

Gold Supported on Iron Oxy-Hydroxides: a Versatile Tool for the Synthesis of Fine Chemicals

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Abstract

A comprehensive overview on gold supported on iron oxy-hydroxides as tool for the synthesis of fine chemicals is given. We will discuss on the catalytic activity of gold supported on iron oxy-hydroxides in several reactions of potential industrial interest, comprising the selective oxidation of primary alcohol to aldehyde, the selective reduction of α,β unsaturated aldehydes and ketones to the corresponding α,β unsaturated alcohols. Furthermore, a significant application of gold supported on iron oxy-hydroxides is the direct synthesis of hydrogen peroxide from H_2 and O_2 .

The versatility showed by Au supported on oxy-hydroxides catalysts is an aspect of great importance for industrial applications.

Keywords

Gold catalysts, selective hydrogenation, selective oxidation, hydrogen peroxide, α,β unsaturated alcohols, iron oxy-hydroxides.

Introduction

The production of fine chemicals and chemical intermediates involves the selective activation of certain chemical bonds to obtain the desired products.

Most of the fine chemicals have a much shorter market lifetime than bulk chemical, therefore the need of the industry is the manufacture of the product at right time and for a limited period.

It is therefore strategic to develop catalysts able to be employed for different processes and easily adaptable to the industrial existing equipments.

Taking in mind these considerations, gold supported on iron oxy-hydroxides catalysts shows a high adaptability because they can be efficiently used for selective oxidation and hydrogenation reactions.

Gold catalysts prepared by coprecipitation or deposition precipitation have demonstrated to be very selective in the oxidation, with gaseous oxygen or air, of o-hydroxybenzylalcohol (salicylic alcohol) to o-hydroxybenzaldehyde (salicylic aldehyde) [1,2] and in the selective hydrogenation, with gaseous hydrogen, of α,β unsaturated aldehyde, such as citral (3,7-dimethyl-2, 6-octadien-1al) and cinnamaldehyde (trans,3-phenyl,propenal), and of α,β unsaturated ketones, such as trans, 4-phenyl, 3-buten, 2-one (benzalacetone), 4-methyl, 3-penten, 2-one and 3-penten, 2-one, to the corresponding primary and secondary α,β unsaturated alcohols, respectively [3-6].

Furthermore, gold supported on iron oxy-hydroxides is effective for the direct synthesis of hydrogen peroxide from H_2 and O_2 . [7,8]

All the reactions investigated show a relevant industrial interest. o-Hydroxybenzylalcohol is a very interesting raw material for the synthesis of o-hydroxybenzaldehyde (salicylic aldehyde) which is used as an ingredient in agricultural, chemicals, perfumes, polymers and fibres.

The processes for the manufacture of o-hydroxybenzaldehyde are mainly chemical, (Reimer-Tiemann process, formylations or carbonylation of phenol), rather than catalytic [9-11]. However, all these processes have one or more of the following disadvantages: formation of isomers difficult to separate, multistage synthesis, low yield, formation of large amount of waste.

The catalytic routes for the synthesis of o-hydroxybenzaldehyde are mainly covered by patent and are based on the oxydation of o-hydroxybenzylalcohol by oxygen gas, in alkaline medium, on Pt or Pd catalysts in the presence of modifiers such as lead, bismuth which avoid the formation of large amount of tar improving the lifetime of catalysts [12-14].

With respect to Pd or Pt, the use of gold catalyst show the advantage that gold is less expensive and more stable than Pt and Pd under reaction conditions, the lifetime of Pt and Pd catalysts being reduced also by over-oxidation.

The selective hydrogenation of α,β unsaturated aldehydes such as citral and cinnamaldehyde to α,β unsaturated

alcohols are important for their interest as fragrances in the perfumery industries.

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 none or low selectivity towards the hydrogenation of 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), Ga(III), 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 effect [15].

Gold supported on iron oxy-hydroxides, hydrogenates, citral and cinnamaldehyde to the corresponding α,β unsaturated alcohols with a selectivity higher than 85%, without the addition of promoters [3,5].

The catalytic hydrogenation of α,β 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 [16]. The main routes for the synthesis of unsaturated alcohols from α,β unsaturated ketones are the classical homogeneous reduction with LiAlH_4 or reduction by hydride transfer to the enone C=O group [17,18].

In contrast to the α,β 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 [19]. 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/SiO₂ catalyst, whereas the rate of hydrogenation of acetone is only hardly increased [20]. Selective hydrogenation of α,β unsaturated ketones to the corresponding unsaturated alcohols, with molecular H₂, has been instead achieved on Au supported on iron oxy-hydroxides catalysts [4-6]. In particular, in the hydrogenation of benzalacetone and 4-methyl,3-penten,2-one the selectivity towards the formation of unsaturated alcohol was higher than 60% up to quantitative conversion of the substrates.

Another reaction for which gold catalysts supported on iron oxy-hydroxides are attracting attention is the local generation of hydrogen peroxide through the direct synthesis from H₂ and O₂.

Hydrogen peroxide is one of a large number of liquid phase oxygen donors that are commercially available. Hydrogen peroxide is the best oxygen donor for the mild oxidation by virtue of its high active oxygen content and the formation of an environmentally benign co-product, water. However, its use is strongly limited due to safety problems.

Currently, hydrogen peroxide is produced on a large scale

(over 20,000 tonnes per annum) by the sequential hydrogenation and oxidation of an alkyl anthraquinone. Hydrogen peroxide is a hazardous material and transportation from point of manufacture to point of use is expensive. The identification of direct route for the synthesis of H₂O₂ from the reaction of O₂ and H₂ would be highly beneficial. There is evidence in the literature and in the patent application that gold based catalysts are applied effectively for this purpose [7,8,21,22]. Hutchings has reported the use of Au catalysts supported on various supports, included iron oxy-hydroxides, for the direct synthesis of hydrogen peroxide from O₂ and H₂. [7,8,21].

In this paper we will show in detail the results obtained in the oxidation of alcohol and hydrogenation of α,β unsaturated carbonyl compounds carried out on Au supported on oxy-hydroxides. A brief description of the results obtained in the direct synthesis of the H₂O₂ from O₂ and H₂ will be also given.

Experimental

Samples preparation

Au supported catalysts were prepared by coprecipitation and deposition-precipitation. The coprecipitation was carried out using HAuCl₄ (Fluka) and Fe(NO₃)₃·9H₂O (Fluka) as starting materials. An aqueous mixture of HAuCl₄ and Fe(NO₃)₃·9H₂O was poured into an aqueous solution of Na₂CO₃ 1M (pH=11.9) and kept at 353 K under vigorous stirring. The solids were digested overnight at room temperature and then washed with water until free of chloride ions (AgNO₃ test) and then dried under vacuum at 353 K for one day.

The deposition-precipitation of gold onto the supports was carried out in agreement with the Haruta's procedure [23], by adding 5 g of the support to 400 ml of an aqueous solution containing 5 g of HAuCl₄. The temperature of the solution was 343 K and the pH was previously adjusted in the range 7-8 by addition of NaOH 0,2 M. Upon addition of the support the pH slightly decreases, then when the equilibrium was reached it was increased up to 7-8 by further addition of NaOH. The slurry was maintained at 343 K, under vigorous stirring, for 2 hours. Then the samples was filtered, washed with deionized water until elimination of chloride then dried under vacuum at 353 K for one day.

The iron oxide support was prepared by precipitation of the hydroxides by adding Fe(NO₃)₃·9H₂O to an aqueous solution of Na₂CO₃ 1M and kept under vigorous stirring at a temperature of 353 K. The precipitate was digested overnight at room temperature, washed several times with water then dried under vacuum at 353 K.

