Effect of Au in the hydrogenation of Citronellal 0ver Ir/TiO$_2$ catalysts

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Abstract

In this paper, the liquid phase hydrogenation of citronellal was studied using Ir, Au, and Ir-Au catalysts. The bimetallic catalysts were prepared by co-deposition-precipitation with urea (CDPU). The catalysts were reduced either at 573 and 773 K. The catalysts were characterized by EDX, XRD, N$_2$-physisorption, and H$_2$-chemisorption at 303 K. The results indicate that the textural properties of supported catalysts not change respect to metal, while the dissociation of H$_2$ varies depending on the supported metal. For Ir-Au/TiO$_2$ catalysts an increase in the reduction temperature favored the conversion of citronellal, however, decreases the selectivity to unsaturated alcohol.

Keywords: citronellal, hydrogenation, DPU, Ir-Au catalysts

Efecto del Au en la hidrogenación de Citronelal sobre catalizadores Ir/TiO$_2$

Resumen

Se estudió la hidrogenación en fase líquida del citronelal usando catalizadores Ir, Au, and Ir-Au. Los catalizadores bimetálicos fueron preparados por deposito-coprecipitación con urea (CDPU). Los catalizadores fueron reducidos a 573 y 773 K, y caracterizados mediante EDX, XRD, fisisorción de N$_2$ y quimisorción de H$_2$ a 303 K. Los resultados indicaron que las propiedades texturales de los catalizadores soportados no cambian respecto al metal, mientras que la disociación de H$_2$ varía dependiendo del metal soportado. Para los catalizadores Ir-Au/TiO$_2$ un incremento en la temperatura de reducción favorece la conversión del citronelal, sin embargo, disminuye la selectividad hacia el alcohol insaturado.

Palabras clave : citronellal, hydrogenation, DPU, Ir-Au catalysts

Efeito da Au na hidrogenação de citronelal em catalisadores Ir/TiO2

Resumo

Estudou-se a hidrogenação em fase líquida utilizando catalisadores citronelal Ir, Au, Au e Ir. Os catalisadores bimetálicos foram preparados por co-precipitação de depósito-ureia (CDPU). Os catalisadores foram reduzidos a 573 e 773 K, e caracterizada por EDX, XRD, fisissorção de N2 e quimissorção de H2 a 303 K. Os resultados indicaram que as propriedades texturais de catalisadores suportados em que o metal não se altera, enquanto que a dissociação de H2 suporte varia de acordo com o metal. Ir-Au/TiO2 catalisadores para uma temperatura de redução crescente favorece a conversão do citronelal, no entanto, diminui a selectividade para o álcool insaturado.

Palavras-chave: citronelal, hidrogenação, DPU, Ir-Au catalisadores

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4

Introducciòn

Selective hydrogenation reactions are of special interest in the field of fine chemistry(1). An example of this type of reaction is the hydrogenation of citronellal (3,7-dimethyl-6-octenal). The figure 1, displays the main reaction pathways that can occur; the reduction of either the C=O or the conjugated C=C bond to conjugated C=C bond to produce citronellol or 3,7-dimethyloctanal, respectively. The consecutive hydrogenation of this products leads to 3,7-dimethyloctanol. Apart from these reactions, secondary processes of cyclization can lead to other by-products like isopulegols. The chemoselective hydrogenation of the carbonyl group of citronellal to citronellol (3,7-dimethyl-6-octene-1-ol) is desirable due to the fact that it is widely used in the perfume industry and as an important reactant in the synthesis of chiral compounds(2-3). Some heterogeneous catalysts have been used to improve the selectivity towards unsaturated alcohol. For instance, Rh/TiO_2 shows high selectivity to citronellol (4) as well as Ir/TiO_2 (5). However, it is possible to modify the product distribution of the hydrogenation of citronellal using acid supports. Other studies indicated that isopulegols are preferentially formed as primary products when Ru supported on acids solids are used(6).Similar results were reported recently, using $Ir/Nb_2O_5-SiO_2$ catalysts (5). On the other hand, gold heterogeneous catalysts can show very high selectivity for the selective hydrogenation of unsaturated molecules (7-8) due to their low capacity of dissociation of molecular H_2, which facilitate the selective hydrogenation of citronellal, however, for this reaction, it has not been yet demonstrated. The catalytic activity of gold heterogeneous catalysts depends not only on the size of the gold nanoparticles, but also on the nature of the support and even the preparation methods of the catalysts (9). Additionally, the presence of a metal of group VIII in gold catalysts has been used to increases the rate of H_2 dissociation, resulting an enhancement in the catalytic activity with respect to monometallic catalyst(10). The presence of a second metallic component can significantly improve the catalytic performance in several cases, attributed to "ensemble" or ligand effects.

