

## First example of selective hydrogenation of unconstrained $\alpha,\beta$ -unsaturated ketone to $\alpha,\beta$ -unsaturated alcohol by molecular hydrogen

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Selective hydrogenation of unconstrained  $\alpha,\beta$ -unsaturated ketones to the corresponding unsaturated alcohols has been achieved on Au supported on  $\text{Fe}_2\text{O}_3$  catalysts.

Benzalacetone (*trans*-4-phenyl-3-buten-2-one) has been hydrogenated to unsaturated alcohol (4-phenyl-3-buten-2-ol) with a selectivity higher than 60% up to 100% conversion.

The catalytic hydrogenation of  $\alpha,\beta$ -unsaturated ketones to the corresponding unsaturated alcohols by molecular hydrogen is a very intriguing challenge for people working in catalysis. Up to now studies on this topic have been almost unsuccessful. The main routes for the syntheses of unsaturated alcohols from  $\alpha,\beta$ -unsaturated ketones are the classical homogeneous reduction with  $\text{LiAlH}_4$  or reduction by hydride transfer from isopropanol to the enone C=O group (Meerwin–Pondorf–Verley reduction).<sup>1,2</sup>

In contrast to the  $\alpha,\beta$ -unsaturated aldehydes, for which the selective hydrogenation of the C=O bond can be achieved by promoting noble metal catalysts with s,p non-transition elements such as Sn(II), Ge(IV), Ga(III) or transition metal elements such as Fe(III), the hydrogenation of unsaturated ketones always leads to the formation of the saturated ketone.<sup>3</sup> Ponec *et al.* have reported that the rate of hydrogenation of the C=O bond of propanal is dramatically enhanced by addition of Sn(II), Ga(III) or Fe(III) to a Pt/SiO<sub>2</sub> catalyst, whereas the rate of hydrogenation of acetone is only slightly increased.<sup>4</sup>

A direct evidence of the low efficacy of the addition of promoters to noble metal catalysts for the selective hydrogenation of  $\alpha,\beta$ -unsaturated ketones has also been obtained in this present study.

The hydrogenation of benzalacetone, carried out on Ru/C and Pt/C catalysts (Me = 2 wt.%) and on Sn(II) promoted Ru and Pt catalysts, Ru = 2 wt.%; Sn = 1.56 wt.% and Pt = 2 wt.%; Sn = 0.58 wt.%, led to saturated ketone as the main reaction product, regardless of the presence of the promoter. It should be noted that the above catalysts are highly selective towards the formation of the unsaturated alcohol in the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes as cinnamaldehyde and citral.<sup>5–7</sup>

Recently, an example has been reported of selective hydrogenation of the C=O bond of ketoisophorone, an  $\alpha,\beta$ -unsaturated ketone having a sterically hindered carbonyl group, to the corresponding unsaturated alcohol over Pd/Al<sub>2</sub>O<sub>3</sub>.<sup>8</sup> However the authors have pointed out that when the catalyst has been employed for the reduction of an  $\alpha,\beta$ -unsaturated ketone having unconstrained C=O bond, no unsaturated alcohol has been obtained.

In the present work we demonstrate that gold supported on  $\text{Fe}_2\text{O}_3$  catalysts can be successfully used for the selective hydrogenation of  $\alpha,\beta$ -unsaturated ketones, having an unhindered C=O group, to the correspondent  $\alpha,\beta$ -unsaturated alcohols. It has already been reported that gold dispersed on a nanometric scale shows a remarkable intrinsic selectivity, with respect to the Group VIII metal catalysts, towards the hydrogenation of the C=O bond in the hydrogenated  $\alpha,\beta$ -unsaturated aldehydes,<sup>9</sup> and that the rate of hydrogenation of C=O is strongly influenced by the nature of the support, Au/Fe<sub>2</sub>O<sub>3</sub> and Au/ZrO<sub>2</sub> being much more selective than Au/SiO<sub>2</sub>.<sup>9–12</sup>

The catalytic activity of Au supported on  $\text{Fe}_2\text{O}_3$  and Al<sub>2</sub>O<sub>3</sub> in the liquid phase hydrogenation of *trans*-3-buten-4-phenyl-2-one (benzalacetone) has been investigated. Gold catalysts have been prepared by classical co-precipitation and deposition–precipitation methods. The co-precipitation was carried out by adding an aqueous solution of HAuCl<sub>4</sub> (Fluka) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Fluka) to a solution of Na<sub>2</sub>CO<sub>3</sub> 1 M (pH = 11.9) kept at 80 °C, under vigorous stirring. The solid was digested overnight at room temperature and then washed with water until free of chloride ions (AgNO<sub>3</sub> test). The deposition–precipitation method, described elsewhere,<sup>13</sup> consists of the addition of the support to a solution of HAuCl<sub>4</sub> previously adjusted at pH 8–9 with NaOH and kept at 70 °C. The slurry was vigorously stirred for two hours then filtered off and washed with water until chloride free. Catalysts were dried under vacuum ( $p = 10^{-2}$  mbar) at 80 °C for one day.