Samples characterization

The morphologic and chemical properties of all samples investigated have been evaluated with several techniques.

The gold content was determined by measuring the absorbance of gold solutions at $\lambda=400$ nm [24]. The solutions were prepared dissolving the catalysts in HCl-HNO₃ (3:1 by volume), then adding a solution of tin(II) chloride in hydrochloric acid.

Surface area measurements were made using the BET nitrogen adsorption method in a conventional volumetric apparatus.

XRD studies were carried out with an Itai-Structures diffractometer using nickel filtered Cu K α radiation.

TEM analysis were performed on a Philips instrument Model CM12 electron microscopy, operating at 120kV and directly interfaced with a computer for real time image processing.

The ⁵⁷Fe Mossbauer spectra were measured with a ⁵⁷Co source in rhodium matrix. The source was kept at the same temperature as the adsorber (293 or 4.2K).

The ¹⁹⁷Au Mossbauer spectra were taken with a ¹⁹⁷Pt source in isotopically enriched ¹⁹⁶Pt metal. Both the source and the adsorber were kept at liquid helium temperature (4.2 K).

XPS analyses were carried out in a conventional ultra high vacuum system equipped with a VG Microtech spectrometer with a standard twin-anode Al/Mg X-ray source.

XPS data were collected using the Al-K α (1486.6 eV) radiation a 105° concentric hemispherical analyser operating in the constant pass-energy mode ($E_{\text{pass}} = 20$ eV).

Catalytic activity

Catalytic activity measurements were carried out in a 100 ml four-necked batch reactor fitted with a reflux condenser, dropping funnel, thermocouple and magnetic stirrer head coupled with a gas stirrer (Mod. MRK 1/20 – BR purchased by Premex Reactor).

Protocol in the oxidation reaction

The reaction temperature was 323 K, unless otherwise specified. The o-hydroxybenzylalcohol was a commercial analytical product (Fluka, Assay 99%).

The catalyst (0.5-1.8 g) was added to 25 ml of solvent (distilled water). Before catalytic activity measurements the catalysts were treated at 323 K for 10 minutes under gaseous O₂. The substrate ($5.5 \cdot 10^{-4}$ 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 sampling a sufficient number of microsamples and analysing them by HPLC (Waters model 510) equipped with a Photo Diode Array detector (PAD).

The reaction products were separated on a Symmetry C18 column, (5 μ m, 4.6 x 250 mm), using a water / acetonitrile solution (gradient method). The total flow was kept a 0.8 ml/min. Calibration curves for the reagent and reaction

products were obtained analysing reference samples under the above reported experimental conditions. The salicylic alcohol was detected at 273.4 nm, the salicylic aldehyde at 212.2 nm and salicylic acid at 202.8 nm.

Protocol in the hydrogenation reactions

The catalyst (weight 0.5÷1g; particle size = 160-200mesh) was added to 25 ml of solvent (ethanol) and treated at 343 K for 1 hour under gaseous H₂.

The substrate ($6 \cdot 10^{-4}$ mol) was injected through one arm of the flask. The reaction mixture was stirred at 700 rpm.

The α,β unsaturated ketones, trans,4-phenyl,3-buten,2-one (benzalacetone) was supplied by ACROS. and 4-methyl,3-penten,2-one and 3-penten,2-one were supplied by Fluka.

The α,β unsaturated aldehydes, citral (purity >98%) and cinnamaldehyde (purity >98%) were supplied by Aldrich.

The progress of the reaction was followed by sampling a sufficient number of microsamples and analysing them by means of GC - FID(Shimadzu GC-QP5000 Mod.), equipped with an EC-WAX wide bore column (60m, 0.53 mm i.d.). The analysis has been carried out under isotherm conditions at 413 K.

Preliminary tests carried out with different amounts of catalysts (0.2-1.0 g) grain size (80-200 mesh) and stirring rate (500-1000 rpm) indicated that under the conditions used the reaction is carried out in the absence of mass-transfer limitation.

Results and discussion

Characteristics of the gold catalysts

In Table 1 are listed the preparation method, the gold loading and the chemical state of gold and iron oxide of all the gold preparations.

A detailed characterisation by ¹⁹⁷Au and ⁵⁷Fe Mossbauer spectroscopy and XPS spectroscopy of gold catalysts prepared by coprecipitation (entries 2-9) have revealed that gold is present as Au(III) and Au (metal) and the support is a mixture of ferrihydrite, and hematite [25,27]. The amount of ferrihydrite on such catalysts has been found to increase with the gold loading. XRD analysis have shown that all the samples, but AF046/b, are amorphous [28].

On the iron oxide support (entry 1), the XRD analysis shows the presence of different crystalline iron oxyhydroxides phases. Hematite (α -Fe₂O₃) is the prevailing crystallographic phase, but goethite (α -FeOOH) and ferrihydrite have been also found [5]. Upon dispersing gold, through the deposition-precipitation, the ferrihydrite phase almost disappears (entry 10). It is likely that during the deposition of gold, ferrihydrite is transformed into the more ordered hematite phase [29]. It is interesting to note that

Table 1

Chemical composition, preparation method and chemical state of gold and iron oxide of all gold preparations

Entry	Code	Preparation method	Au (wt. %)	Chemical state of iron oxide	Chemical state of gold
1	Fe ₂ O ₃	Precipitation	-	Ferrihydrite, goethite, maghemite, hematite [5]	-
2	AF046/b	Coprecipitation	0.46	Ferrihydrite, hematite [25]	Au(III), Au metal [25]
3	AF056/b	Coprecipitation	0.56	Ferrihydrite, hematite [25]	Au(III), Au metal [25]
4	AF117/b	Coprecipitation	1.17	Ferrihydrite, hematite [25]	Au(III), Au metal [25]
5	AF126/b	Coprecipitation	1.26	Ferrihydrite, hematite [25]	Au(III), Au metal [25]
6	AF359/b	Coprecipitation	3.59	Ferrihydrite, hematite [25]	Au(III), Au metal [25]
7	AF3.1	Coprecipitation	3.1	Ferrihydrite, hematite [27]	Au(III), Au metal [26]
8	AF5.3	Coprecipitation	5.3	Ferrihydrite, hematite [27]	Au(III), Au metal [26]
9	AF16.6	Coprecipitation	16.6	Ferrihydrite, hematite [27]	Au(III), Au metal [26]
10	AF5dp	Deposition-precipitation	5.4	Goethite, maghemite, hematite [5]	n.d.
11	AF5dpr ^(a)	Deposition-precipitation	5.4	Goethite, maghemite, hematite [5]	Au(metal) [6]
12	Au/Fe ₂ O ₃ *	Coprecipitation	4.4	Hematite [5]	Au metal [6]

*Gold "reference" catalyst, Type C, Lot No. Au/Fe₂O₃ #02-3;

^(a) A suspension of the catalyst in ethanol, was treated for 1 h in H₂ flow (20 cc/min) at 343 K.

after 1 h reduction of the catalyst in H₂, at 343 K in ethanol (entry 11), the chemical state of iron oxide is substantially unmodified with respect to that of the "as prepared sample" [5]. Au(III), instead is converted to Au metal [6].

In table 1 is also reported the chemical and structural data of the Au/Fe₂O₃ reference catalyst, supplied by the World Gold Council, used as reference catalyst. On this catalyst the support is present as crystalline hematite, α-Fe₂O₃ and gold is under metallic state [5,6].