One very interesting system investigated for its anomalous interactions with hydrogen is Ir-Au which is considered to be near-surface alloys. Such alloys bind atomic hydrogen (H) as weakly as the noble metals, while retaining the ability to dissociate molecular hydrogen (H_2) much easier than the noble metals (11). Recently, studies reported that using Ir-Au/TiO_2 catalyst, prepared by deposition-precipitation, the activity in CO oxidation when compared to Au/TiO_2 was remarkable enhanced (12). In this sense, the aim of this paper is to get a better insight on the influence of gold in the liquid phase hydrogenation of citronellal on the products distribution without affecting the high catalytic activity of iridium.

Experimental

Preparation of catalysts

The Au/TiO_2 and Ir/TiO_2 catalysts were prepared by deposition precipitation using urea (DPU)(13). Ir-Au catalyst (atomic relation: 0.3) was obtained by co-impregnation by urea. In a standard experiment, the desired amount of $HAuCl_4$ ($1.951x10^{-3}$ M) and H_2IrCl_6 ($6.35\times$

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ISSN 0120-4211   **3-11**

5

10^{-4} M) was added into 100 mL of urea solution (2.54 x10^{-3} M) with 5 g of TiO$_2$ (Degussa P-25), and the mixture was then gently heated to 353 K for 16 h, and washed using deionized water to remove the chlorine residues. The solids were dried under vacuum at 373 K and calcined at 673 K for 4 h. All samples were reduced in H$_2$ at 573 K (LT) and 773 K (HT) for 2 h in flowing hydrogen.

Catalyst characterization

Chemical analysis of Au and Ir in the samples was determined by energy dispersive X-ray spectroscopy (EDS) using an Oxford-ISIS detector coupled to a scanning electron microscope (JEOL JSM-5900-LV) over more than 50 different areas of the catalyst. X-ray diffraction were measured in a Philips Analytical X-Pert-Pro diffractometer using nickel-filtered Cu kα radiation (λ = 1.54056 Å). Spectra were obtained in the 2θ range of 10–85º, using a scan rate of 4º min^{-1} and a 0.02º data interval. The crystalline phases were identified using the JCPDS files. N$_2$ adsorption-desorption isotherms at 77 K were measured in a Micromeritics ASAP 2020. Samples were previously evacuated at 623 K for 16 h. The metal dispersion Ir, Au and Ir-Au catalysts were evaluated by H$_2$ chemisorption performed on a Micromeritics ASAP 2020 apparatus at 308 K (14). The catalysts were activated under vacuum at 403 K for 1 h, and then were reduced in H$_2$ at 573 or 773 K for 2 h, followed by evacuation at these same temperatures for 60 min. After cooling to 308 K, the catalysts were evacuated again for 2 h followed by analysis at 308 K. The difference between the total and reversible uptakes was ascribed to irreversible hydrogen uptake. The metal dispersion, surface area, and metal particle size were determined from the irreversible uptake. The dispersion was obtained(15) by using the equations (1)-(3), in which V is the hydrogen uptake, SF is the calculated stoichiometry factor, assuming an H/metal stoichiometry of 2, $\%weight$ is the percentage of the sample weight, and A_m is the effective area of one active metal atom

