

Liquid-phase hydrogenation of citral over Ir-supported catalysts

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Received 8 June 2001; received in revised form 16 August 2001; accepted 5 October 2001

Abstract

The hydrogenation of citral over a series of supported iridium catalysts was investigated. The nature of the support (TiO₂ and SiO₂), the effect of additives (Fe and Ge), and the influence of the reduction temperature on catalyst performance have been examined. It was found that the presence of ionic species, such as, promoters or species generated upon reduction at high temperature of the reducible TiO₂ support, i.e. TiO_x moieties, leads to catalysts active and highly selective to the hydrogenation of the carbonyl bond. This is explained in terms of the presence of positively charged (Fe³⁺, Ge⁴⁺) species in intimate contact with Ir, which are responsible for the polarisation of the C=O bond. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Citral; Hydrogenation; Iridium; Catalysts; SMSI effect

1. Introduction

Selective hydrogenation of organic substrates containing a number of unsaturated functional groups is an important step in the preparation of various fine chemical products. Significant attention have received the hydrogenation of α,β unsaturated aldehydes to produce allylic alcohols. The widest hydrogenations studied are the hydrogenation of acrolein [1,2], crotonaldehyde [3–5] and cinnamaldehyde [6,7] over single metallic-supported catalysts. The hydrogenation of α,β unsaturated carbonyl compounds on single metal catalysts, mainly conducted in vapour phase hydrogenation (acrolein and crotonaldehyde) usually leads to the reduction of the conjugated C=C double bond with a high selectivity, close to 100%.

Several attempts have been made to develop a suitable catalytic system to improve the selectivity to the unsaturated alcohol. Thus, the use of reducible supports that present the SMSI effect, such as TiO₂ or Nb₂O₅ [8,9] has been successfully used to increase the selectivity to the hydrogenation of the C=O group of the crotonaldehyde when high temperature reduction of Pt–TiO₂ was used [10]. Similar results have been obtained in the hydrogenation of acrolein over Pt and Ir metals deposited on Nb₂O₅. From these studies, it is clear that the presence of reduced TiO_x ($1.5 < x < 2$) moieties at the metal interface region is responsible for the polarisation of the C=O group that increases to a large extent the selectivity of the reaction. The morphology of the particles has been also claimed to have an important effect on the selectivity. In fact, Gallezot and Richard [11] have found a strong dependence of selectivity on the metal particle size in the liquid-phase hydrogenation of cinnamaldehyde over Pt catalysts. Large platinum particles, over 5 nm, gave a selectivity

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of 98% to the cinnamylalcohol at 50% conversion, whereas small platinum particles of 1.3 nm size gave 83% selectivity at the same conversion level. Similar effects were observed with Rh and Ru catalysts [12,13]. The behaviour has been explained in terms of the hindered adsorption of the olefinic bond by the unsaturated aldehyde group due to a steric repulsion between the flat metal surface in large metal particles and the aromatic ring leading to an increase in the selectivity towards C=O group hydrogenation. The addition of a second metal such as Sn, Ge or Mo [14–16] also produces an enhancement of the selectivity towards the allylic alcohols. Claus [17] has shown that the addition of Sn to Rh, Pt or Ru catalysts produce also an increase in the selectivity to crotylalcohol. Moreover, when the bimetallic catalysts are prepared by controlled surface reaction of $n\text{-(C}_4\text{H}_9)_4\text{Sn}$ on the surface of group 8 metals deposited on a carrier, a Rh–Sn

alloy is formed and an electron transfer occurs between Rh and Sn in the alloy state. On the other hand, Pt–Sn catalysts prepared by impregnation of a support with H_2PtCl_6 and SnCl_2 lead to catalysts in which the tin is mainly present as Sn(IV) and Sn(II) and only a minor proportion of tin in a zero-valent state. However, these catalysts also produce an enhancement in the selectivity to crotyl alcohol. Similar results were obtained by Reyes et al. [18], in the liquid-phase hydrogenation of cinnamaldehyde on supported Rh catalysts when the catalysts are promoted by the addition of Mo. The presence of Mo^{4+} and Mo^{6+} and $\text{Rh}^{\delta+}$ species are responsible for the significant enhancement of the selectivity to cinnamylalcohol.

Dealing with the cationic promoters, the addition of iron chloride to platinum catalysts for cinnamaldehyde hydrogenation led to an important improvement in the activity and selectivity to the desirable product [19].