Selective oxidation of o-hydroxybenzylalcohol

Table 2 shows the preparation method, the gold loading and the total surface area (SA) of gold catalysts supported on iron oxy-hydroxides used in the oxidation of salicylic alcohol.

The oxidation of the alcohol leads to o-hydroxybenzaldehyde (salicylic aldehyde) and o-hydroxybenzyl acid (salicylic acid) as main reaction products.

On all the catalysts investigated the liquid phase oxidation

of salicylic alcohol follows a first order reaction rate law with respect to the alcohol concentration.

The first order dependence of the rate of reaction on the salicylic alcohol concentration is indicated by the linearity of the plot $-\ln(1-\text{conv})$ versus reaction time (Fig.1). The positive value of the intercept indicates that, within the first minutes of the reaction, the concentration of the reagent strongly decreases but the formation of any products has been observed. The reactant is partially adsorbed on the solid, and the amount of adsorbed alcohol in the first minutes of reaction was calculated from the value of the intercept of the plot $-\ln(1-\text{conv})$ versus reaction time.

The specific activity, K (min⁻¹ g⁻¹), increases with the noble metal loading (Table 2). In the absence of gold, the support does not show any measurable activity.

The apparent activation energy, E_a, calculated in the range of temperature 323–353 K is comprised between 13 -15 Kcal mol⁻¹, regardless of the gold loading.

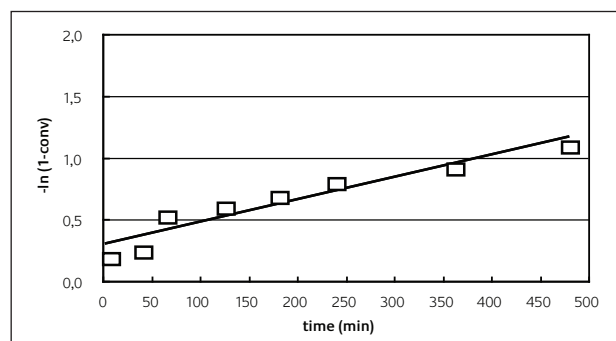
These results indicate that the reaction occurs with a similar mechanism on all the Au supported on oxy-hydroxides catalysts. Therefore, the increase of the catalytic activity with the gold content could be due to an increase of the number

Table 2

Gold loading, surface area, and reaction rate constant for the liquid phase oxidation of salicylic alcohol over gold on oxy-hydroxides preparations (Tr= 323 K, P_{O₂} = 1 atm).

Code	Preparation method	Au (wt. %)	S.A. (m ² /g)	K (min ⁻¹ g ⁻¹)10 ³
Fe ₂ O ₃	Precipitation	-	195	n. d.
AF046/b	Coprecipitation	0.46	127	1.29
AF056/b	"	0.56	275	2.99
AF117/b	"	1.17	263	12.99
AF126/b	"	1.26	290	21.11
AF359/b	"	3.59	214	29.98

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**Figure 1**

Plot of first order rate equation (AF046/b) [Reprinted from Ref.1 by permission of Elsevier]

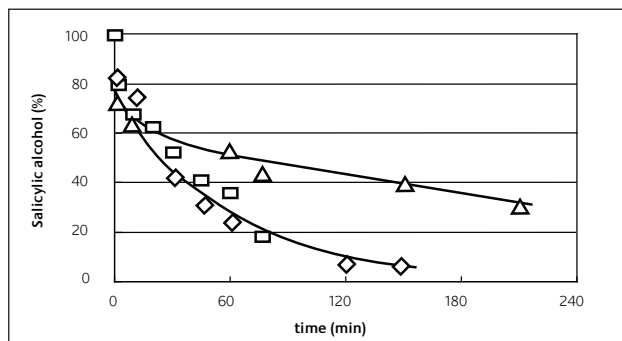


Figure 2

Amount of salicylic alcohol in the reaction mixture as a function of time on the AF359/b catalysts at $P_{O_2} = 1$ atm (◇), $P_{O_2} = 0.2$ atm (□), in absence of oxygen (Δ). Catalyst weight = 0.600 g, $T_r = 323$ K. [Reprinted from Ref. 1 by permission of Elsevier]

of active sites.

Experiments carried out at different O_2 partial pressure, have demonstrated that the rates of oxidation of the salicylic alcohol does not depend on the O_2 partial pressure, indicating that the oxygen adsorption is not the rate-limiting step (Fig. 2).

When the reaction is carried out under N_2 atmosphere, (Fig. 2) two different rates of oxidation can be distinguished. Initially the oxidation occurs as fast as the reaction carried out in the presence of oxygen then it decreases at higher reaction time.

These results suggest that the oxidation of salicylic alcohol occurs on the surface of the catalysts with a heterogeneous mechanism involving the lattice oxygen of the metal oxide. The replacement of the active sites mainly occurs through the adsorption of O_2 from the gaseous feed on the vacancy sites.

This behaviour also indicates that the replacement of the oxygen surface active sites by diffusion of oxygen coming from the bulk occurs at lower extent. The above results suggest that the redox properties of the catalysts play an important role in the liquid phase oxidation of salicylic alcohol.

Previous TPR investigations, carried out on similar Au/Fe_2O_3 catalysts, have demonstrated that the presence of gold promotes the partial reduction of Fe(III) to magnetite [28]. A similar effect of gold on the reducibility of Fe_2O_3 have been also reported by others [30-33].

The reduction temperature is shifted, already at low gold content, at least by 200 K to lower temperature. Moreover, the higher the gold loading the lower is the reduction temperature [28,33]. Several hypotheses have been formulated to explain the increase of the reducibility of Fe_2O_3 in the presence of gold. Ilieva et al have suggested that gold is able to dissociate water forming activated hydroxyl groups which promote the low temperature reduction of Fe_2O_3 support [31]. Minico' et al concluded that the lower reduction temperature on Au/Fe_2O_3 catalysts is due to the ability of highly dispersed gold to activate the oxygen of the iron oxide weakening the Fe-O bonds located nearby the gold atoms [33]. Boccuzzi et al, instead, have reported that small

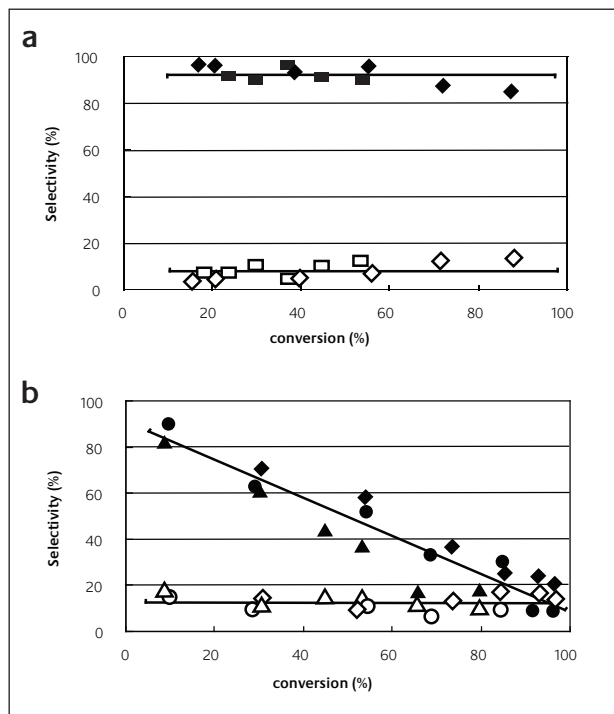


Figure 3

a Products distribution in the oxidation of salicylic alcohol as a function of conversion [Reprinted from Ref. 1 by permission of Elsevier]. Salicylic aldehyde on AF046/b (■), on AF056/b (◆). Salicylic acid on AF046/b (□), on AF055/b (◇)

b Products distribution in the oxidation of salicylic alcohol as a function of conversion [Reprinted from Ref. 1 by permission of Elsevier]. Salicylic aldehyde on AF117/b (◆), AF126/b (▲), AF359/b (●). Salicylic acid on AF117/b (◇), AF126/b (Δ), AF359/b (○)

gold particles dissociate H_2 already at room temperature, giving rise to hydrogen atoms which can react with adsorbed oxygen atoms or spillover on the support where they can facilitate the reduction of the oxide [34].

