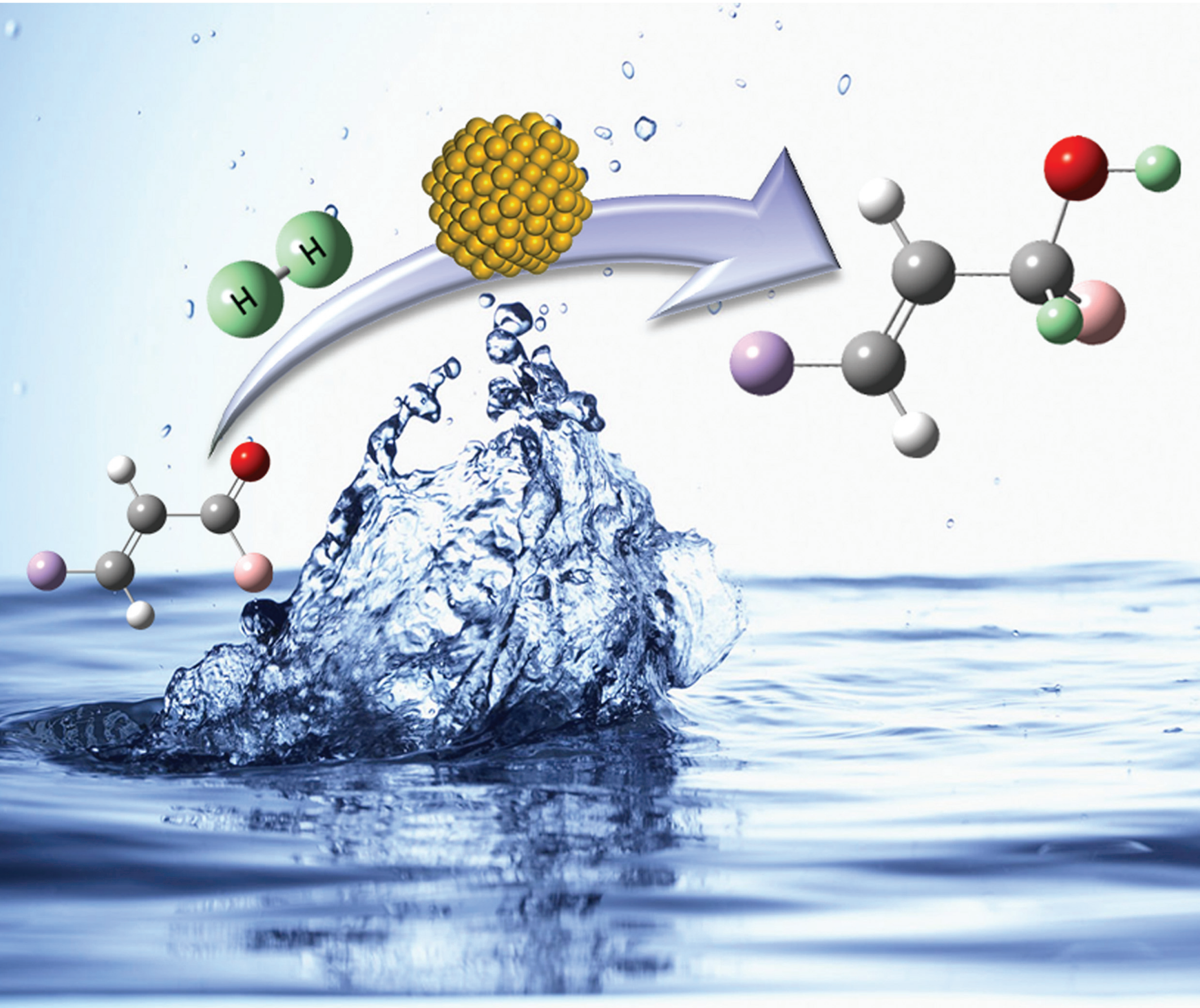
www.rsc.org/greenchem
Volume 13 | Number 3 | March 2011 | Pages 457–724



ISSN 1463-9262

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Cite this: *Green Chem.*, 2011, **13**, 602

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PAPER

Gold supported on mesostructured ceria as an efficient catalyst for the chemoselective hydrogenation of carbonyl compounds in neat water

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Received 21st December 2010, Accepted 17th January 2011
DOI: 10.1039/c0gc00937g

Rapid and efficient selective hydrogenation of a range of α,β-unsaturated carbonyl compounds to their corresponding allylic alcohols was achieved in neat water using gold supported on a mesostructured CeO_2 matrix. Both the activity and chemoselectivity for the reduction of carbonyl compounds improved significantly on going from organic solvents to water for the reaction media. Results in the intermolecular competitive hydrogenation showed that the intrinsic higher rate for the Au-catalyzed aldehyde reduction in water was responsible for the high activity and chemoselectivity observed.