Catalytic experiments were carried out in a batch reactor at atmospheric pressure under H<sub>2</sub> flow, at 60 °C, using a four-necked flask fitted with a reflux condenser, dropping funnel, thermocouple and a stirrer head. Benzalacetone (Aldrich) and solvent (ethanol) were commercial analytical grade products and were used without further purification. The catalyst was added to 25 ml of solvent and reduced “*in situ*” at 70 °C for 1 h. After cooling at reaction temperature the substrate ( $6 \times 10^{-4}$  mol) was injected through one arm of the flask. The reaction mixture was stirred at 700 rpm. The progress of the reaction was followed by analysis of a sufficient number of microsamples by means of GC-MS equipped with a EC-WAX capillary column (60 m, 0.25 mm id).

The reaction products, 4-phenyl-butan-2-one (saturated ketone) and 4-phenyl-butan-2-ol (saturated alcohol) were identified by comparison with commercial products. The unsaturated alcohol, 4-phenyl-3-buten-2-ol, was identified by comparison with a standard compound synthesized according to a method reported in the literature<sup>14</sup> and extensively characterized by mass spectrometry and NMR.

Preliminary runs carried out at different stirring conditions, loading and catalyst grain size demonstrated the absence of external and internal diffusion limitations.

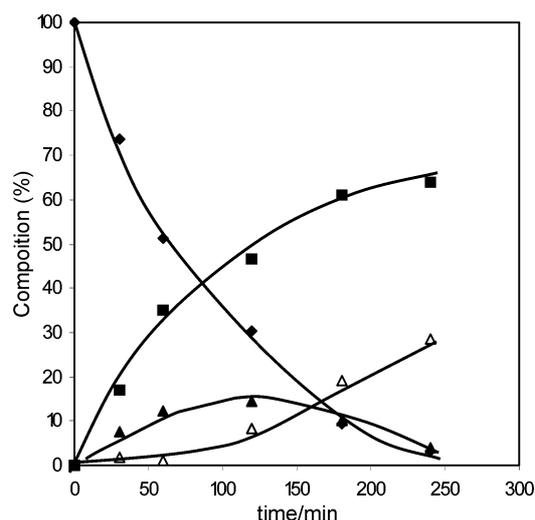
Fig. 1 shows a typical course of the hydrogenation of benzalacetone on Au/Fe<sub>2</sub>O<sub>3</sub> catalysts. It shows that the formation of the saturated ketone and of the unsaturated alcohol occurs through parallel reactions, whereas the saturated alcohol is mainly obtained by the further hydrogenation of the C=O bond of the saturated ketone. The hydrogenation of the unsaturated alcohol is not observed up to 100% of conversion of benzalacetone.

In order to rule out the possibility that the hydrogen atoms are supplied by the alcoholic solvent, the reaction was carried out under N<sub>2</sub>. After activation “*in situ*”, the system was flushed in N<sub>2</sub> at 60 °C for one night then the substrate was introduced into the reaction vessel. Under these conditions, no conversion of benzalacetone was observed up to 3 h of contact time thus indicating that the reaction does not occur through a Meerwin–Pondorf–Verley reduction mechanism. Moreover, when H<sub>2</sub> was readmitted into the reaction vessel, the hydrogenation of benzalacetone occurred.