Taking into account that lattice oxygen is directly involved in the oxidation of salicylic alcohol, it can be suggested that the increase of the specific activity with the gold loading is due to the enhancement of the reducibility of the catalysts.

However, it cannot be ruled out a direct involvement of gold sites in the reaction mechanism.

It is widely reported that a reaction step in the CO oxidation on Au/Fe_2O_3 catalysts is the activation of CO by nanosize gold particles [35,36]. However, gold in a higher oxidation state has been also shown to chemisorb carbon monoxide [37]. ^{197}Au Mossbauer spectroscopy [25] and XPS spectroscopy [26], have revealed that when the catalysts are not calcined at high temperature (as in the case of the catalysts reported in this paper) gold is mainly present as Au(III).

Au(III) sites have been found the most active sites in the hydrochlorination of ethyne on Au/C, but no evidence on the chemisorption of the substrate on gold sites has been reported [38,39].

From our data no suggestion can be given if and how gold sites are directly involved in the chemisorption of the α -hydroxybenzyl alcohol.

As already mentioned, the main reaction products were salicylic aldehyde and salicylic acid. Fig.3a and 3b show the selectivity toward the reaction products as a function of conversion.

The selectivity at different level of conversion has been calculated as follows:

$$S = [i\text{-product}]_{(t)} / ([\text{alcohol}]_{(t_0)} - [\text{alcohol}]_{(t)})$$

where:

$[i\text{-product}]_{(t)}$ = concentration (mM) of the *i*-product at reaction time *t*

$[\text{alcohol}]_{(t)}$ = concentration (mM) of salicylic alcohol at reaction time *t*

$[\text{alcohol}]_{(t_0)}$ = concentration (mM) of alcohol at time zero, calculated from the intercept of $-\ln(1-\text{conv})$ vs time.

It can be observed that on the catalysts with lower gold loading (Fig. 3a) the selectivity towards salicylic aldehyde and salicylic acid remains constant in the whole range of conversion investigated. This indicates that they are end products and are formed from direct oxidation of salicylic alcohol through parallel reactions. It is noteworthy that salicylic aldehyde is obtained with high selectivity, about 90%, even at almost quantitative conversion of the reagent.

On the samples with higher gold content (> 1 wt %) the selectivity towards salicylic aldehyde decreases with the conversion level, while the selectivity to salicylic acid remains constant (Fig. 3b). From the decrease of the yield of the salicylic aldehyde any other product has been detected by HPLC analysis. This leads to a negative material balance, which progressively increases, in absolute value, during the course of the reaction.

The negative material balance has been confirmed by the Total Organic Compounds (TOC) analysis of the solution before and after reaction. The loss of organic compounds determined with the different analytical methods (TOC and HPLC) are in good agreement.

It can be therefore suggested that the disappearance of salicylic aldehyde on the catalysts with high gold loading occurs through its complete oxidation to CO_2 , and/or through the conversion of the substrate to compounds which remain adsorbed on the catalyst. The formation of appreciable amounts of CO_2 during the course of the reaction was ruled out by analysing the gaseous effluent of the reactor.

Temperature Programmed Oxidation (TPO) experiments were carried out on the fresh and used catalysts. The latter have been recovered by filtration after the reaction, washed with cold water and dried under vacuum at 353 K for 2 hours. TPO profile show the presence of a single peak centred at 503 K relative to the evolution of CO_2 on the used catalysts, while the carbon dioxide evolved from the fresh catalysts was always negligible.

A quantitative analysis of the CO_2 evolved during TPO from the used catalysts shows that it corresponds to the oxidation of about 70 wt% - 80 wt.% of the initial amount of salicylic alcohol.

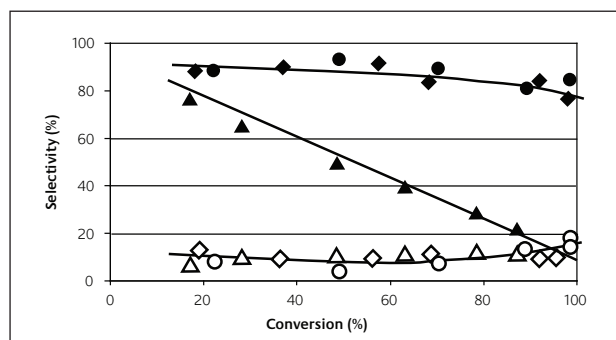


Figure 4

Products distribution in the oxidation of salicylic alcohol on gold supported on oxy-hydroxides as function of conversion for reactions carried out at different pH [Reprinted from Ref.2 by permission of Elsevier].

Salicylic aldehyde: pH = 11.05 (◆), pH = 8.61 (●), pH = 6.87 (▲),
Salicylic acid: pH = 11.05 (◇), pH = 8.61 (○), pH = 6.87 (△)

This result indicates that the material lost from the solution is mainly recovered on the solid.

Further, it was demonstrated that the decrease of selectivity of salicylic aldehyde during the reaction is related to the pH of the reaction medium [2]. When the reaction was carried out at starting pH=7, during the run the pH of solution progressively decreases leading, at the end of reaction, to an acid solution. In this case it was observed a decrease of the selectivity increasing the conversion (Fig. 4).

The decrease of the pH of the solution when the reaction was carried out under neutral condition is obviously due to the progressively increases of the concentration of H^+ generating from the dissociation of salicylic acid which is a quite a strong acid, the first dissociation being $K_{a1(298\text{K})} = 1,07 \cdot 10^{-3} \text{ mol/l}$.

When the reaction was carried out at pH >8 using Na_2CO_3 , the pH remains almost constant during the run and also the selectivity towards the formation of salicylic aldehyde remains constant in the whole range of conversion investigated (Fig.4) [1]. The constancy of the pH during the run, when the reaction is carried out in a solution of Na_2CO_3 , can be explained assuming a buffer effect of the couple $\text{CO}_3^{2-}/\text{HCO}_3^-$. Therefore, the disappearance of salicylic aldehyde is not catalysed by the solids but depends on the pH of the reaction medium. From these observations we concluded that on AF046/b and AF056/b, the catalysts that do not show the disappearance of salicylic aldehyde during the run, there should be residual Na_2CO_3 left on the catalyst after preparation.

From this study it is clearly evidenced that gold supported on iron oxy-hydroxides catalysts are effective for the liquid phase oxidation of salicylic alcohol under mild conditions. When the reaction is carried out at pH >8 the selectivity toward the formation of salicylic aldehyde is 90% up to 100% of conversion.