Introduction

Chemoselective hydrogenation of α,β-unsaturated carbonyl compounds (unsaturated aldehydes or ketones, UALs or UKEs) to the corresponding allylic alcohols is an important step in the industrial synthesis of fine chemicals, particular of pharmaceuticals, perfumes and cosmetics.[1] Although extensively studied, selective allylic alcohol synthesis facilitated by catalytic hydrogenation rather than traditional stoichiometric reduction remains a challenging issue. Conventional hydrogenation catalysts based on supported Pt,[2a] Pd,[2b] Ru,[2c] and Rh[2d] produce mainly saturated aldehydes. Therefore, great efforts have been made to overcome this problem over the past decades, either by the use of special additives or promoters (Lewis acids or bases),[2b] modifying the active metal with a second metal component,[3] or a fine tuning the particle sizes of the catalysts.[4] Although these modified systems are effective, catalyst preparation often remains tedious and elusive, and the amount of the modifying agent must be precisely controlled.[3] Alternative simple and efficient catalyst that would enable the preferential hydrogenation of the C═O group *versus* C═C is highly desirable.

In recent years, catalysts based on supported gold nanoparticles (NPs) have attracted considerable attention as new promising carbonyl hydrogenation materials owing to their high intrinsic selectivity toward the formation of the desired allylic alcohols.[5] This was prompted by Hutchings and coworkers's discovery of exceptionally high selectivity of ZnO and ZrO_2 supported gold NPs for the gas phase hydrogenation of the conjugated C═O bond.[1c,6] Subsequent studies by evaluating gold deposited on other supports, including iron oxides,[7a] TiO_2,[7b] CeO_2[7c] and Mg_2AlO[7d] have revealed that supported gold catalysts are also highly effective for the hydrogenation of UALs to produce the desired allylic alcohols in the liquid phase. Despite their high chemoselectivity, one critical limitation associated with the current Au-catalyzed carbonyl compounds reductions is the limited hydrogen-delivery rate compared to the conventional hydrogenation metals.[5a,5c] Moreover, these Au-based hydrogenation processes suffer from some general drawbacks,[5c,7] including the need of relatively high temperature/pressure and the use of hazardous organic solvents as the reaction media.

During the last decade, the increasing awareness of environmental concerns has stimulated the development of metal-catalyzed reactions in aqueous media,[8] since water represents the most benign, abundant and inexpensive solvent known.[9] In addition, the use of water as the reaction medium has reportedly led to unique reactivity and selectivity that can not be obtained in conventional organic solvents.[10] In this sense, chemoselective reduction of UALs and UKEs with hydrogen in water would lead to a particularly green process. However, as far as we know, few publications are available that address the use of supported metal NPs for producing allylic alcohols from hydrogenation of carbonyl compound in an aqueous environment.[11]

In the continued search for greener methods for chemoselective C═O reduction, there is a definite need for new environmentally benign and clean protocols that enable facile carbonyl reduction in aqueous media. Very recently, we have described an efficient and selective reduction method of UALs using supported gold catalysts in the presence of CO/H_2O.[12] The improved performance of Au catalysts for aqueous CO/H_2O-mediated reduction has prompted us to investigate the possibilities offered by Au for environmentally clean selective reduction of UALs and UKEs with H_2 under aqueous conditions. Herein, we demonstrate for the first time that gold supported on

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mesostructured ceria can catalyze the reduction of UALs and UKEs to the corresponding allylic alcohols in high yields in aqueous media. Our results have shown that the replacement of organic solvents with neat water can result in a significant improvement in both the activity and selectivity of gold-catalyzed conjugated C=O hydrogenation.