$$(1)$$

$$D = \frac{100\% \times 100\%}{22414} \times \frac{V \times SF}{\frac{\%weightIr}{W_{atomic}Ir} + \frac{\%weightAu}{W_{atomic}Au}}$$

$$Ms = (6,023 \times 10^{23}/22414)(V)(SF)(A_m) \quad (2)$$

$$(3) Msm = Ms \times \frac{100\%}{\%weightIr + \%weightAu}$$

Catalytic activity

Catalytic reactions were conducted in a batch reactor at a constant stirring rate (1000 rpm). For all reactions, hydrogen partial pressure was of 0.62 MPa, catalyst weight of 200 mg, 25 ml of a 0.10 M solution of (R)-citronellal in n-heptane and reaction temperature of 363 K. The absence of oxygen was assured by flowing He through the solution, as well as when the reactor was loaded with the catalyst and reactants at atmospheric pressure during 30 min. Prior to the experiment, all catalysts were reduced in situ under hydrogen flow of 20 cm^3×min^{-1} at atmospheric pressure and temperature of 363 K. Blank experiment showed no catalytic activity due to the supports under these conditions. Reaction products were analyzed in a GC-Varian 3800- mass spectrometer Saturn 2000, using a β-Dex Column.

6

Results and Discussion

Catalyst characterization

Table 1 displays the metal loading of the catalysts studied obtained by EDS analysis, it can be observed that the method used to prepare monometallic catalysts allows the deposition close to the nominal metal loading (1 wt %). In the case of bimetallic sample, the metals were not deposited completely, which may be attributed to the washing process to eliminate chlorine residues or the adsorption competition between Au and Ir species over the TiO_2 surface as has been reported by (12). N_2 isotherms of adsorption-desorption are shown in the Figure 2. It can be seen that all the adsorption isotherms were of the type IV in the classification of Brunauer, Deming, Deming and Teller (BDDT). In all materials, a type H4 hysteresis was observed (16). The textural properties, BET specific surface areas and the total pore volumes of the catalysts are summarized in Table 2. The impregnation with the aqueous solution of metal precursors does not affect significantly the surface area (S_{BET}), pore volume (V_p) and pore size (r_p) of the support, due to its low metallic content. Figure 3 displays the profiles of XRD, which exhibit the same XRD diffraction lines due to the support. The absence of lines due to Ir and Au is indicative of highly dispersed species (16) . Metallic dispersions were expressed in terms of the quantity H/Ir, and hydrogen uptake as $\mu molg^{-1}$. The results are summarized in Table 1. The values expressed could be explained taking into account that gold apparently spreads over the iridium surface,

considering that Au has lower surface free energy (16), this causes an increases in the particle size and a decrease in H_2-chemisorption. This behavior is clearly observed in the LT series, contrary to catalysts submitted to HT reduction. Au LT and HT and Ir-Au HT catalysts did not show hydrogen adsorption. The hydrogen uptake of gold catalysts is weak, principally determined by the particle size (17). The absence of chemisorption values for HT catalysts reflects a loss in the number of surface sites, suggesting either the development of SMSI (strong metal-support interactions) or a state of sintering of the metal particles. The decreasing in the H/Ir ratio is frequently reported when partially reduced. The decreasing in the H/Ir ratio is related with partially reduced species of the support that migrates on the metallic particle, covering part of the metal sites generating a surface decoration(5,18).

Catalytic activity

Figure 4 shows the evolution of the conversion level with time on stream for both studied series (LT and HT). It can be seen that the reaction rate is higher during the first hour of reaction, being lower the conversion levels in the LT series compared to the HT counterpart. Catalytic properties for citronellal hydrogenation over LT and HT catalysts are summarized in Table 4, taking into account that the selectivity may be affected by the conversion level, the results of initial activity at 5 % of conversion are shown in Table 4.