With respect to Pd or Pt catalysts, the use of gold supported on iron oxy-hydroxides catalysts in the selective oxidation of salicylic alcohol show the advantage to achieve a high selectivity to salicylic aldehyde avoiding the addition of

promoters such as $\text{Bi}_2(\text{SO}_4)_3$ or $\text{Pb}(\text{NO}_3)_2$. When the reaction is carried out in aqueous solution of NaOH on 10wt% Pd/C or 10 wt% Pt/C the selectivity to aldehyde at 100% of conversion is 80% and 77,6% respectively [12]. An increase of the selectivity up to 90% is obtained upon addition of 0,2 g/l of promoters. On gold catalysts, indeed, the selectivity to aldehyde is higher than 90% already without addition of promoters. However, gold catalysts shows a lower catalytic activity than Pd or Pt supported catalysts. The residence time to achieve 100% of conversion at 323 K with a weight ratio Au:alcohol 0,03:1 is 3h 30' whereas at 303 K with a weight ratio Pt or Pd:alcohol 0,01:1 is 3h [12].

Selective hydrogenation of α,β unsaturated aldehydes

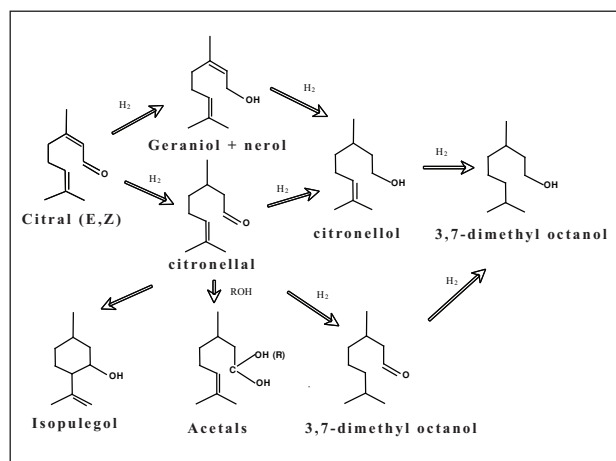
The catalytic activity in the hydrogenation of citral and cinnamaldehyde on gold supported on iron oxy-hydroxides was also investigated.

Citral is an aliphatic aldehyde containing three double bond, isolated C=C bond and conjugated C=C and C=O bond and its hydrogenation occurs through a complex pathways represented in Scheme 1.

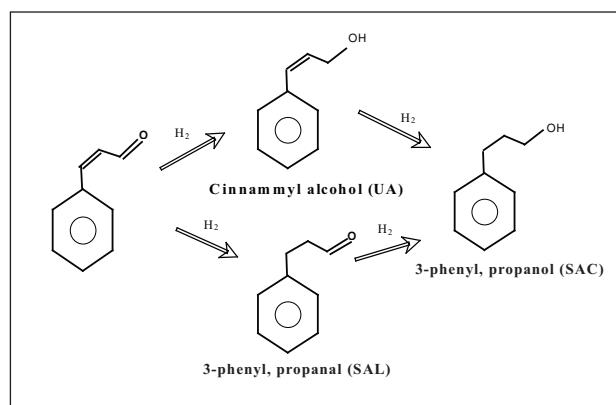
Cinnamaldehyde is an aromatic aldehyde containing a bulky phenil group on the C=C double bond and its hydrogenation occurs through a simpler pathway reported in Scheme 2.

In Table 3 are reported the catalytic activity in the hydrogenation of citral on Au supported on iron oxy-hydroxides support.

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 has not been 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 [40,41], were not detected.



Scheme 1



Scheme 2

The catalytic activity, measured as initial rate of disappearance of citral per g of catalyst, increases with the gold loading while the products distribution is similar regardless of the amount of the 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%.

Recycle test 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 out on Pt on iron oxy-hydroxides catalyst prepared by Metal Vapor Deposition on the preformed support. As it is

Table 3

Catalytic activity and selectivity in the hydrogenation of citral

Code	Preparation method	Au (wt. %)	Pt (wt. %)	V_i (mol $g_{cat}^{-1}s^{-1}$) 10^8	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
PtMVS	Metal Vapor Deposition	-	0.9	140.5	0.79	12.85	86.36
AAI2.3dp*	Deposition-precipitation	2.3	-	0.1	32.01	16.13	51.86

Selectivity was measured at conv = 20%.

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Table 4

Selectivity towards the formation of α,β unsaturated alcohol in the hydrogenation of cinnamaldehyde

Entry	Catalyst	Preparation method	Me wt. %	Mean particle size d(nm) ^(a)	Conv (%)	Sel(%) SAL	Sel(%) UA	Sel(%) SAC
1	AF5.3	Coprecipitation	5.3	6.3	50.2	13.6	83.8	2.6
2	AF5dp	Deposition-precip.	5.4	3.2	56.3	3.3	86.9	9.8
3	Au/Fe ₂ O ₃ *	Coprecipitation	4.4	3.7	48.2	25.3	73.2	1.6
4	AAI2.3dp	Deposition-precip.	2.3	4.3	50.1	33.9	60.3	5.8
5	Ru/Fe ₂ O ₃	Depos. of Ru ^o colloids	2	n.d.	50.3	8.1	74.9	17.0

(a) Measured by TEM. *Gold "reference" catalyst, Type C, Lot No. Au/Fe₂O₃ #02-3.

SAL = Saturated Aldehyde; UA = Unsaturated Alcohol; SAC = Saturated Alcohol;

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shown in Table 3, Pt catalyst is more active than gold catalysts but less selective towards the formation of unsaturated alcohol. It should be noted that the selectivity obtained on Pt catalysts is similar to that obtained, at the same conversion, in the hydrogenation of citral on Pt promoted by Snⁿ⁺ [40]. Therefore, gold catalysts are more selective than the classical noble metal promoted catalysts, but show a lower activity [41].

Table 4 reports the product distribution obtained in the catalytic hydrogenation of the cinnamaldehyde. Au supported on iron oxy-hydroxides are the most selective samples regardless the gold loading and preparation method (entries 1,2). For comparison, the hydrogenation of cinnamaldehyde has been carried out on Ru on iron oxy-hydroxide catalyst prepared by deposition of colloids of metallic ruthenium on the preformed support (entry 5). Once more, it has been observed that the selectivity to unsaturated alcohol is lower than that obtained on Au dispersed on iron oxy-hydroxides. It should be also noted that the Au/Fe₂O₃ reference catalysts supplied by the World Gold Council, made of Au dispersed on well crystallized hematite shows a lower selectivity than gold supported on iron oxy-hydroxides (entry 3). This difference cannot be ascribed to differences in gold particle size. Indeed, Au/Fe₂O₃ reference and AF5dp show similar gold particle size but very different selectivity to unsaturated alcohol (Table 4).

The high selectivity towards the formation of unsaturated alcohols in the hydrogenation of citral and cinnamaldehyde on Pt, Ru and Au catalysts based on iron oxy-hydroxides can be explained claiming the active role of Feⁿ⁺ which acts as Lewis adsorption site and can activate the C=O bond of the unsaturated aldehydes increasing its hydrogenation rate. This type of mechanism is widely reported in the literature [15,19].

However, it also reported that metallic iron acts as promoter in the selective hydrogenation of α,β unsaturated aldehydes to unsaturated alcohols on Pt catalysts [15]. The mechanism of promotion by metallic iron has been explained considering an electron transfer from the more electropositive Fe to Pt and the electron deficient iron atoms acts as Lewis adsorption sites for the C=O bond [15]. However, it should be also considered that the electron transfer from iron to platinum can increase the hydridic

character of chemisorbed hydrogen and thus the nucleophilic attack by H⁻ species on the positively charged carbon of the polarized C=O bond [15].