Results and discussion

Catalyst characterization

Mesostructured ceria was synthesized through a surfactant-assisted precipitation method, with the use of cetyltrimethyl ammonium bromide (CTAB) as templating agent.[8b,13] Fig. 1 shows the nitrogen adsorption-desorption isotherm and the pore-size distribution of the resultant material. According to the IUPAC classification, the isotherm can be classified as a type IV one, typical of mesostructured materials and the hysteresis loop is type H1 indicating a complex mesoporous structure. The Brunauer-Emmett-Teller (BET) surface area of the CeO_2 was 150 m^2 g^{-1} and the mean pore diameter was 3.8 nm with a narrow distribution. The X-ray diffraction (XRD) pattern for the support was shown in Fig. 2a. The diffraction pattern of the mesostructured CeO_2 sample was found to be very broad, showing a semicrystalline nature of this material. The peak intensities and their 2θ angles have been identified as characteristic of the cubic fluorite structure of CeO_2 (JCPDS no. 34-0394). The average crystallite size of CeO_2 sample was 4.5 nm.

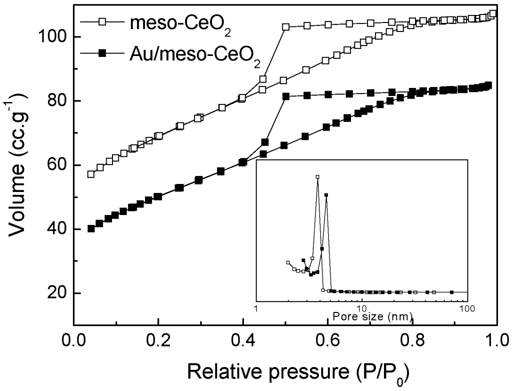


Fig. 1 N_2 adsorption-desorption isotherms of meso-CeO_2 and Au/meso-CeO_2. The inset shows BJH pore size distribution.

When gold NPs were deposited onto the as-synthesized support (denoted as Au/meso-CeO_2; see details in the Experimental section), the surface area decreased slightly to 138 m^2 g^{-1} while the mean pore size increased to 4.6 nm. An almost identical XRD pattern was obtained for Au/*meso*-CeO_2 comparing with *meso*-CeO_2 (Fig. 2b), indicating the crystalline structure and the average size of the crystalline domain of the support were well maintained in the gold samples. No peaks due to metallic Au were detected, owing to the fact that the gold particle sizes were very small (<5 nm). Transmission electron microscopy (TEM) experiments have been carried out to observe a possible structure of the metallic Au particles (Fig. 3a). The image does not clearly show the presence of ordered mesopores, but reveal a rather foam-like structure resulting from closely aggregated metal oxide nanoparticles,[13] which is further supported by the N_2 adsorption-desorption isotherm data as illustrated in Fig. 1. The size of the nanoparticles is around 5 nm, consistent with the crystallite size obtained by XRD. However, the identification of the small Au particles was unsuccessful, possibly due to the poor contrast between Au and ceria support.[14]

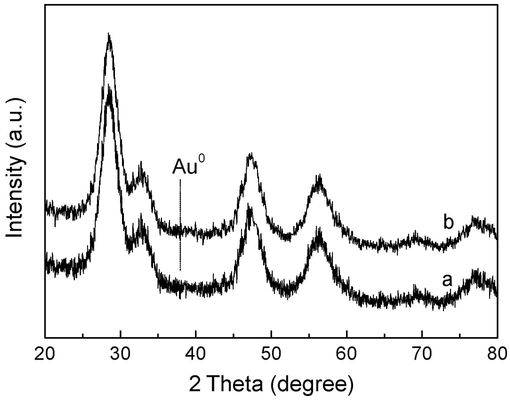


Fig. 2 XRD diffractograms: (a) meso-CeO_2 and (b) Au/meso-CeO_2.

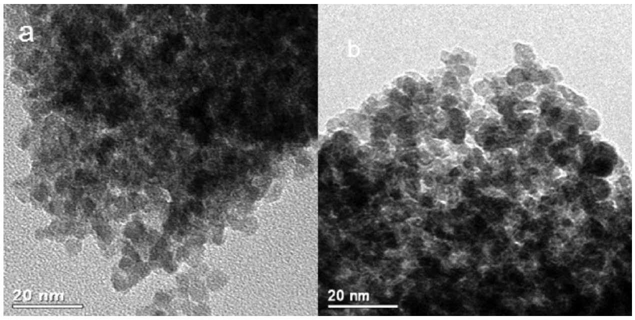


Fig. 3 TEM images of Au/meso-CeO_2: (a) before reaction; (b) after four runs.

Catalytic hydrogenation

The catalytic properties of the Au/meso-CeO_2 catalyst in various solvents were investigated using chemoselective hydrogenation of crotonaldehyde (CAL) as a model reaction. The hydrogenation reactions were carried out in a 50 mL Parr stainless-steel reactor.