**Table 1** Catalytic activity and selectivity for the hydrogenation of benzalacetone<sup>a</sup>

Catalyst	Metal load (wt.%)	Preparation method	$V_i \times 10^8/\text{mol g}_{\text{cat}}^{-1} \text{ s}^{-1}$	Conversion (%)	Selectivity (%)	Selectivity (%)	Selectivity (%)
					S.K.	U.A.	S.A.
Au/Fe <sub>2</sub> O <sub>3</sub>	5.3	Coprecipitation	1.6	28.7	35.8	<b>57.3</b>	6.9
Au/Fe <sub>2</sub> O <sub>3</sub>	16.6	Coprecipitation	3.5	99.1	1.5	<b>56.2</b>	42.3
Au/Fe <sub>2</sub> O <sub>3</sub>	4.2	Deposition–Precipitation	10	26.5	28.4	<b>64.2</b>	7.4
Au/Al <sub>2</sub> O <sub>3</sub>	5.1	Deposition–Precipitation	0.2	90.5	11.2	<b>67.5</b>	21.2
Ru/Fe <sub>2</sub> O <sub>3</sub>	2.0	Impregnation	20	27.7	30.1	<b>66.6</b>	3.3
				70.2	24.4	<b>65.8</b>	9.8
				26.7	85.3	<b>10.9</b>	3.8
				36.3	97.5	<b>1.7</b>	0.8
				92.1	94.8	<b>1.4</b>	3.8

<sup>a</sup> S.K. = saturated ketone, U.A. = unsaturated alcohol, S.A. = saturated alcohol.



**Fig. 1** Hydrogenation of benzalacetone on Au/Fe<sub>2</sub>O<sub>3</sub> (Au = 16.6 wt.%). (Reaction conditions:  $T = 60$  °C,  $P_{\text{H}_2} = 1$  atm, ethanol = 25 ml, benzalacetone =  $6 \times 10^{-4}$  mol, catalyst = 0.500 g). Benzalacetone (◆), saturated ketone (▲), unsaturated alcohol (■), saturated alcohol (△)

Table 1 reports the initial rate of disappearance of benzalacetone  $V_i$  ( $\text{mol g}_{\text{cat}}^{-1} \text{ s}^{-1}$ ) and the product distribution, at low and high conversion, during the hydrogenation of the unsaturated ketone.

On Au supported on Fe<sub>2</sub>O<sub>3</sub> catalysts, the activity and selectivity towards the formation of the unsaturated alcohol depend on the gold content and on the preparation method. On catalysts prepared by co-precipitation the catalytic activity and the selectivity increases with the gold loading. Moreover, Au/Fe<sub>2</sub>O<sub>3</sub> prepared by deposition–precipitation is more active and selective towards the formation of unsaturated alcohol than an analogous sample prepared by co-precipitation.

The activity and selectivity towards the formation of the unsaturated alcohol are strongly influenced by the nature of the support, with Au supported on Fe<sub>2</sub>O<sub>3</sub> being much more selective than the analogous catalyst dispersed on Al<sub>2</sub>O<sub>3</sub>.

It should be noted, however, that on Ru/Fe<sub>2</sub>O<sub>3</sub> the selectivity to the unsaturated alcohol was less than 2% (Table 1), thus indicating the high specificity of gold for this reaction.

Gold catalysts reported in Table 1 have also been used for the hydrogenation of cinnamaldehyde (*trans*-3-phenyl-2-propen-1-al), the  $\alpha,\beta$ -unsaturated aldehyde having the same structure as the benzalacetone. It has been found that on Au/Fe<sub>2</sub>O<sub>3</sub> the selectivity towards the formation of the cinnamyl alcohol is higher than 85% up to 100% of conversion, whereas on Au/Al<sub>2</sub>O<sub>3</sub> it is 60% at 40% of conversion. The high selectivity of

the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts towards the hydrogenation of the C=O bond for the hydrogenation of an unsaturated aldehyde agrees with our previous findings on the hydrogenation of citral (3,7-dimethyl-2,6-octadien-1-al) on similar catalysts.<sup>12</sup>

The enhancement of the selectivity towards the formation of the cinnamyl alcohol on Au/Fe<sub>2</sub>O<sub>3</sub> with respect to Au/Al<sub>2</sub>O<sub>3</sub> can be explained by considering that iron sites on the surface of the support act as promoters, activating the C=O bond of the unsaturated aldehyde.<sup>12</sup>

By analogy, it can be speculated that for the hydrogenation of benzalacetone, the higher selectivity towards the formation of unsaturated alcohols on Au supported on Fe<sub>2</sub>O<sub>3</sub> with respect to Al<sub>2</sub>O<sub>3</sub> is due to the activation of the C=O bond on the iron sites of the support. However, it cannot be ruled out that the role of the support is to modify the electronic properties of the metal which in turn leads to an increase in the hydrogenation rate of the C=O bond.

In conclusion, we would like to remark that the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts are the first examples of heterogeneous catalysts able to selectively hydrogenate unconstrained unsaturated ketones to unsaturated alcohols with a yield higher than 60%.

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