In the case of Au supported on iron oxy-hydroxides, due to the mild conditions at which catalysts are reduced (T = 343 K), it can be ruled out that, iron oxide are reduced, even partially to metallic iron. This conclusion is supported by TPR experiments, on similar catalysts, where it is shown that the presence of gold mainly promotes the partial reduction of Fe(III) oxide to magnetite (Fe₃O₄) whereas the further reduction to metallic iron, that occurs at temperature higher than 800 K, is less influenced by the presence of gold [28].

Therefore it can be concluded that Feⁿ⁺ acts as promoter in the selective hydrogenation of citral and cinnamaldehyde.

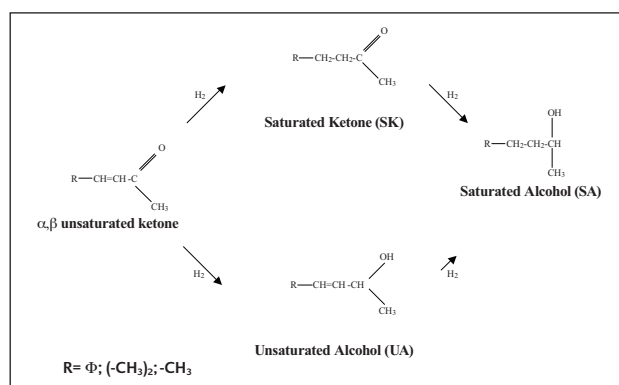
Indeed the hydrogenation of citral and cinnamaldehyde, carried out on Au supported Al₂O₃ shows a lower selectivity to unsaturated alcohols (Table 3 and 4).

The highest selectivity of gold compared with Ru and Pt, dispersed on iron oxy-hydroxides is due to the the lower capability of gold to interact with the C=C bond [4].

In conclusion, we have demonstrated that gold supported on iron oxy-hydroxides are more selective than analogous Ru and Pt catalysts for the selective hydrogenation of citral and cinnamaldehyde to the corresponding unsaturated alcohols.

Selective hydrogenation of α,β unsaturated ketones

Addition of H₂ to the α,β unsaturated ketones can be described through the simplified Scheme 3.



Scheme 3

Table 5

Chemical composition, surface area (S.A.), mean gold particle size (nm) and catalytic activities (V_i) of gold supported catalysts used in the hydrogenation of benzalacetone.

Entry	Catalyst	Preparation method	Au (wt. %)	Mean gold particle size d(nm) ^(b)	S.A. (m ² /g)	V_i^a (10 ⁷)
1	AF3.1	Coprecipitation	3.1	– ^c	68	3.5±0.2
2	AF5.3	Coprecipitation	5.3	6.3	122	3.0±0.2
3	AF16.6	Coprecipitation	16.6	6.6	178	2.1±0.1
4	AF5dp	Deposition-precipitation	5.4	3.2	121	27.9±1.4
5	Au/Fe ₂ O ₃ *	Coprecipitation	4.4	3.7	39	1.1±0.1
6	AAI2.3dp	Deposition-precipitation	2.3	4.3	124	1.0±0.1

^a V_i = initial rate of hydrogenation of benzalacetone (moles converted · g_{Au}⁻¹ · s⁻¹);

^b Measured by TEM;

^c Not determined due to the poor contrast with the support background;

*Gold “reference” catalyst, Type C, Lot No. Au/Fe₂O₃ #02-3.

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It has to be highlighted that the reduction of benzalacetone occurs by means of molecular H₂ and any mechanism involving the hydrogen transfer from the alcohol to the substrate was ruled out. This conclusion was drawn through a series of experiments carried out in the absence of hydrogen. Catalysts were pre-reduced “in situ” at 343 K for 1 h in the presence of ethanol; the reactor was cooled down at the reaction temperature (333 K). In order to eliminate any residual H₂, the reactor was flushed with N₂ for several hours. At this point the substrate was introduced into the reaction vessel. Under these conditions no conversion of benzalacetone was observed up to 3 hours of contact time. When H₂ was readmitted into the reactor, the hydrogenation of benzalacetone occurred thus indicating that the reducing agent is molecular H₂.

In Table 5 is reported the rate of hydrogenation of benzalacetone (C₆H₅CH=CHCOCH₃) on gold preparations, expressed as initial rate of reaction per gram of metal.

Catalytic activity data of the gold catalysts supported on iron oxy-hydroxides (entries 1-4) prepared by coprecipitation and deposition precipitation clearly show that the rate of reaction is strongly influenced by the preparation method. Catalyst prepared by coprecipitation (entry 2) is much less active than analogous sample prepared by deposition-precipitation (entry 4). Within the same preparation method, instead, the catalytic activity decreases with increasing the gold content (entries 1-3).

The higher catalytic activity of the sample prepared by deposition-precipitation AF5dp, with respect to the AF5.3 sample could be due to the higher dispersion of gold (Table 5) and/or to a higher amount of gold exposed on the external surface of the support. It is well known that in the solids prepared by coprecipitation and dried at 353 K, gold is mainly buried into the iron oxy-hydroxide matrix [42], whereas a higher amount of exposed gold is obtained through the deposition-precipitation method [43].

The Au/Fe₂O₃ “reference” catalyst shows a lower catalytic activity.

The formation of the unsaturated alcohol has been observed on all gold supported catalysts and the selectivity measured at low and high conversion are reported in Table 6.

It can be noted that the selectivity to the unsaturated alcohol (UA) remains almost constant regardless of the level of conversion whereas the selectivity to the saturated alcohol (SA) increases as that of the saturated ketone decreases (SK). This indicates that the formation of the saturated ketone (SK) and of the unsaturated alcohol (UA) occurs through parallel reactions, whereas the saturated alcohol is mainly obtained by the further hydrogenation of the C=O bond of the saturated ketone (Scheme 3).

All the Au catalysts supported on oxy-hydroxides (entries 1-4) show a remarkable selectivity towards the hydrogenation of the C=O bond in the whole range of conversion investigated.

The “reference” sample shows the lowest selectivity towards the formation of the unsaturated alcohol.

It seems that the selectivity to the unsaturated alcohol cannot be univocally correlated to the gold particles size. If we compare the results obtained on the AF5dp and AF5.3 catalysts, we could conclude that the dimensions of the metal particles do not influence the selectivity. Indeed, the selectivity of the two samples towards the hydrogenation of the conjugated C=O bond is quite similar (Table 6), notwithstanding the difference in the mean gold particles size (Table 5). A further confirmation of the independency of the selectivity to UA from the gold particle size is given from the comparison of selectivity data obtained on AF5dp and Au/Fe₂O₃ reference. Both catalysts, indeed, have similar gold particle size (Table 5) but very different selectivity to UA (Table 6).

It should be noted that the chemical nature of the support strongly influences the activation of the conjugated C=O bond. Gold supported on Al₂O₃ shows the lowest selectivity towards the formation of the unsaturated alcohol indicating that iron oxide promotes the hydrogenation of the C=O bond with an increase of the selectivity towards the formation of the unsaturated alcohol (Table 6). Among the Au supported on iron oxide catalysts, those containing poor crystallized or amorphous iron oxy-hydroxides phase are the most selective. Indeed Au/Fe₂O₃ reference sample, containing well crystallized hematite is the less selective.

