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Chemoselective C=O Hydrogenation of α,β-unsaturated Carbonyl Compounds over Quasihomogeneous and Heterogeneous Nano-Au^0 Catalysts Promoted by Lewis Acidity

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Abstract Lewis-acid promoted Au^0 clusters were used as quasihomogeneous or as heterogeneous metal catalysts for the chemoselective hydrogenation of α,β-unsaturated carbonyl compounds. Addition of Lewis-acid cations like Zn^{2+} to amidic dispersions of size-optimized Au^0 nanocolloids led to an enhanced hydrogenation rate and allylic alcohol chemoselectivity in the hydrogenation of e.g., crotonaldehyde (83% selectivity at 92% conversion). Heterogeneous Au^0 catalysts were generated by the quantitative immobilization of the Au^0 nanocolloids on a nanosized ZnO support, followed by partial removal of the polyvinylpyrrolidone stabilizer. This deposition preserved the nanodispersed state of Au^0, and resulted in a heterogeneous metal catalyst with stable activity and high C=O chemoselectivity in e.g., the hydrogenation of mesityl oxide (66% selectivity at 91% conversion).

Keywords Hydrogenation · Unsaturated aldehyde · Unsaturated ketone · Allylic alcohol · Gold catalyst · Heterogeneous catalyst · Lewis-acid promotion

1 Introduction

Chemoselective C=O hydrogenation of α,β-unsaturated carbonyl compounds to allylic alcohols is an important step in the preparation of fine chemicals [1, 2], and heterogeneous Au catalysts have recently been introduced as catalysts for this hydrogenation by gaseous H_2. Most of the attention has been devoted to α,β-unsaturated aldehydes [3–11]. Less data are available regarding the hydrogenation of the more challenging α,β-unsaturated ketones [12–15]. It has been shown that Au has a much stronger preference for C=O hydrogenation than other metals like Pt or Ru etc. predominantly catalyzing C=C saturation. As further chemoselectivity increases are desirable, particularly for α,β-unsaturated ketones, there is a strong needed to understand the reasons for the encouraging allylic alcohol selectivities obtained with nano-sized Au. Potentially important factors are the size of the Au clusters, their geometrical structure and surface morphology, and the electron density of the metallic clusters. Substantial support effects have been encountered, with oxides like ZnO and Fe_2O_3 giving the best performance. Generally, such supported Au catalysts are produced by incipient wetness impregnation, by deposition-precipitation or by co-precipitation. Such metal oxide supports can influence the catalyst activity in at least two principal ways. First, the support can exert an active promoting effect during the reaction itself, e.g., by activation of a C=O group on a Lewis-acid center [16]. Alternatively, the support can influence the formation process of the Au clusters, and this could as well result in metal catalysts with different performance. This complex situation calls for alternative catalyst preparation procedures, in which a size-controlled, pre-reduced Au phase is contacted with a support.

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We have previously addressed this challenge by preparing polyvinylpyrrolidone (PVP) stabilized sols of Au or other metals (e.g., Ag, Co) via borohydride reduction in amide solvents, e.g., *N*,*N*-dimethylformamide (DMF) [17, 18]. The cluster size in such metal sols can be varied by changing the PVP/Au ratio in the synthesis. In the hydrogenation of crotonaldehyde in amide solvents, optimized Au^0 nanocolloids with an average cluster diameter of 7 nm were used as quasihomogeneous catalysts, resulting in a selectivity of 75% to crotyl alcohol (**1b**) at 90% crotonaldehyde (**1a**) conversion (Scheme 1) [18].

In the present work, we study the promotion of these size-optimized Au^0 nanocolloids by Lewis-acid cations in the crotonaldehyde hydrogenation. An activation of the carbonyl bond could lead to an increase of the specific C=O hydrogenation rate, and thus of the chemoselectivity [16, 19]. Next, it will be attempted to immobilize the PVP-stabilized Au^0 clusters on metal oxide supports, with the aim of quantitatively deposing the Au clusters, and of satisfactorily preserving the Au nanodispersion and the hydrogenation chemoselectivity obtained by promotion with Lewis-acid cations. Finally the generated heterogeneous nano-Au^0 catalysts will be not only being tested for various α,β-unsaturated aldehydes, but also for ketone substrates.