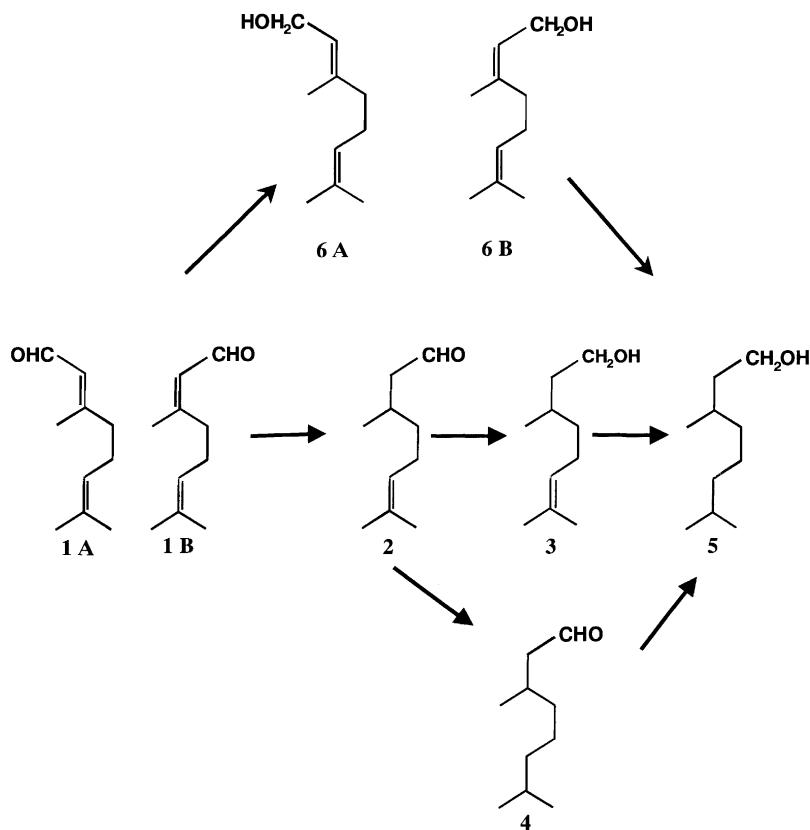


Fig. 1. Reaction network for citral hydrogenation. 1A: citral (E); 1B: citral (Z); 2: citronellal; 3: citronellol; 4: 3,7-dimethyloctanal; 5: 3,7-dimethyloctanol; 6A: nerol; 6B: geraniol.

This behaviour may be attributed to the presence of cationic species on the metal crystal, which contributes to the polarisation of carbonyl groups.

Among the α,β unsaturated carbonyl compounds, citral is a particularly attractive molecule, because it possesses an isolated C=C bond in addition to the conjugated C=O and C=C bonds. In addition, studies dealing with the hydrogenation of citral are rather scarce [20–22]. Fig. 1 shows the reaction scheme of citral hydrogenation.

The aim of the present contribution is to study the effect of the support, the addition of a second metal and the reduction temperature on the activity and selectivity for the hydrogenation of citral in liquid phase. Iridium catalysts supported on SiO₂ and TiO₂ with the addition of cationic promoters, Fe or Ge prepared by impregnation and reduced at 473 and 723 K are compared. The catalysts have been characterised by nitrogen adsorption at 77 K, H₂ chemisorption measurements at 298 K, TEM studies for particle size evaluation and XPS experiments to estimate surface composition. The liquid-phase hydrogenation of citral was studied in a batch reactor at 340 K and 60 psi (14.7 psi = 1 atm).

2. Experimental

Ir/SiO₂ catalysts were prepared by impregnation of a silica (BASF D11-11, $S_{\text{BET}} = 142 \text{ m}^2 \text{ g}^{-1}$) and TiO₂ (Degussa P-25, $S_{\text{BET}} = 72 \text{ m}^2 \text{ g}^{-1}$) with an aqueous solution of H₂IrCl₆ to give an Ir loading of 1 wt.%. The impregnates were dried at 393 K for 6 h, calcined in air at 723 K for 4 h, and reduced in situ at 473 (LTR) or 773 K (HTR) for 2 h prior to characterisation or catalyst testing. A portion of the reduced samples was then impregnated with GeCl₄(l) or an aqueous solution of FeCl₃ in an appropriate amount to give an atomic ratio of Ir:Ge or Ir:Fe of 1:1.

Nitrogen physisorption at 77 K and hydrogen chemisorption at 298 K were carried out in a Micromeritics ASAP 2010 apparatus. TEM micrographs were obtained in a JEOL Model JEM-1200 EXII System and XRD in a Rigaku apparatus. Photoelectron spectra (XPS) were recorded using an Escalab 200 R spectrometer provided with a hemispherical analyser, and using non-monochromatic Mg K α X-ray radiation ($h\nu = 1253.6 \text{ eV}$) source. The surface Ir/Si and

Ir/Ti atomic ratios were estimated from the integrated intensities of Ir 4f and Si 2p lines after background subtraction and corrected by the atomic sensitivity factors [23]. The spectra were fitted to a combination of Gaussian–Lorentzian lines of variable proportion. The binding energy of the Si 2p peak at 103.4 eV was taken as an internal standard.