Table 6

Catalytic activity and selectivity towards the formation of the unsaturated alcohol in the hydrogenation of benzalacetone

Entry	Catalyst	Au (wt. %)	Conv (%)	Sel(%) SK	Sel(%) UA	Sel(%) SA
1	AF3.1	3.1	23.9	42.4	51.8	5.8
			95.1	1.4	57.0	41.6
2	AF5.3	5.3	21.6	35.8	57.3	6.9
			95.1	1.5	56.2	42.3
3	AF16.6	16.6	20.4	28.4	64.2	7.4
			90.4	11.2	67.5	21.2
4	AF5dp	5.4	17.3	35.8	61.3	2.9
			91.2	18.6	58.5	23.0
5	Au/Fe ₂ O ₃ *	4.4	17.6	77.9	20.4	1.7
			84.0	77.3	19.8	1.9
6	AAI2.3dp	2.3	21.9	85.1	11.4	3.5

SK = Saturated Ketone; UA = Unsaturated Alcohol; SA = Saturated Alcohol;

*Gold reference catalyst, Type C, Lot No. Au/Fe₂O₃ #02-3.

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It should be highlighted that the presence of iron oxide is not sufficient to enhance the hydrogenation rate of the C=O with respect to the C=C bond in the hydrogenation of the α,β unsaturated ketones, but it is necessary to have both gold and iron oxides. This indicates that the catalytic behaviour rise from a synergic effect between the two constituents. Indeed, when the hydrogenation of benzalacetone was carried out on Ru catalyst prepared dispersing colloids of metallic ruthenium on the same support used to prepare the AF5dp catalyst, the main reaction product was the saturated ketone and the selectivity towards the formation of the UA was less than 2%, whereas on AF5dp the selectivity to UA is 60%.

We have also studied the hydrogenation of 4-methyl,3-penten,2-one [(CH₃)₂C=CHCOCH₃] and of 3-penten,2-one [CH₃CH=CHCOCH₃]. The product distribution, at low and high conversion, is reported in Table 7 It can be seen that Au/Fe₂O₃ catalysts are able to hydrogenate selectively the conjugated C=O bond on substrates having a sterically unhindered C=O bond with respect to benzalacetone. The replacement of the bulky phenyl group of benzalacetone with two methyl groups on the C=C bond in the 4-methyl,3-penten,2-one does not lead to substantial differences in the product distribution. The α,β unsaturated alcohol remains the main reaction product with a selectivity higher than 60% in the whole range of conversion investigated. In the hydrogenation of the 3-penten,2-one, which has only one methyl group as a

substituent on the C=C bond, the selectivity towards the formation of the unsaturated alcohol drops to almost 15%. In analogy with the behaviour observed in the hydrogenation of the α,β unsaturated aldehydes, the presence of less bulky substituents on the conjugated C=C bond favours its adsorption on the catalytic sites leading to the preferential formation of the saturated carbonyl compound [15,19].

From the results presented here, it is clearly demonstrated that gold shows an unique catalytic behaviour in the hydrogenation of α,β unsaturated ketone by molecular H₂. Gold is a metal with a high intrinsic selectivity toward the hydrogenation of the C=O in α,β unsaturated carbonyl compounds. The selectivity towards the formation of UA is strongly influenced by the support. Among the iron oxide used Au supported on poor crystallized or amorphous iron oxy-hydroxides is more selective than gold supported on well crystallized hematite. We argue that the intrinsic selectivity of gold can be due to the adsorption mode of the conjugated systems on this metal. Among the different adsorption mode of the conjugated systems gold is likely a metal on which the 1,2 -C=O adsorption mode, which in turn leads to the formation of the UA, is preferred with respect the 1,4-C=C-C=O adsorption mode, which is responsible for the formation of the saturated carbonyl compound. Further studies are necessary in order to better elucidate the nature of the active and selective sites.

Table 7Catalytic activity and selectivity towards the formation of the unsaturated alcohol in the hydrogenation of α,β unsaturated ketones

Substrate	Catalyst	Conv (%)	Sel (%) SK	Sel (%) UA	Sel (%) SA
Benzalacetone	AF5dp	17.3	35.8	61.3	2.9
		91.2	18.6	58.5	23.0
4-methyl, 3-penten,2-one	“	22.1	34.6	60.7	4.7
		89.1	9.8	64.9	12.3
3-penten,2-one	“	20.3	83.3	14.3	2.4
		90.2	59.8	16.2	24.0

SK = Saturated Ketone; UA = Unsaturated Alcohol; SA = Saturated Alcohol.

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Direct synthesis of H₂O₂ from H₂ and O₂

The identification of a direct route for the synthesis of H₂O₂ from O₂ and H₂ has been a research target for many years. At present, some success has been achieved using Pd as catalyst, especially when halides are used as promoters [44,45]. The key problem that remains is the selectivity to H₂O₂, since the conditions that are required to produce H₂O₂ also promoted its decomposition or hydrogenation or the non selective formation of H₂O.

Recently, there is evidence in the literature and in the patent application that gold based catalysts are applied effectively for this purpose [7,8,21,22]. Hutchings et al. has reported the use of Au catalysts supported on various supports for the direct synthesis of hydrogen peroxide from O₂ and H₂ [7,8,21].

The results obtained by the authors are very promising. With regard to the catalytic performance of 1.3 wt% Au/TiO₂ patented catalyst [22], the most active catalyst, 5 wt% Au/Al₂O₃, reported by Hutchings et al. is much more active in the synthesis of H₂O₂. The productivity, expressed as moles H₂O₂ h⁻¹ Kg_{cat}⁻¹, is 3,6 for 1.3 wt% Au/TiO₂ at reaction temperature of 303 K [22], whereas 5wt% Au/Al₂O₃ show a similar productivity but at lower temperature (Tr = 275 K) [8].

Au supported on oxy-hydroxides catalysts are also effective in the direct synthesis of hydrogen peroxide, but their catalytic activity is lower than that obtained for 5% Au/Al₂O₃.

The catalytic activity of gold catalysts supported on iron oxy-hydroxides is strongly influenced by the preparation method and the catalysts thermal treatment [8]. 5%Au/Fe₂O₃ prepared by impregnation is more active than catalysts prepared by coprecipitation. Moreover, among the catalysts prepared by coprecipitation, the productivity increases with the temperature of calcination from 0.126 moles H₂O₂ h⁻¹ Kg_{cat}⁻¹ of the non calcined catalyst to 0.366 moles H₂O₂ h⁻¹ Kg_{cat}⁻¹ of the catalyst calcined at 873 K [8]. The increase of the rate of hydrogen peroxide formation has been related to the increase of the Au particle size [8]. The addition of Pd to Au/αFe₂O₃ prepared by impregnation (weight ratio Pd:Au 1:1) significantly enhances the catalyst performance for the synthesis of H₂O₂. The catalyst containing a weight ratio Pd:Au 1:1 shows a rate of synthesis of H₂O₂ 30 times higher than that obtained on gold catalyst, and give similar performance to the alumina Pd-Au catalysts [8].

STEM and HREM microscopy indicate that the most active Pd-Au/αFe₂O₃ catalysts have core-shell type alloy nanoparticles with Pd rich shell [8].

Remarks

This overview on the catalytic activity of Au supported on iron oxy-hydroxides clearly demonstrate that those catalysts are highly versatile because they can be used either for selective oxidation of alcohol to aldehyde, selective hydrogenation of

α,β unsaturated carbonyl compounds to α,β unsaturated alcohols and the direct synthesis of hydrogen peroxide from H₂ and O₂ (Fig. 5).

With this respect they show potentiality to be used as catalysts for the synthesis of fine chemicals.

Au supported on iron oxy-hydroxides is the first example of heterogeneous catalyst on which it is possible to realize the selective hydrogenation of α,β unsaturated ketones to α,β unsaturated alcohols with molecular H₂ as reductant.

Furthermore, the catalytic activity of gold supported on iron oxy-hydroxides in the direct synthesis of hydrogen peroxide is of particularly relevance, and open a new route for studies on selective oxidation reactions with H₂O₂ produced "in situ".