2 Experimental

2.1 Preparation of Au^0 Nanocolloids

The Au^0 sols were prepared as described previously [18]. Briefly, 0.2 mmol $HAuCl_4.3H_2O$ was added to 8 mL DMF containing 0.133 g polyvinylpyrrolidone (MW = 10.000, PVP-10, Sigma-Aldrich), at a molar ratio PVP monomer/Au of 6. After 2 h stirring at 298 K, 1 mmol $NaBH_4$ in 2 mL DMF was added. The Au^0 sols were stirred in a closed vessel for 2 h prior to further use, either in the hydrogenation or immobilization experiments.

2.2 Immobilization of Au^0 Clusters on Metal Oxide Supports

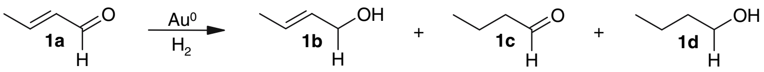
For immobilization of the Au^0 colloids, 2.5 mL of the as-prepared Au^0 sol was added to 2.5 mL DMF containing 0.5, 1.0 or 2.0 g of suspended metal oxide support. The mixture was stirred for 2 h. To enhance the efficiency of the Au^0 heterogenization, 0.1–0.5 ml of a 0.1 M HCOOH solution in DMF was added to the metal oxide dispersion in 2.4–2.0 ml DMF prior to the Au immobilization. In case of quantitative Au immobilization, the heterogenization results in Au loadings of respectively 2.0, 1.0 or 0.5 wt.%. As supporting materials, Fe_2O_3 and ZnO with different particle sizes were taken, all supplied by Aldrich. Fe_2O_3 was used as a powder (Fe_2O_3, <5 µm) or nanopowder (nano-Fe_2O_3, 5–25 nm; maghemite or γ-Fe_2O_3), while ZnO as well was applied in its powder (ZnO, <5 µm) and nanopowder form (nano-ZnO, 50–70 nm). In order to remove excess PVP from the heterogeneous catalyst, 0.5–2 g of the solid was stirred with 5 mL DMF for 15 min and isolated by centrifugation. A next washing cycle was started by resuspending the solid in 5 mL DMF.

2.3 Catalyst Characterization

The colloidal and immobilized Au^0 clusters were characterized by TEM at 200 kV. A droplet of the Au^0 colloid dispersion or a droplet of the well-homogenized heterogeneous Au^0 catalyst suspension was dried on a carbon film supported by a copper grid. The size of the Au^0 clusters was estimated as the number-average diameter (d_p) for an ensemble of 200 Au^0 particles observed in the TEM. Fourier transform infrared spectroscopy (FT-IR) was used to study the presence of surface hydroxyl groups on the metal oxide supports. Metal oxide supports pretreated with organic acids were dried at 473 K under vacuum for 6 h prior to pelletization. The heterogeneous Au^0 catalysts were subjected to thermogravimetric analysis (TGA) in O_2 to obtain information on the amount of PVP deposited on the metal oxide supports. Prior to TGA, the heterogeneous Au^0 catalysts were dried in a vacuum oven at 453 K for 24 h to remove organics like the solvent. The TGA temperature program started at 303 K with a 5 K/min increase up to 873 K. The PVP burned off between 513 K and 593 K. The efficiency of the Au immobilization and the degree of Au leaching from the supported Au^0 catalysts in the hydrogenation experiments were investigated by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4 Hydrogenation Experiments and Product Analysis

A reaction mixture for the hydrogenations catalyzed by the quasihomogeneous Au^0 catalysts consisted of 0.5 mL of as-prepared Au^0 sol, 0.5 mL of DMF, and 2 mmol crotonaldehyde **1a**. Prior to the addition of the substrate, the Au^0 dispersions were pressurized for 1 h with 2.0 MPa H_2 at 298 K in order to avoid surface reoxidation of Au^0 [20].



Scheme 1 Hydrogenation of crotonaldehyde **1a**

The actual reaction mixture was pressurized with 4.0 MPa H_2 and was kept at 333 K while stirring at 1,000 rpm. All reactions were performed in high throughput mode using a multi-reactor unit from TOP containing mini-reactors with an individual volume of 4 mL.