Table 1 presents the initial activities and selectivities to crotyl alcohol (CROL) at 50% conversion for CAL hydrogenation at 100 °C and 1.0 MPa H_2 over Au/meso-CeO_2 in water and a range of organic solvents. When employing the most commonly used isopropanol as the solvent, Au/meso-CeO_2 catalyzed CAL to CROL with an initial activity of 78.4 μmol g_{Au}^{-1} s^{-1} and 38% selectivity. Note that this result is fully comparable with the work of Campo *et al.*,[7b] who found that ceria-supported gold NPs gave similar activity and selectivity for CAL hydrogenation in isopropanol solution. The use of other organic solvents was much less effective with lower than 30% selectivity being achieved for the chemoselective hydrogenation of CAL under identical reaction conditions. Surprisingly, when neat water was applied as the solvent, the specific rate of the initial activity is dramatically boosted to an unprecedented value of 226.4 μmol g_{Au}^{-1} s^{-1}, which is almost 3 times that of the

Table 1 Catalytic performance of various catalysts for the reduction of crotonaldehyde by H_2 in various solvents[a]

Entry	Catalyst	Solvent	Initial activity[b]/ μmol g_{Au}^{-1} s^{-1}	CROL selectivity (%)[c]
1	Au/meso-CeO_2	water	226.4	90
2[d]	Au/meso-CeO_2	water	202.8	88
3	Au/meso-CeO_2	isopropanol	78.4	38
4	Au/meso-CeO_2	ethanol	52.5	29
5	Au/meso-CeO_2	dioxane	43.8	25
6	Au/meso-CeO_2	cyclohexane	22.0	25
7	Au/CeO_2	water	146.2	81
8[e]	Au/TiO_2	water	68.4	24
9[e]	Au/Fe_2O_3	water	31.0	33
10[e]	Au/Al_2O_3	water	24.8	21
11	meso-CeO_2	water	—	—

[a] Reaction conditions: 1 mmol CAL, 1.0 mol% Au, 15 mL solvent, 100 °C, 1.0 MPa H_2. [b] Measurement at 10 min of reaction. [c] Selectivities were compared at 50% of conversion. [d] Results for the fourth run. [e] Au/TiO_2 and Au/Fe_2O_3 provided by the World Gold Council, Au/Al_2O_3 provided by Mintek. CAL: crotonaldehyde, CROL: crotyl alcohol.

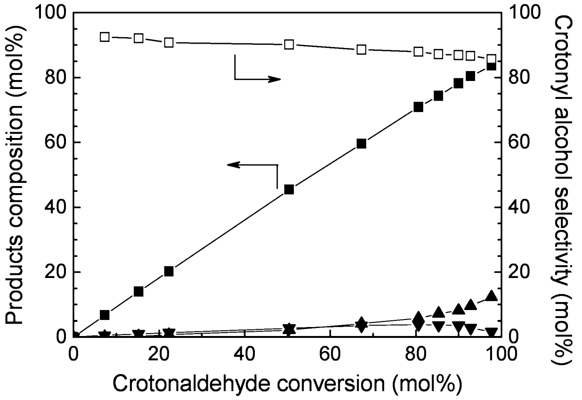


Fig. 4 Composition of products and selectivity for crotonyl alcohol for the hydrogenation of crotonaldehyde over Au/meso-CeO_2 as a function of crotonaldehyde conversion. (■) CROL; (▼) BAL; (▲) BOL; (□) CROL selectivity. Reaction conditions: 1 mmol CAL, Au/meso-CeO_2 (Au: 1.0 mol%), 15 mL H_2O, 100 °C, 1.0 MPa H_2. CROL: crotyl alcohol, BAL: butanal, BOL: butanol.

isopropanol system and nearly one order of magnitude higher than that for cyclohexane, with an excellent selectivity up to *ca.* 90% can be achieved for CROL production. No conversion was found in the absence of catalysts or in the presence of Au-free meso-CeO_2 under identical conditions (Table 1, entry 11), illustrating that the presence of gold was indispensable for high catalytic activity.