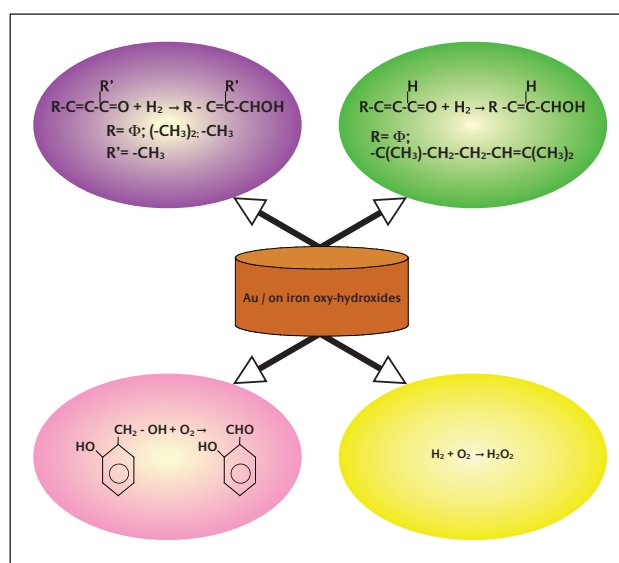


Figure 5

References

- 1 C. Milone, C. Gangemi, G. Neri, A. Pistone and S Galvagno, *Applied Catalysis A: General*, 2001, **211**, 251
- 2 C. Milone, R. Ingoglia, A. Pistone, G. Neri, S. Galvagno, *Catalysis Letters*, 2003, **87**, 201
- 3 C. Milone, M.L. Tropeano, P. Gulino, R. Ingoglia, G. Neri, S. Galvagno, *Chemical Communication*, 2002, **8**, 868
- 4 C. Milone, R. Ingoglia, M.L. Tropeano, G. Neri, S. Galvagno, *Chemical Communication*, 2003, **7**, 868
- 5 C. Milone, R. Ingoglia, A. Pistone, G. Neri, F. Frusteri, S. Galvagno, *Journal of Catalysis*, 2004, **222**, 348
- 6 C. Milone, R. Ingoglia, L. Schipilliti, C. Crisafulli, G. Neri, S. Galvagno, *Journal of Catalysis*, 2005, **236**, 80
- 7 P. Landon, P.J. Collier, A.F. Carley, D. Chadwick, A.J. Papworth, A. Burrows, C.J. Kiely, G.J. Hutchings, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1917
- 8 J.K. Edwards, B. Solsona, P. Landon, A.F. Carley, A. Herzing, M. Watanabe, C.J. Kiely, G.J. Hutchings, *J. of Mater. Chemistry*, 2005, **15**, 4595
- 9 K. Hamada; G. Suzukamo, US Patent 4,469,894, 1984

- 10 K. Hamada; G. Suzukamo, US Patent 4,584,410, 1984
- 11 L. Weisse, R. Neunteufel, B. Nenndorf, H. Strutz, US Patent 5,395,978, 1995
- 12 J. Le Ludec, US Patent 4,026,950, 1977
- 13 B. Kurt, M. Reiner, F. Helmut, W. Karlfried, US Patent 4,119,671, 1978
- 14 H. Lanfranc, US Patent 5,689,009, 1997
- 15 P. Gallezot, D. Richard, Gallezot, *Catal. Rev.-Science Engineering*, 1998, **40**, 81
- 16 J. Kaspar, M. Graziani, G. Picasso Escobar, A. Trovarelli, *Journal of Molecular Catalysis*, 1992, **72**, 243
- 17 M. Gargano, V. D'Orazio, N. Ravasio, M. Rossi, *Journal of Molecular Catalysis*, 1990, **58**, L5
- 18 S.N. Coman, V.I. Parvulescu, M. De Bruyn, D.E. De Vos, P. Jacobs, *Journal of Catalysis* 2002, **206**, 218
- 19 V. Ponec, *Appl. Catal. A: General*, 1997, **149**, 27
- 20 G.M.R. van Druten, L. Aksu, V. Ponec, *Appl. Catal. A: General*, 1997, **149**, 181
- 21 P. Landon, P.J. Collier, A.J. Papworth, C.J. Kiely, G.J. Hutchings, *Chem. Commun.* 2002, 2058
- 22 A. Jones, R.A. Grey, Patent Application n° WO 02/064500, 2002
- 23 M. Haruta, *Cat. Tech.* 2002, **63**, 102
- 24 F.E. Beamish and J.C. van Loon, in *Analysis of Noble Metals*, Academic Press, New York, 1977
- 25 F.E. Wagner, S. Galvagno, C. Milone, A.M. Visco, L. Stievano, S. Calogero, *J. Chem. Soc. Faraday Trans.*, 1997, **93**, 3403
- 26 A.M. Visco, F. Neri, G. Neri, A. Donato, C. Milone and S. Galvagno, *Physical Chemistry and Chemical Physics*, 1999, **1**, 2869-2873
- 27 *Ph.D Thesis*, University of Padova (Italy)
- 28 G. Neri, A.M. Visco, S. Galvagno, M. Panzalorto, *Thermochimica Acta*, 1999, **329**, 39
- 29 U. Schewertmann, R.M. Cornell, in *Iron Oxides in the Laboratory: Preparation and Characterization*, VCH, Weinheim, 1991
- 30 N.M. Gupta and A.K. Tripathi, *J Catal.*, 1999, **187**, 343
- 31 L.I. Ilieva, D.H. Andreeva, A.A. Andreev, *Thermochimica Acta*, 1997, **292**, 169
- 32 G. Munteanu, L. Ilieva, D. Andreeva, *Thermochimica Acta*, 1997, **291**, 171
- 33 S. Minicò, S. Scirè, C. Crisafulli, R. Maggiore, S. Galvagno, *Appl. Catal. 34 B: Environmental*, 2000, **28**, 245
- 34 F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, *J. Catal.* 1999, **188**, 176
- 35 F. Boccuzzi, A. Chiorino, T. Tsubota, M. Haruta, *J. Phys. Chem.* 1996, **100**, 3625
- 36 F. Boccuzzi, G. Cerrato, F. Pinna, G. Strukul, *J. Phys. Chem.*, 1998, **102**, 5733
- 37 S. Minicò, S. Scirè, C. Crisafulli, A.M. Visco, S. Galvagno, *Cat. Letters*, 1997, **47**, 273
- 38 G.J. Hutchings, *Gold Bulletin*, 1996, **29**, 123
- 39 G.J. Hutchings, M.R.H. Siddiqui, A. Burrows, C.S. Kiely, R. Whyman, *J. Chem. Soc. Farad. Trans.* 1997, **93**, 187
- 40 G. Neri, C. Milone, A. Donato, L. Mercadante, A.M. Visco, *J. Chem. Tech. Biotechnol.*, 1994, **60**, 83
- 41 C. Mohr, H. Hofmeister M. Lucas P. Claus, *Chem. Eng. Technol*, 2000, **23**, 4
- 42 M. Haruta, H. Kageyama, N. Kamijo, T. Kobayashi, F. Delannay, *Successful Design of Catalysts, Studies in Surface Science*, ed. T. Inui, Elsevier Amsterdam, 1988, **44**, 33
- 43 S. Scirè, S. Minicò, C. Crisafulli, C. Satriano, A. Pistone, *Applied Catalysis B: Environmental*, 2003, **40**, 43
- 44 J. Wanngard, Patent Application n° 0816286, 1998
- 45 K.T. Chuang, B. Zhou, US. Patent n°5338531, 1984