In order to study the effect of Lewis-acid cations (M^{n+}), the 0.5 mL volume of DMF was substituted with 0.5 mL of a solution of $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $SnCl_4$ or $ZnCl_2$ in DMF. The molar M^{n+}/Au ratio was varied between 5/1 and 1/5 (5/1, 5/2, 5/3, 5/4, 5/5, 4/5, 3/5, 2/5, 1/5). In control experiments the metal chloride salts were substituted with the corresponding nitrate or sulfate salts.

For the hydrogenations catalyzed by the heterogeneous Au^0 catalysts, 2 mmol α,β-unsaturated aldehyde (substrate/Au = 200) or 1 mmol α,β-unsaturated ketone (substrate/Au = 100) was added to a 1 mL of DMF suspension containing the metal oxide powder loaded with Au^0 nanoclusters.

For the recycling experiments with the heterogeneous Au^0 catalysts, the reaction mixtures were centrifuged; the supernatant was removed for reaction analysis and the catalyst powder was washed four times with 1 mL DMF. The reaction was restarted by addition of 1.0 mL of a 2.0 M substrate solution in DMF.

Product analysis was performed on a gas chromatograph equipped with a 0.32 mm i.d. by 50 m WCOT fused silica column coated with a Chrompack CP-WAX 58 CB stationary phase (1.2 µm d_f) and a FID detector. Peak assignment of the hydrogenation products was done by comparison of the retention times with those of commercial reference compounds. Allylic alcohols that were not commercially available were prepared from the corresponding carbonyl compounds by reduction according to the Luche protocol [21–22]. In some cases, product identification was aided by GC-MS analysis.

3 Results and Discussion

3.1 Addition of Metal Cations to Au^0 Nanocolloids

As in previous work, size-optimized Au^0 nanocolloids were employed in DMF as the reaction medium [18]. Using these optimum metal colloids, the influence of the addition of Lewis-acid metal cations was investigated in the hydrogenation of crotonaldehyde **1a**, for which crotyl alcohol **1b** is the desired product (Scheme 1). The chloride salts of Co^{2+}, Fe^{3+}, Sn^{4+} and Zn^{2+} were added in a low molar ratio of 1/5 (M^{n+}/Au^0). These metal cations have previously been successfully applied as activity and chemoselectivity promoters for hydrogenation metal catalysts [23, 24].

All Lewis-acid cations truly acted as activators inducing a rise in the conversion rates and turnover frequencies, at low as well as at high crotonaldehyde conversion level. This is proven in detail by the turnover frequency values given in Table 1. The hydrogenation rate with the promoted Au^0 nanocolloids increased in the order $Sn^{4+} < Fe^{3+} < Zn^{2+} < Co^{2+}$ and the order of these TOF values is maintained over the full course of the crotonaldehyde hydrogenation. Since the maximization of the selectivity towards the formation of crotyl alcohol **1b** was our major objective, the effect of the metal cations on the chemoselectivity was primarily evaluated at high crotonaldehyde conversion (Table 1, entries 6–10). This allowed a fair comparison of the induced improvement on the crotyl alcohol selectivity for the different metal cations. The strongest enhancement in C=O hydrogenation chemoselectivity was observed for Fe^{3+} and Zn^{2+}. In line with literature, the selectivity promotion by Fe^{3+} and Zn^{2+} can be ascribed to the specific activation of the C=O bond by interaction with cations adsorbed on the Au^0 surface and concomitant acceleration of the C=O hydrogenation [23]. The addition of Sn^{4+} led only to a small promoting effect, whereas the presence of Co^{2+} even had a negative effect on the chemoselectivity. Promotion by Co^{2+} and Sn^{4+} was therefore not considered further.

The detailed evolution of the chemoselectivity with the crotonaldehyde conversion is given in Table 2, both for the Au sols and for Au sols with added Fe^{3+} or Zn^{2+}. As expected, in all cases the selectivity for the primary products crotyl alcohol (**1b**) and butanal (**1c**) decreases with conversion, while the selectivity for the secondary product 1-butanol (**1d**) increases. The crotyl alcohol selectivity decrease is similar in all reactions, showing that the added ions do not really affect the susceptibility of crotyl alcohol to secondary reaction. Noteworthily, the decrease of the butanal selectivity with conversion is much sharper for the

Table 1 Influence of Lewis-acid cations (M^{n+}) on the hydrogenation of crotonaldehyde **1a** catalyzed by Au^0 nanocolloids