Reactions were conducted in a Parr Instruments Model 4561 autoclave at a constant stirring rate (500 rpm). Prior the experiments, the catalysts were reduced in situ under hydrogen flow of 20 cm³/min at atmospheric pressure and temperature of 473 or 723 K (LTR or HTR, respectively). For all reactions the conditions were: 40 ml of a solution 0.5 M citral in ethanol, 200 mg of catalyst and hydrogen pressure of 60 psi under H₂ flow of 20 cm³/min at constant temperature. Moreover, internal diffusion limitations were also shown to be absent by applying the Weisz-Prater parameter [24] over Ir/TiO₂-HTR catalyst, which gave a value of 0.18 and assure the absence on internal diffusion limitations. Therefore, all these results indicate the absence of any transport limitations from the kinetics dated included in this paper. Blank experiments showed no catalytic activity due to the supports under these conditions. Reaction products were analysed on an HP 4890D GC furnished with an HP 5 semicapillary column of 15 m and 0.53 mm ID. The GC analyses was performed using a flame ionisation detector, using He as carrier, and the column was kept at a constant temperature, 393 K. Under these analytical conditions, the retention time (min) of the reported products for the citral hydrogenation were: citral (E): 30.7; citral (Z): 35.4; nerol: 28.2; geraniol: 32.2; citronellal: 21.3; citronellol: 27.6 and 3,7-dimethyloctanol: 25.6. The product selectivity was calculated as follows:

$$S_i = \frac{\text{concentration of species } i}{\sum_{\text{product}} \text{concentration of species } i}$$

3. Results and discussion

Table 1 summarises H/Ir ratios and the estimated particle sizes as derived from H₂ chemisorption and TEM. The average particle size of Ir crystallites (d) has been calculated from the equation [25] $d = 1.11/(\text{H/Ir})$ (nm), where H/Ir is the estimated

Table 1
H/Ir ratio and particle sizes obtained by hydrogen chemisorption and TEM of supported Ir catalysts

Catalyst	H/Ir _{Chem}	Particle size (nm)	
		Chem	TEM
Ir/TiO ₂ -LTR	0.25	3.7	2.6
Ir-Fe/TiO ₂ -LTR	0.05	19	2.7
Ir-Ge/TiO ₂ -LTR	0.07	13	2.7
Ir/SiO ₂ -HTR	0.276	3.3	1.7
Ir-Fe/SiO ₂ -HTR	0.056	16	1.7
Ir-Ge/SiO ₂ -HTR	0.095	9.7	1.7
Ir/TiO ₂ -HTR	0.16	7.9	2.5
Ir-Fe/TiO ₂ -HTR	0.02	46	2.7
Ir-Ge/TiO ₂ -HTR	0.02	46	2.8

metal dispersion. It can be seen that the H/Ir ratios are comparable for monometallic Ir/SiO₂ and Ir/TiO₂ reduced at low temperature (LTR), whereas the Ir/TiO₂-HTR sample exhibits a substantially lower H/Ir value. However, TEM results indicate that particle size of Ir/TiO₂-LTR and Ir/TiO₂-HTR samples are similar (2.5–2.6 nm) and somewhat smaller (1.7 nm) for Ir/SiO₂ sample. The differences may be explained considering the surface decoration of Ir crystals by TiO_x moieties, which produce a drop in the hydrogen uptake without changes in the particle size. It is emphasised that hydrogen chemisorption provides only the amount of exposed Ir surface atoms and, therefore, catalysts showing lower H/Ir ratios indicates a partial surface coverage effect and not a change in metal dispersion. The higher specific area of the support may be responsible for the small particle size measured on the silica-supported catalysts. The incorporation of Fe or Ge promoters to the reduced Ir catalysts produces a significant drop in the hydrogen

uptake, which can be attributed to a partial coverage of the Ir metal crystal by the Fe₂O₃ and GeO₂ oxides, without changes in metal particle size as shown by TEM. Metal particle size distribution for Ir/SiO₂ catalysts, obtained from TEM micrographs, revealed a very narrow distribution centred at about 1.5 nm and having metal crystal sizes in the range 1.0–3.0 nm. For Ir/TiO₂ catalysts, the distribution is wider having a maximum close to 2.0 nm and particle sizes in the range 1.0–4.0 nm. Consistent with TEM data, no X-ray diffraction lines attributable to Ir⁰ crystallites were observed for Ir/SiO₂ catalysts. No changes were observed upon incorporation of Ge and Fe additives. This observation indicates clearly that the dispersion degree of Ir is very high on the silica surface. For Ir/TiO₂ catalysts, besides the lines coming from the support, a wide and very weak line due to the metal component ($2\theta = 41^\circ$) can be discerned, indicating that metal particles with sizes larger than that formed on the silica support are present, in agreement with TEM and chemisorption results.