The remarkable activity of the Au/meso-CeO_2 catalyst for the chemoselective hydrogenation of CAL in aqueous media can be further seen from the product evolution profiles as a function of CAL conversion as shown in Fig. 4. The high selectivity for CROL (up to 85%) is maintained even at 100% CAL conversion. The by-products, mainly butanal (BAL, product of C═C hydrogenation) and butanol (BOL, reduction of C═O and C═C bonds), did not exceed 15% with no detectable amount of other side products. To the best of our knowledge, this is the highest CROL yield (*ca.* 85%) reported to date in the literature for liquid phase CAL hydrogenation over Au-based catalysts (Table 2). Of particular note is that this value compares favorably with 82% reported recently on the CO/H_2O–Au/CeO_2 system.[12]

We also compared the activity and selectivity of Au/meso-CeO_2 with those of gold deposited on commercial CeO_2 (Evonic, Adnano 90, surface area: 90 m^2 g^{-1}), TiO_2, Fe_2O_3 and Al_2O_3 in aqueous medium. Results from Table 1 indicated that gold deposited on meso-CeO_2 was the most active and selective catalyst. The Au/TiO_2, Au/Fe_2O_3 and Au/Al_2O_3 lead to low activity (*ca.* 25–70 μmol g_{Au}^{-1} s^{-1}) and very poor selectivity to CROL (*ca.* 21–33%). Note that Au/CeO_2 gave a much higher activity (148.1 μmol g_{Au}^{-1} s^{-1}), with 81% selectivity to CROL. Comparing the results of Au/CeO_2 with those corresponding to Au/meso-CeO_2 indicated that an increased surface area of ceria support (meso-CeO_2, 150 m^2 g^{-1}) is favorable for obtaining a gold catalyst with enhanced catalytic activity and selectivity. A similar phenomenon has also been found by Campo and co-workers in their work on the liquid phase hydrogenation of CAL over Au/CeO_2 catalysts with isopropanol as the solvent.[7b]

Furthermore, Au/meso-CeO_2 was easily separated by simple filtration after CAL hydrogenation, and could be reused four times without appreciable loss of its catalytic activity and selectivity (Table 1, entry 2). This was consistent with the characterization results for this catalyst. XPS results (Fig. 5) showed essentially no changes in the dispersion of the Au NPs and in the metallic state of Au, respectively, after the four successive runs. No gold particles were detected on the same sample after four repeated hydrogenation by TEM (Fig. 3b).

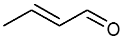
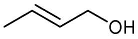
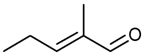
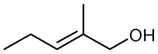
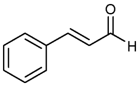
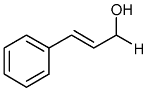
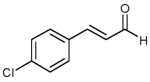
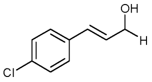
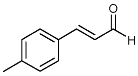
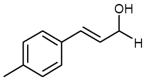
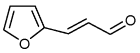
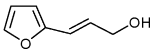
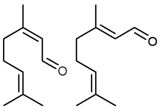
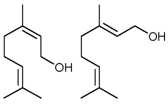
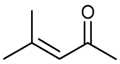
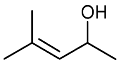
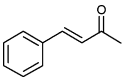
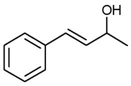
To examine the scope of the present aqueous hydrogenation system with Au/meso-CeO_2, we extended our studies to a range of UALs. Results in Table 3 showed that aliphatic, aromatic aldehydes were smoothly hydrogenated to give the corresponding unsaturated alcohols in high yields, and the Au/meso-CeO_2 was also effective for a heterocyclic aldehyde. CAL displayed a significantly higher activity than 2-methyl-2-pentene aldehyde (entries 1, 2), revealing that the activity is largely influenced by the presence of a β-bulky group due to steric

Table 2 Catalytic results reported recently for crotonaldehyde hydrogenation over Au catalysts

Catalyst	Solvent	Reaction conditions	CAL conv. (%)[a]	CROL sel. (%)[a]	Reference
Au/α-Fe_2O_3	Isopropanol	100 °C, 1.0 MPa	62	31	Lenz *et al.*, 2009[7a]
Au/CeO_2	Isopropanol	80 °C, 1.0 MPa	31	29	Volpe *et al.*, 2009[7b]
Au/Mg_2AlO	Ethanol	120 °C, 0.9 MPa	52	62	Chen *et al.*, 2010[7c]
Au–In/APTMS-SBA-15	Hexane	120 °C, 2.0 MPa	76	75	Yang *et al.*, 2009[7d]
Au/meso-CeO_2	Water	100 °C, 1.0 MPa	88	87	This work

[a] Conversion and selectivity measured at 3 h of reaction. CAL: crotonaldehyde, CROL: crotyl alcohol.