	M^{n+}	Time [h]	$C_{unsat.carb}$ [%]	$S_{all.alc.}$ [%]	$Y_{all.alc.}$ [%]	*TOF* $[h^{-1}]^a$
1	/	5	28	78	22	11.0
2	Co^{2+}	5	39	74	29	15.7
3	Fe^{3+}	5	32	81	26	13.0
4	Sn^{4+}	5	31	78	24	12.3
5	Zn^{2+}	5	35	85	30	14.1
6	/	40	92	74	68	4.6
7	Co^{2+}	28	93	66	61	6.7
8	Fe^{3+}	32	91	78	71	5.7
9	Sn^{4+}	36	92	76	70	5.1
10	Zn^{2+}	28	90	81	73	6.4

Reaction conditions: $HAuCl_4 \cdot 3H_2O$, DMF, PVP/Au = 6, M/Au = 0.2, **1a**/Au = 200, 4.0 MPa H_2, 333 K

[a] TOF = (moles of substrate converted) (moles of metal)$^{-1}$ h^{-1}, calculated over the entire reaction

Table 2 Influence of Lewis-acid cations (Fe^{3+},Zn^{2+}) on the product distribution in the hydrogenation of crotonaldehyde **1a** over Au^0 nanocolloids

	M^{n+}	$C_{unsat.carb.}$ [%]	$S_{all.alc.}$ [%]	$S_{sat.carb.}$ [%]	$S_{sat.alc.}$ [%]
1	/	26	79	11	10
2		48	77	9	14
3		73	76	8	16
4		91	74	6	20
5	Fe^{3+}	25	83	9	8
6		51	82	8	10
7		74	80	6	14
8		90	79	5	16
9	Zn^{2+}	27	87	7	6
10		49	85	5	10
11		76	82	4	14
12		91	81	2	17

Reaction conditions: $HAuCl_4 \cdot 3H_2O$, DMF, PVP/Au = 6, M/Au = 0.2, **1a**/Au = 200, 4.0 MPa H_2, 333 K

reaction in the presence of Zn^{2+} (entries 9–12) than in the absence of added metal ions (entries 1–4). This indicates that Zn^{2+} activates not only the C=O group in crotonaldehyde, but also the carbonyl group of the saturated aldehyde.

To verify the role of the chloride counteranions, the nitrate and sulfate salts of Fe^{3+} and Zn^{2+} were also evaluated as promoters. As the crotyl alcohol yields were essentially the same as those obtained with the chloride-based promoters, one can state that the different anions merely act as spectators [24].

Next the molar Fe^{3+}/Au^0 and Zn^{2+}/Au^0 ratios were varied between 5/1 and 1/5, in order to locate the optimum ratio for maximum crotyl alcohol chemoselectivity. At 90% crotonaldehyde conversion, the plots of crotyl alcohol selectivity versus promoter cation content reach maxima at Fe^{3+}/Au^0 and Zn^{2+}/Au^0 ratios of 3/5 and 2/5, respectively. This corresponds to chemoselectivity improvements of approximately 5 and 10% in comparison with the unpromoted Au^0 nanocolloids, for which the selectivity amounts to 75% at equal conversion.

Figure 1a, b shows the TEM image of the as-prepared, size-optimized Au^0 nanocolloids and that of Au^0 nanocolloids promoted by an optimum amount of Zn^{2+}. The micrographs prove that the dispersion of the Au is not changed by the metal salt.

