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Selective liquid phase hydrogenation of citral on Au/Fe_2O_3 catalysts

C. Milone, M. L. Tropeano, G. Gulino, G. Neri, R. Ingoglia and S. Galvagno*
Dipartimento di Chimica Industriale e Ingegneria dei Materiali, Salita Sperone 31, 98166 Messina, Italia.
E-mail: galvagno@ingegneria.unime.it

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Gold supported on iron oxide hydrogenates citral (an α,β-unsaturated aldehyde) to the corresponding α,β-unsaturated alcohols (geraniol and nerol) with a selectivity higher than 95%.

Beside CO oxidation, several studies have demonstrated that gold supported catalysts show a remarkable catalytic activity for a wide number of reactions including hydrogenations.[1,2]

Of great interest are the few literature data concerning the activity showed by gold supported catalysts in the hydrogenation of complex systems such as α,β-unsaturated aldehydes.[3–6]

Shibata *et al.*[3] have reported that an oxidized amorphous Au–Zr alloy (30 atom% Au) catalyses the hydrogenation of but-2-enal and 2-methylprop-2-enal with a maximum selectivity towards the formation of unsaturated alcohols of 59.4 and 47.3%, respectively. Moreover it was found that Au/ZrO_2 prepared by impregnation shows a much lower activity with respect to Au–Zr alloy. The influence of the preparation method on the hydrogenation activity of gold supported catalysts has been pointed out by Hutchings *et al.*[4] in their study on the hydrogenation of crotonaldehyde on Au/ZnO and Au/ZrO_2. They found that catalysts prepared by coprecipitation are more active than analogous catalysts prepared by impregnation. The maximum selectivity towards the formation of crotyl alcohol was almost 50% on both catalytic systems, however, the conversion is lower than 20%.

The selective hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols is a reaction of great importance in the synthesis of fine chemicals. The selectivity of this reaction presents some difficult challenges, since one is attempting to enhance the rate of hydrogenation of the C=O bond while suppressing that of hydrogenation of the C=C bond. It is well known that classical hydrogenation metal catalysts show no or low selectivity towards the hydrogenation of the C=O bond and that the selectivity of the metal catalysts can be improved by addition of promoters such as Fe(III), Sn(II), Ge(IV). Also effective are electron donating ligand effects from the support, steric constraints in the metal environment, strong metal–support interaction, selective poisoning, presence of substituents on the C=C bond, solvent and pressure effects.[7]

Taking into account the hydrogenation activity showed by gold supported catalysts, we thought that Au/Fe_2O_3 prepared by coprecipitation should be in principle a suitable catalyst for the selective hydrogenation of α,β-unsaturated aldehydes to α,β-unsaturated alcohols. Iron on the surface of the support would act as a promoter activating the C=O bond thus increasing its hydrogenation activity. Moreover dispersed gold shows a weaker interaction with the C=C bond with respect to noble metals such as Pt or Pd.[2,8] Therefore this could contribute to a decrease of the rate of formation of saturated aldehyde during the hydrogenation of an α,β-unsaturated aldehyde.

Liquid phase hydrogenation of citral (3,7-dimethyl-2,6 octadienal) was taken as a reaction model to investigate the catalytic activity of gold supported on Fe_2O_3 catalysts. The catalytic activity of gold supported catalysts was also compared with that of Pt supported on Fe_2O_3 catalysts.

Au/Fe_2O_3 catalysts with low (Au wt% = 3.1) and high (Au wt% = 16.6) gold loading were prepared by coprecipitation using $HAuCl_4$ (Fluka) and $Fe(NO_3)_3{\cdot}9H_2O$ (Fluka) as starting materials. An aqueous mixture of $HAuCl_4$ and $Fe(NO_3)_3{\cdot}H_2O$ was poured into an aqueous solution of 1 M Na_2CO_3 (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 ($AgNO_3$ test).

Catalysts were dried under vacuum ($p = 10^{-2}$ mbar) at 80 °C for one day. Gold content has been determined by a spectrofotometric method.[9] Pt supported on Fe_2O_3 catalysts were prepared by either metal vapor deposition (code: PtMVS) or wetness impregnation of iron oxide with a solution of H_2PtCl_6 (code: PtI). The support was prepared by precipitation of iron hydroxide following the same procedure used for the preparation of the coprecipitated gold catalysts. Pt/Fe_2O_3 prepared by wetness impregnation was reduced under H_2 flow at 300 °C.