Comparison of the reactivity of monometallic catalysts shows that Ir/TiO_2 is more active compared to Au/TiO_2

7

catalyst, which it is in agreement with the results of chemisorption. For the LT series, an important hydrogenation of citronellal occurs during the first few minutes, with a rapid deactivation after this earlier period. This behavior is attributed to decarbonylation reaction of aldehyde yielding irreversible adsorbed CO that blocks metallic active sites(19). This result suggests that the decarbonylation process poisons mainly the C=C hydrogenation sites and modifies the C=C/C=O adsorption competition, changing the selectivity obtained. Particularly, for Au catalysts the selectivity towards the carbonyl group (SC=O) decrease with the increase of conversion, this can explain the results of table 5. Conversely, the deactivation occurs in a lower extent over HT catalysts and bimetallic catalysts except for Au monometallic catalyst (Figure 4). This could be an indication of some modification of the adsorption properties of the reactive surface due to the presence of gold as has been recently reported by(20) in the hydrogenation of citral over Ir-Au catalysts prepared by sequential impregnation(21).

Table 5 shows the selectivity towards different reaction products at 3 h of reaction. The different behavior in terms of selectivity for Ir monometallic catalysts is mainly due to the SMSI effect of solids submitted to HT(22). This is explained considering the Ir/TiO_2 and catalysts possess active sites in which the metallic component exhibit a partial decoration, with the creation of $Ir^{\delta+}$ species, which are more active in the polarization of the C=O bond(23,24), this has been well established for the hydrogenation of aldehydes α,β-unsaturated as citral or furfural(25). Earlier reports by our group in the hydrogenation of citronellal indicated that the $S_{C=O}$ is lower with catalysts of Ir/TiO_2 HT prepared by incipient impregnation ($S_{C=O}$ = 60)(25), suggesting with these results that the preparation method affects the selectivity level. In this study the elimination of chlorines residues by DPU modified the ratio of products favoring the formation of citronellol, due to a lower acidity on the catalysts. Ir-Au LT showed a higher the selectivity to SC=O, probably due to the type of active sites formed. Catalysts obtained by co-impregnation can develop particles of core-shell type, considering that Au has lower surface free energy than Ir (16), it is possible that the gold covers the iridium surface and thus a increases the probability of adsortion of carbonyl group. However, when is compared with Ir-Au HT catalysts, the decreasing capacity of dissociation of H_2 due to the SMSI effect with a partial coverage of Au over the crystallites of Ir, causes an alteration on the surface and therefore the formation of others products. Thus the role of gold presumably is dependent on the temperature of reduction used.

Conclusions

For $Ir-Au/TiO_2$ catalysts an increase in the reduction temperature favors the conversion of citronellal, however, decreases the selectivity to unsaturated alcohol, due to the modification of surface. In this sense, the catalytic behavior in Ir-Au catalysts is highly dependent of the reduction temperature used. Although, not was observed a drastic change in the textural properties of supported catalysts with the deposition

8

of the metals, as well as, not were evidenced lines diffraction of DRX of gold or iridium, a decrease in H_2-chemisorption values with respect to iridium catalyst monometallic, can explain the conversion levels and selectivity differences between Ir and Ir-Au catalysts.

Acknowledgements

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9

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10

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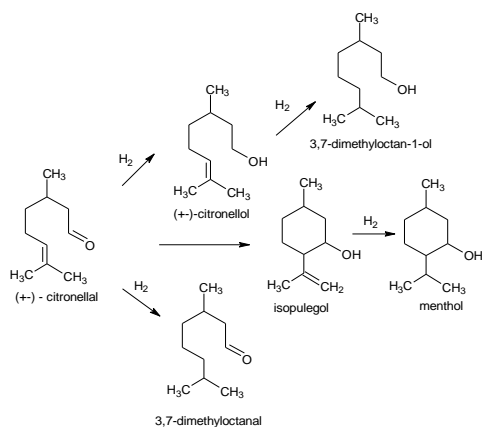
Figure 1. Routes of hydrogenation of citronellal

Figure 2. Nitrogen adsorption-desorption of Ir-Au catalysts
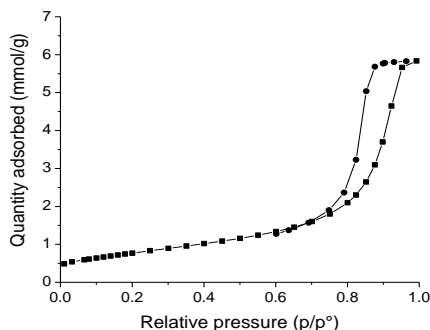