3.2 Au^0 Clusters Immobilized on Metal Oxide Supports

In a second approach, the size-optimized Au^0 clusters were immobilized on metal oxide supports such as iron oxide (Fe_2O_3) and zinc oxide (ZnO). As discussed in the previous section, addition of the corresponding metal cations (Fe^{3+} and Zn^{2+}) to the Au^0 nanocolloids turned out beneficial both in terms of hydrogenation rate and chemoselectivity. Adsorption of the PVP polymer, stabilizing the Au^0 clusters, on the metal oxide support may occur through hydrogen-bonding or via acid-base interactions with the surface hydroxyl groups [25, 26]. The availability of such groups on the Fe_2O_3 and ZnO supports was clearly demonstrated by monitoring the $\nu_{O\text{–}H}$ vibrations by FT-IR spectroscopy. For Fe_2O_3, a characteristic peak was observed at ~3,350 cm^{-1} and for ZnO this band appeared at ~3,410 cm^{-1} [27, 28]. In order to obtain catalysts with a reasonable specific activity, it was attempted to load 2 wt.% of Au on the supports. With the conventional metal oxide powders (<5 μm), it proved impossible to reach Au loadings exceeding 0.5 wt.%. The limited immobilization capacity for Au^0 clusters must be related to the low surface area of these metal oxides. We therefore resorted to the same metal oxides but with nanodimensions (<70 nm). Using nano-ZnO as the support and offering 2 wt.% of Au, the Au^0 nanocolloids were quantitatively immobilized as evidenced by ICP-AES. For the corresponding nano-Fe_2O_3 support, which contains even smaller particles, the same Au immobilization procedure resulted in an Au deposition efficiency of only ~80%. The higher Au immobilization capacity of the ZnO nanopowder is presumably related to the higher point of zero charge for nano-ZnO in comparison with Fe_2O_3 [29]. This implies that at any pH, the protonation degree of a ZnO surface is higher than that of a Fe_2O_3 surface; a higher number of surface hydroxyl groups on nano-ZnO support might lead to a better adsorption of the PVP-protected Au^0 nanoclusters.

To improve the Au immobilization capacity of the nano-Fe_2O_3 support, formic acid was added during the catalyst preparation. This could result in a stronger interaction between the support and the PVP surrounding the Au^0 nanoclusters. As previously observed [30], interaction of organic acids (e.g., formic acid) with the surface hydroxyl groups of metal oxides results in a solid polyacid which can strongly bind with PVP [31]. A molar formic acid/Au^0 ratio

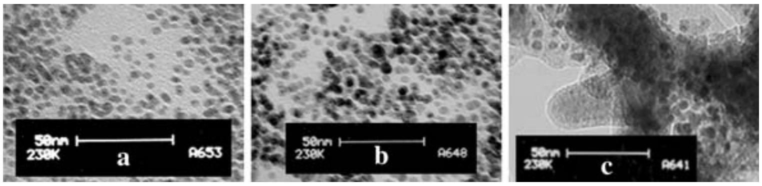


Fig. 1 TEM images of the size-optimized Au^0 nanosol (**a**), the same Au^0 nanosol promoted by the optimum amount of Zn^{2+} (**b**), and the optimum Au^0/nano-ZnO catalyst (2 wt.% Au) with reduced PVP content (**c**)

of 3/5 proved sufficient to achieve quantitative immobilization of the Au^0 nanocolloids on the nano-Fe_2O_3 support at an Au loading of 2 wt.%. In order to allow better comparisons, the formic acid/Au^0 ratio of 3/5 was employed for all further preparations of supported 2 wt.% Au^0 catalysts. Figure 1c shows a TEM image of Au^0/nano-ZnO (2 wt.% Au loading), which has been treated with the appropriate amount of formic acid during the preparation. The Au^0 nanoparticles are well dispersed on the surface of the nano-ZnO support and the size of the Au^0 clusters remains unchanged throughout the immobilization.

The heterogeneous 2 wt.% Au^0 catalysts were then applied in the hydrogenation of crotonaldehyde **1a** and their catalytic performance was compared with the 'quasihomogeneous' Au^0 sol, either unpromoted or promoted by Fe^{3+} or Zn^{2+} at the optimum M^{n+}/Au^0 ratio (Table 3).

The heterogenized Au^0 clusters displayed a lower catalytic activity in comparison with the corresponding unpromoted Au^0 nanocolloids (Table 3, entries 1–5). This effect is less pronounced for the nano-ZnO catalyst. The reduced activity may be due to more severe diffusion limitations because of compaction of the protective PVP polymer surrounding the Au^0 clusters; or the immobilization on the support might block part of the active Au^0 sites. On the other hand, in comparison with the original Au^0 sol, immobilization of nano-sized Au^0 resulted in an increase of the chemoselectivity (Table 3, entries 6–10). This evidences a substrate C=O activation by the nano-sized metal oxide supports. The largest improvement was observed for the 2 wt.% Au^0/nano-ZnO catalyst, even if the chemoselectivity enhancement was smaller than for promotion by dissolved Zn^{2+}. The nano-Fe_2O_3 support had a less pronounced beneficial effect. The promoting role of Lewis acidity in such chemoselective C=O hydrogenations of α,β-unsaturated carbonyl compounds is in agreement with literature work.[15, 32]