Catalytic experiments were carried out at atmospheric pressure under H_2 flow, at 60 °C, in a four-necked flask fitted with a reflux condenser, dropping funnel, thermocouple and a stirrer head. Citral (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 (0.5 ml) was injected through one arm of the flask. The reaction mixture was stirred at 700 rpm. The progress of the reaction was followed by sampling a sufficient number of microsamples. Chemical analyses were performed by means of GC-FID. The gas chromatographic column was a EC-WAX wide-bore capillary column (60 m, 0.53 mm i.d.).

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

On all catalysts, hydrogenation of citral leads mainly to the formation of unsaturated alcohols (geraniol and nerol, the *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) is the other main reaction product. A further addition of hydrogen to citronellal gives citronellol (3,7-dimethyl-6-octenol). Up to 100% of citral conversion, the further hydrogenation of the unsaturated alcohols to citronellol was not observed. Products of hydrogenation of the isolated C=C double bond as well as isopulegol, a cyclic isomer of citronellal, previously reported in the hydrogenation of citral on Ru catalysts,[10,11] were not detected. The results obtained for the hydrogenation of citral on gold supported catalysts are reported in Table 1. The catalytic activity increases with the gold loading while the products distribution is similar regardless of the amount of the noble metal. It is noteworthy that the unsaturated alcohols, geraniol and nerol, are the main reaction products thus indicating the high activity of these catalysts towards the hydrogenation of the C=O bond with respect to the conjugated C=C bond. Selectivity to unsaturated alcohols, measured at 90% of conversion of citral, is higher than 95% regardless of the gold loading.

Recycle tests of gold supported catalysts have shown a loss of activity of 20% with respect to the fresh catalysts with no changes in the products distribution.

For comparison, the hydrogenation of citral has been carried

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Table 1 Catalytic activity and selectivity in the hydrogenation of citral on Fe_2O_3 supported catalysts

					Selectivity (%)		
Code	Preparation method	Au (wt%)	Pt (wt%)	10^8 V_i^a/mol g_{cat}^{-1} s^{-1}	Citronellal	Citronellol	Nerol + Geraniol
AF3.1	Coprecipitation	3.1	—	3.0	0.18	2.84	96.98
AF16.6	Coprecipitation	16.6	—	66.5	0.53	3.54	95.93
Pt MVS	Metal vapor deposition	—	0.9	140.5	0.79	12.85	86.36
Pt I	Impregnation	—	2	9.4	0.93	11.04	88.03

[a] V_i is the initial rate of hydrogenation of citral.

out on Pt/Fe_2O_3 catalysts prepared by metal vapor deposition and wetness impregnation. The results are also reported in Table 1. Notwithstanding the lower amount of noble metal, PtMVS is much more active than PtI and gold catalysts. The higher activity of PtMVS may be due to a higher degree of dispersion of the noble metal onto the support. However, the product distribution on platinum catalysts is quite similar regardless the preparation method. It is noteworthy that on Pt catalysts the selectivity towards the formation of unsaturated alcohol is lower than that observed on gold catalysts. On the Pt catalysts, citronellal, formed through the hydrogenation of the conjugated C=C double bond is obtained with higher yield than on Au/Fe_2O_3 catalysts and at higher reaction times citronellal is hydrogenated to citronellol.

The high selectivity towards the formation of unsaturated alcohols obtained on all Fe_2O_3 supported catalysts can be explained assuming the active role of iron which, in agreement with previous findings,[12] can activate the C=O bond of the unsaturated aldehydes increasing its hydrogenation rate. The role of iron as promoter has been already reported in the hydrogenation of citral on Pt/C catalysts.[13] Moreover, the hydrogenation of citral carried out on Au supported on carbon (iron free) shows a much lower activity and selectivity to unsaturated alcohols (selectivity = 4%, conversion = 10%) than Au/Fe_2O_3 catalysts.

To verify if the lower yield to citronellal obtained on Au/Fe_2O_3 with respect to Pt/Fe_2O_3 is due to the lower capability of gold to interact with the C=C bond, the hydrogenation of geraniol (3,7 dimethyl-2,6-octenol) to citronellol (3,7-dimethyl-6-octenol) has been investigated under the same reaction conditions.

The results have shown that the hydrogenation rate of C=C on gold catalysts was 20 times lower than on Pt catalysts, thus indicating the validity of the starting hypothesis.

In conclusion, we have demonstrated that gold supported on Fe_2O_3 are suitable catalysts for the selective hydrogenation of citral to the correspondent unsaturated alcohols.

To our knowledge this is the second example of catalyst, the other an Rh–Sn system prepared by a controlled surface reaction,[14] which shows such a high selectivity in the hydrogenation of citral.

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