Figure 3. X-ray diffraction of (a) TiO₂, (b) Ir/TiO₂, (c) Ir-Au/TiO₂, (d) Au/TiO₂
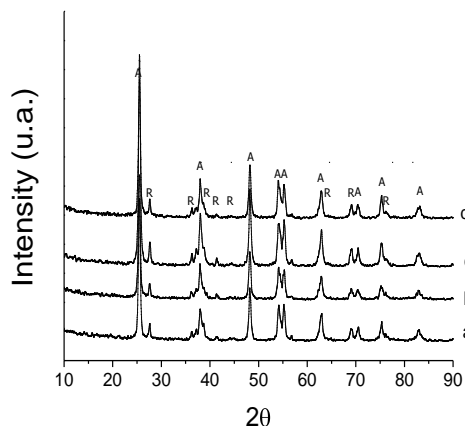

Figure 4. Conversion level as function of time during 0.1 M citronellal hydrogenation on Ir, Au and Au-Ir/TiO₂ catalysts at 363 K and 0.62 MPa, 0.2 g catalyst.
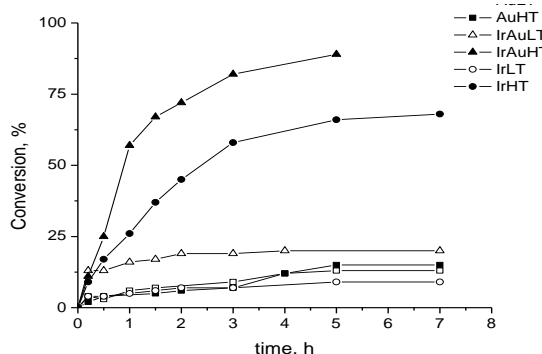

Table 1. Chemical composition obtained by EDS analysis, textural properties of Ir, Au, Ir-Au catalysts and H/Me ratio and metal particle size (d) obtained from H₂-chemisorption of Ir, Ir-Au and Au catalysts reduced in H₂ at 573 K.

Catalyst	Ir%	Au%	S_{BET} m²/g	V_p cm³/g	S_p nm	H/Me	D,nm
Ir	1.0	----	51	0.21	12.7	0.26	3.5
Ir-Au	0.44	0.08	51	0.21	11.8	0.14	6.3
Au	-----	0.89	51	0.21	10.7	0.017	n.r**

*n.r.: not reported, due to low value of H/Ir the value of size crystal not is real Typical isotherms of H₂ chemisorption at 308 K were obtained for reduced catalysts at LT catalysts of Ir and Ir-Au.

Table 2. Catalytic activity in citronellal hydrogenation at 363 K and 0.62 MPa, expressed as initial activity and conversion (X)

Catalyst	Initial activity ($\mu mol\ s^{-1}g^{-1}_{cat}$	X, (%) at 3h
Ir/TiO₂, LT	1.09	7
Ir/TiO₂, HT	2.34	58
Au/TiO₂, LT	0.47-	9
Au/TiO₂, HT	0.24	7
Ir-Au/TiO₂, LT	0.37	
Ir-Au/TiO₂, HT	3.53	82

Table 5. Selectivity of reaction. COL: cynnamil alcohol,
DMAL: 3,7 dimethyl-octanal, DMAL dimethyl-octanol,
ISP: isopulegol

Catalyst	COL	DMAL	DMOL	ISP	Others
Ir/TiO$_2$, LT	60	10	13	6	11
Ir/TiO$_2$, HT	96	0	0	0	4
Au/TiO$_2$, LT	48	20	31	0	1
Au/TiO$_2$, HT	35	23	32	9	1
Ir-Au/TiO$_2$, LT	86	4	6	0	4
Ir-Au/TiO$_2$, HT	24	25	36	10	5