Table 3 Hydrogenation of α,β-unsaturated carbonyl compounds in water[a]

Entry	Substrate	Product	Time/h	Conv. (%)	Sel. (%)
1			0.5 3.5	45 >99	90 86(84)
2			0.5 6.0	28 90	84 81(68)
3[b]			0.5 3.0	48 96	97
4[b]			0.5 2.0	50 94	95 92(85)
5[b]			0.5 4.0	32 97	90 87(82)
6[b]			0.5 3.5	39 96	72 66(62)
7			0.5 2.5	48 >99	95 92(90)
8			0.5 4.5	29 94	64 59(52)
9[c]			0.5 4	34 97	67 66(63)

[a] Reaction conditions: 1 mmol substrate, Au/meso-CeO_2 (Au: 1.0 mol%), 15 mL H_2O, 100 °C, 1.0 MPa H_2. [b] 1 mmol substrate, Au/meso-CeO_2 (Au: 1.0 mol%), 12 mL H_2O, 3 mL EtOH, 100 °C, 1.0 MPa H_2. [c] 1 mmol substrate, Au/meso-CeO_2 (Au: 1.0 mol%), 12 mL H_2O, 3 mL EtOH, 100 °C, 2.0 MPa H_2. Numbers in parenthesis refer to isolated yield of products.

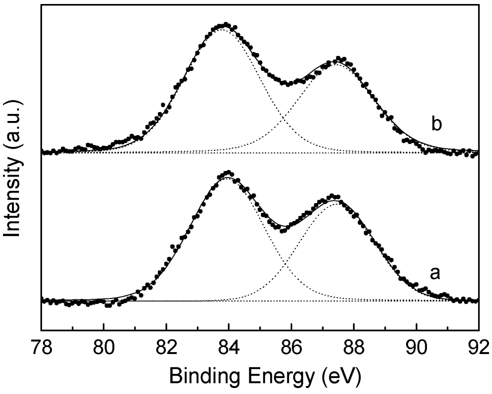


Fig. 5 XP spectra of the Au (4f) signal for Au/meso-CeO_2: (a) before reaction; (b) after four runs.

hindrance. In the case of aromatic UALs, owing to its substantial electro-donating effect, 4-methylcinnamaldehyde was relatively difficult to hydrogenate as compared with cinnamaldehyde and 4-chlorocinnamaldehyde, which was manifested in the required reaction time and a shift in selectivity from unsaturated alcohol to saturated alcohol (entries 3–5). Notably, the chemoselective hydrogenation of furan-2-acrolein also gave the corresponding aldehyde isolated yield of 62% (entry 6). To the best of our knowledge, this study presents the first chemoselective hydrogenation of furan-2-acrolein in the presence of heterogeneous catalysts.

Moreover, it is noteworthy that citral, which is considered one of the most difficult UALs to hydrogenate to the allylic alcohol due to including three unsaturated bonds[15] (conjugated C=O and C=C bonds as well as an isolated C=C bond), was also smoothly converted to give highly valuable geraniol/nerol in excellent yield (Table 3, entry 7). It is remarkable that a high degree of chemoselectivity (*ca.* 92%) in terms of geraniol/nerol production can be achieved for close to 100% conversion of citral. Such reaction efficiency, notably the absence of citronellal owing to C=C hydrogenation, is unique when compared with the conventional catalytic systems.[2c,2d]

α,β-Unsaturated ketones were more challenging as substrates because of the steric hindrance in the carbonyl-component.[16] The chemoselective hydrogenation of UKEs in aqueous media with Au/meso-CeO_2 was also studied by hydrogenation of benzalacetone and 4-methyl-3-penten-2-one. In the case of benzalacetone (Table 3, entry 9), Au/meso-CeO_2 gave 97% conversion with 66% selectivity to 4-phenyl-3-buten-2-ol at higher pressure (2.0 MPa). It is of note that the initial activity of 152.3 μmol g_{Au}^{-1} s^{-1} in this process was more than 50 times higher than that of the alcohol system catalysed by Au/Fe_2O_3 (2.8 μmol g_{Au}^{-1} s^{-1}) with 61% selectivity to the unsaturated alcohol[17b] indicating the high efficiency of the aqueous media with Au/meso-CeO_2. Similar results were also obtained in chemoselective hydrogenation of 4-methyl-3-penten-2-one to the corresponding allylic alcohol (Table 3, entry 8). All these results clearly showed the efficiency of the Au/meso-CeO_2 system in the chemoselective hydrogenation of both UALs and UKEs in water.