Table 3 Influence of Lewis-acid cations and metal oxide supports on the hydrogenation of crotonaldehyde **1a** catalyzed by Au0 nanoclusters

	Catalyst	Time [h]	$C_{\text{unsat.carb}}$ [%]	$S_{\text{all.alc.}}$ [%]	$Y_{\text{all.alc.}}$ [%]
1	Au^0	5	29	78	23
2[a]	$Au^0 + Fe^{3+}$	5	35	81	28
3[b]	$Au^0 + Zn^{2+}$	5	37	86	32
4[c]	Au^0/nano-Fe_2O_3	5	22	80	18
5[c]	Au^0/nano-ZnO	5	25	81	20
6	Au^0	40	92	73	67
7[a]	$Au^0 + Fe^{3+}$	28	90	79	71
8[b]	$Au^0 + Zn^{2+}$	28	92	83	76
9[c]	Au^0/nano-Fe_2O_3	48	91	76	69
10[c]	Au^0/nano-ZnO	42	90	78	70

Reaction conditions: $HAuCl_4.3H_2O$, DMF, PVP/Au = 6, **1a**/Au = 200, 4.0 MPa H_2, 333 K

[a] M/Au = 0.6

[b] M/Au = 0.4

[c] 2 wt.% Au

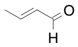
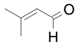
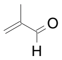
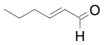
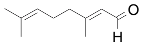
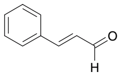
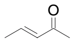
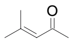
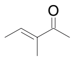
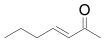
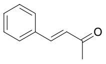
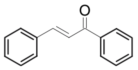
Next, the performance of Au^0/nano-ZnO catalysts with Au loadings of 0.5, 1.0 and 2.0 wt.% was compared in the hydrogenation of crotonaldehyde. The supported nano-Au^0 catalyst with a Au loading of 2 wt.% displayed the highest activity on Au basis, while the obtained hydrogenation chemoselectivities were comparable for the different Au loadings. In an additional control experiment the effect of the formic acid addition on the performance of the 2 wt.% Au^0/nano-ZnO was verified. No significant difference in catalytic performance was observed between catalysts prepared with or without formic acid. Thus, while acid addition is effective in improving the PVP retention on the solid, it can be supposed that excess acidity is to some extent captured by the amide solvent or by the PVP.

In order to alleviate a potentially negative effect of the PVP chains on the Au activity, it was attempted to partially remove the protective polymer from the metal oxide support. Since amide solvents like DMF have a high affinity for PVP, we expected that rinsing the 2 wt.% Au^0/nano-ZnO catalyst with DMF would result in PVP desorption and an enhanced contact between the Au^0 and the ZnO support. The PVP leaching during successive washing cycles was monitored by means of thermogravimetric analysis. Fivefold washing of the 2 wt.% Au^0/nano-ZnO catalyst resulted in a reduction of the PVP content from ~6.5 wt.% to 2.2 wt.%. Importantly, it was confirmed by ICP-AES that no Au species were lost during the successive rinsing steps. The activity of the resulting 2 wt.% Au^0/nano-ZnO catalyst was approximately ~10% higher in comparison with the original catalyst. The chemoselectivity of the treated catalyst also slightly improved, and this might be indicative of an enhanced interaction between the Au^0 clusters and the metal oxide surface. Repeating the PVP washing another 5 times did not result in a further loss of PVP from the Au^0/nano-ZnO catalyst, with a residual PVP loading of 2.0 wt.% after ten rinsing steps with DMF.

Re-use of the optimized 2 wt.% Au^0/nano-ZnO catalyst was studied in the hydrogenation of crotonaldehyde. In the fifth catalyst recycling, 90% of the hydrogenation activity observed in the first run was maintained, without a decrease in the crotyl alcohol selectivity.