To rationalize the beneficial effect achieved by using H_2O as a solvent, an intermolecular competitive hydrogenation of benzaldehyde and styrene using the Au/meso-CeO_2 catalyst in different media under similar reaction conditions has been investigated (Fig. 6). It is revealed that the preferential reduction

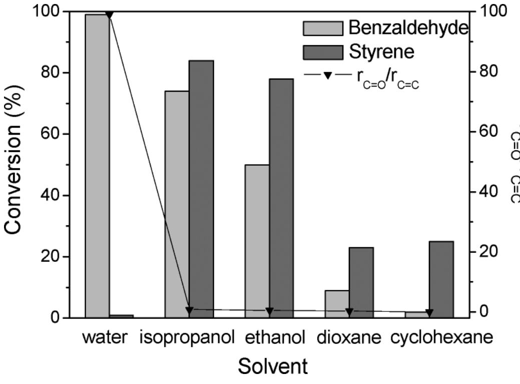


Fig. 6 Competitive reductive hydrogenation of benzaldehyde and styrene over Au/meso-CeO_2 in various solvents. Reaction conditions: 1 mmol benzaldehyde, 1 mmol styrene, Au/meso-CeO_2 (Au: 1.0 mol%), 15 mL H_2O, 100 °C, 1.0 MPa H_2, 1 h.

Table 4 H_2 solubility of various solvents[17]

Solvent	H_2 solubility[a]/μmol cm^{-3}
Water	0.80
Isopropanol	3.90
Ethanol	3.59
Dioxane	1.95
Cyclohexane	3.72

[a] The H_2 solubility (c_L) is related to the Bunsen coefficient (α) by $c_L = \alpha/v_0$, where v_0 is the molar volume of the gas in cm^3 mol^{-1} at 0 °C, α is calculated at 293.15 K and 101.325 kPa (1 atm) partial pressure of the gas.

of benzaldehyde proceeds much more rapidly in water, in sharp contrast to that occurred in organic solvents. Therefore, the intrinsic higher rate for the Au-catalyzed aldehyde reduction in water is responsible for the high chemoselectivity observed.

Previous investigations concerning the use of gold-based catalysts for selective UALs and UKEs reduction have shown that a number of factors such as the reaction conditions and operation mode (*e.g.* gas or liquid phase system),[5b,18] metal and support nature[19] as well as the use of solvents[20] have to be considered in order to account for the phenomena involved in the chemoselective reduction of UALs and UKEs. Presumably, the superior performance of the present aqueous Au-hydrogenation system can be attributed to a beneficial water-assisted orientation of the hydrophilic C═O moiety[2d,21] on the specific surface active sites of Au/meso-CeO_2 which favored chemoselective hydrogenation. It should be mentioned here that the differences cannot be attributed to hydrogen availability since the solubility of H_2 in water is significantly lower than that in organic solvents (Table 4).[17a,22]

Conclusion

In summary, we have described a green and efficient gold-catalyzed reaction system for the chemoselective reduction of α,β-unsaturated carbonyl compounds *via* hydrogenation in aqueous medium. This new catalytic system has been demonstrated to be suitable for the environmentally clean reduction of a range of unsaturated aldehydes or ketones. The unprecedented high efficiency achieved for the clean synthesis of allyl alcohols *via* aqueous Au-catalyzed hydrogenation is preliminarily attributed to a significant beneficial effect of water as a solvent in facilitating the preferential hydrogenation of the hydrophilic C═O group *vs.* C═C.

Experimental

Catalytic preparation

1.5 wt% Au/TiO_2 (type A, lot no. Au/TiO_2 no. 02-1) and 4.5 wt% Au/Fe_2O_3 (type C, lot no. Au/Fe_2O_3 no. 02-5) were supplied by the World Gold Council (WGC). 1.0 wt% Au/Al_2O_3 (Strem catalogue number: 79-0160) was supplied by Mintek.

Preparation of mesostructured ceria materials

Meso-CeO_2 was prepared by a template-assisted precipitation method.[7b] Typically, a NaOH solution (2 g in 300 mL of distilled water) was added to a stirred solution of $Ce(NO_3)_3·6H_2O$ (4.34 g) and CTAB (2.19 g) in 200 mL distilled water at room temperature. The mixture was then maintained in a sealed glass vessel under stirring for 24 h. After thermal aging at 90 °C for 3 h, the pale yellow precipitate was filtered and washed with hot water (80 °C) to remove the residual CTAB. The resultant powder was dried at 100 °C for 6 h and then calcined at 450 °C for 4 h. The Brunauer-Emmett-Teller (BET) surface area of the as-synthesized meso-CeO_2 was 150 m^2 g^{-1}.

Preparation of Au/CeO_2 catalysts

Au/CeO_2 catalysts were prepared by a routine deposition-precipitation (DP) method. An appropriate amount of aqueous solutions of chloroauric acid ($HAuCl_4$) was heated to 70 °C under vigorous stirring. The pH was adjusted to 9 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO_2 powders (Evonic, Adnano 90, specific surface area: 90 m^2 g^{-1}) or meso-CeO_2 was dispersed in the solution. The mixture was aged for 1 h, followed by filtering and washing several times with deionized water to remove Cl^-. The resulting solid product was dried overnight before reduction at 300 °C for 2 h in 5% H_2/Ar. The two catalysts were designated Au/CeO_2 and Au/meso-CeO_2, respectively. The gold loading of the as-prepared catalysts was 1.9 wt% Au/CeO_2 and 2.1 wt% Au/meso-CeO_2 as determined by ICP-AES.

Catalyst characterization

Elemental analysis. The Au loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer (Hitachi 4010).

X-Ray photoelectron spectroscopy (XPS). XPS analysis was performed using a Perkin Elmer PHI 5000 C system equipped with a hemispherical electron energy analyzer. The Mg Kα ($h\nu$ = 1253.6 eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C1s peak at 284.6 eV.

Nitrogen adsorption-desorption measurements. Nitrogen sorption at −196 °C was measured using a Micromeritics TriStar 3000 after the samples were degassed (1.33×10^{-2} Pa) at 300 °C overnight. The specific surface area was calculated using the BET method, and pore size distribution was determined by the BJH method.

X-Ray diffraction (XRD) measurements. The X-ray powder diffraction (XRD) of the catalysts was carried out on a German Bruker D8 Avance spectrometer using nickel filtered Cu-Kα (λ = 0.15418 nm), operated at 40 kV and 20 mA. CeO_2 particle size was determined from the half-height width of the (111) fluorite phase diffraction peak (2θ = 28.5°) by using the Scherrer equation.

Transmission electron microscopy (TEM) analysis. TEM images for supported gold catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator.

Catalytic activity measurements

General procedure for the reduction of UALs and UKEs. Supported gold catalyst (1.97 mg Au, 0.01 mmol) was placed in a 50 mL Parr reactor (Model Number. 4792), followed by the addition of solvent (15 mL) and UALs or UKEs (1 mmol), and then the reaction mixture was vigorously stirred (800 rpm with a magnetic stir bar) at 100 °C under 1.0 MPa of H_2 atmosphere. No variation in reduction rate was observed over a rage of stirrer speeds (400–1000 rpm) indicating the lack of external diffusion limitations. After the reaction, the reaction mixture was filtered and the catalyst was washed thoroughly with ethanol. The products were thoroughly extracted with EtOAc (3 × 20 mL) when water was applied as the solvent. In this case, the organic washings were combined, dried over $MgSO_4$, and then the final product was subjected to GC analysis for identification and quantification of the allylic alcohols. The conversion and product selectivity were periodically determined by GC analysis (Agilent 6820 equipped with a HP-WAX capillary column (0.25 μm, 30 m, 0.32 mm) and a flame ionization detector (FID)) using n-decane as an internal standard. For isolation, the combined organic layer was concentrated under reduced pressure by using a rotator evaporator. The crude product was purified by column chromatography on silica gel (EtOAc–hexane as eluant) to afford the product. All the products were characterized by GC-MS and further confirmed by the comparison of their GC retention time, mass with those of authentic samples.

Recovery and reuse of Au/meso-CeO_2. The catalyst was collected after filtration washed with acetone for three times and then with distilled water for several times. The catalyst was then dried at 100 °C for 12 h before used for next reaction.

Competitive reaction of benzaldehyde and styrene. Au/meso-CeO_2 (1.97 mg Au, 0.01 mmol) was placed in a 50 mL Parr reactor (Model Number. 4792), followed by the addition of solvent (15 mL), benzaldehyde (1 mmol) and styrene (1 mmol), and then the reaction mixture was vigorously stirred (800 rpm with a magnetic stir bar) at 100 °C under 1.0 MPa of H_2 atmosphere.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20873026, 21073042), New Century Excellent Talents in the University of China (NCET-09-0305), the State Key Basic Research Program of PRC (2009CB623506), and Science & Technology Commission of Shanghai Municipality (08DZ2270500).

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