Finally, the optimum Au^0/nano-ZnO catalyst (2 wt.% Au, reduced PVP loading) was applied in the chemoselective hydrogenation of different α,β-unsaturated aldehydes and ketones (Table 4). All reactions were run towards a substrate conversion of 90%. This allowed a fair comparison of the allylic alcohol selectivities for the

Table 4 Comparative study of substrate reactivity and hydrogenation chemoselectivity over Au^0/nano-ZnO catalyst (2 wt.%, reduced PVP loading)

	Substrate		Time [h]	$C_{unsat.carb}$ [%]	$S_{all.alc.}$ [%]
1[a]		**1a**	40	91	79
2[a]		**2a**	72	92	87
3[a]		**3a**	48	90	83
4[a]		**4a**	54	91	85
5[a]		**5a**	60	90	78
6[a]		**6a**	84	91	95
7[b]		**7a**	36	93	37
8[b]		**8a**	54	91	66
9[b]		**9a**	60	90	72
10[b]		**10a**	60	93	55
11[b]		**11a**	40	93	69
12[b]		**12a**	60	90	44

Reaction conditions: $HAuCl_4.3H_2O$, DMF, PVP/Au = 6, 2 wt.% Au, 4.0 MPa H_2, 333 K

[a] substrate/Au = 200

[b] substrate/Au = 100

different substrates. On the other hand, the reaction time required to achieve a conversion level of 90% was a good estimate for the reactivity of each α,β-unsaturated carbonyl compound.

By studying a large number of substrates, significant effects of the substrate substitution pattern on the allylic alcohol selectivity could be discerned. Firstly, the hydrogenation of α,β-unsaturated ketones proceeds with markedly lower chemoselectivity compared to the hydrogenation of the corresponding aldehydic substrates. This was clearly shown in the hydrogenation of prenal **2a** versus mesityl oxide **8a,** and leaf aldehyde **4a** versus 3-hepten-2-one **10a** (Table 4, Entries 2, 8 and 4, 9). As proposed by Ponec [16], this effect must essentially be steric, due to repulsion between the electrons in the metal and the fully occupied σ-orbitals in the substituent on the C=O group. Consequently, a larger substituent on the C=O group decreases its chances to be adsorbed and reduced. For substrates with a β-phenyl substitution on the C=C bond, such as cinnamaldehyde **6a**, benzalacetone **11a** and chalcone **12a**, a similar trend was observed: the chemoselectivity gradually decreases as the H-substituent on the carbonyl group is replaced with a methyl or an even more bulky phenyl group. Secondly, α-methyl substitution of the C=C bond results in higher chemoselectivities compared to β-methyl substitution. This was found in the hydrogenation of methacrolein **3a** versus crotonaldehyde **1a**, and 3-methyl-3-penten-2-one **9a** versus mesityl oxide **8a** (Table 4, entries 1, 3, 8 and 9). In addition, an extension of the alkyl chain in the β-position leads to a higher chemoselectivity. For instance, substitution of the methyl group in crotonaldehyde **1a** with the more bulky *n*-propyl group in leaf aldehyde **4a** causes an increase of the allylic alcohol yield of 5% at similar conversion (Table 4, entries 1 and 4). Finally, substitution of the β-methyl group on the C=C bond by a phenyl ring markedly increases the allylic alcohol selectivity. This selectivity gain seems partly due to steric shielding of the C=C bond; on the other hand, the large polarizability of the Ph–CH=CH–C(H)=O conjugated system makes activation of the carbonyl group more likely, and thus increases the chances for C=O reduction. Allylic alcohols yields of respectively 72%, 70%, 86%, 60% and 64% were obtained over the optimized 2 wt.% Au^0/nano-ZnO catalyst in the hydrogenation of well-studied substrates like crotonaldehyde (**1a**), citral (**5a**), cinnamaldehyde (**6a**), mesityl oxide (**8a**) and benzalacetone (**11a**) at 90% conversion.

4 Conclusions

The high intrinsic chemoselectivity of polyvinylpyrrolidone-stabilized Au^0 clusters in the reduction of α,β-unsaturated carbonyl compounds can be further enhanced by interaction with Lewis acids such as cationic Zn or Fe. Of all promoters tested, Zn^{2+} gives the best performance in terms of chemoselectivity. Promotion of the Au^0 clusters by dissolved Zn^{2+} is slightly more effective than promotion at the surface of nanosized ZnO crystals. A facile procedure was designed for the deposition of PVP-wrapped Au on ZnO or Fe_2O_3. Formic acid addition during preparation improves the retention of the Au; washing with DMF partially removes excess PVP. A broad screening of potential substrates shows that the α,β-unsaturated aldehydes are converted with allylic alcohol selectivities between 78% and 95% at 90% conversion. For the ketone substrates, the selectivity is around 70% at high conversion, which is among the best results reported so far for a heterogeneous metal catalyst.

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