Binding energies of core-level electrons and metal surface composition were obtained from XP spectra. The binding energies of Si 2p, Ti 2p, Ir 4f_{7/2}, Fe 2p_{3/2} and Ge 3d core-level spectra are given in Table 2. For the Ir/SiO₂ and Ir/TiO₂ catalysts, the binding energy of Ir 4f_{7/2} peak is approximately 60.4 eV, which corresponds to Ir⁰ species. A slight increase in the BE of Ir 4f_{7/2} peak is consistent with the general trend observed for small particles of transition metals deposited on inorganic substrates, and agrees with TEM data. Catalysts promoted by Fe or Ge and titania-supported iridium catalysts reduced at high temperature show similar BE values. However, a slight broadening to higher

Table 2
Binding energy (eV) of core electrons of promoted and unpromoted Ir catalysts

Catalyst	Ti 2p _{3/2}	Si or Al (2p)	Ir 4f _{7/2}	Fe 2p _{3/2}	Ge 3d
Ir/TiO ₂ -LTR	458.5	–	60.2	–	–
Ir-Fe/TiO ₂ -LTR	458.5	–	60.4	709.6	–
Ir-Ge/TiO ₂ -LTR	458.5	–	60.2	–	31.4
Ir/SiO ₂ -HTR	–	103.4	60.6	–	–
Ir-Fe/SiO ₂ -HTR	–	103.4	61.1	711.2	–
Ir-Ge/SiO ₂ -HTR	–	103.4	60.5	–	32.8
Ir/TiO ₂ -HTR	458.5	–	60.1	–	–
Ir-Fe/TiO ₂ -HTR	458.5	–	60.1	709.2	–
Ir-Ge/TiO ₂ -HTR	458.5	–	60.1	–	31.7

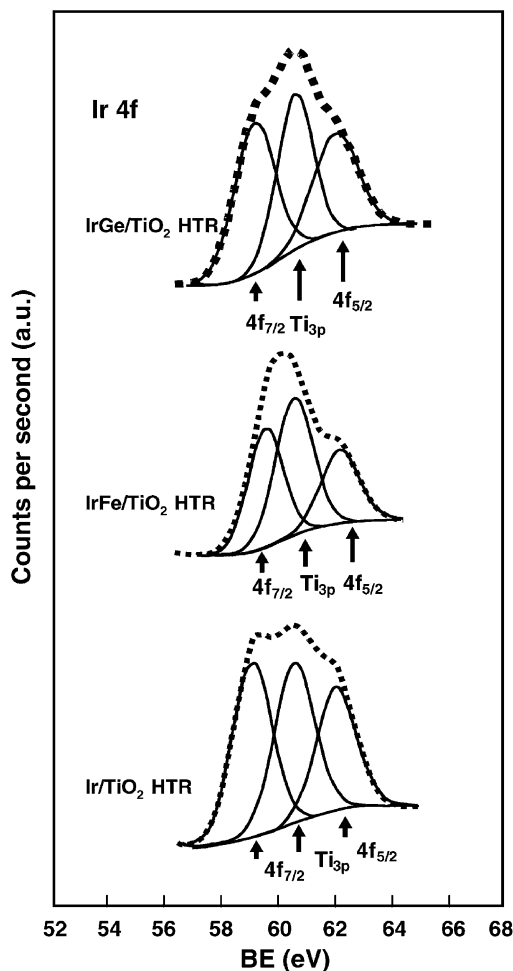


Fig. 2. Ir 4f core-level spectra for Ir-supported catalysts.

binding energies suggests the presence of Ir⁰ and Ir^{δ+} species in these samples. Fig. 2 displays XP spectra for some representative Ir-supported catalysts. It can be seen that three components had to be included to fit the experimental spectra because the Ti 3p peak coming from the support falls just between the two spin-orbit split (Ir 4f_{7/2} and Ir 4f_{5/2}) levels of iridium. Table 3 compiles Ir/M and Fe (or Ge)/M surface ratios for the studied catalysts. The Ir/Si ratio decreases slightly for each series upon the addition of Fe or Ge indicating a partial surface coverage of Ir crystal by Fe or Ge species, in agreement with chemisorption results. The Ir/TiO₂-HTR catalysts show lower Ir/Ti ratios than their LTR counterparts due presumably to

Table 3

XP spectra atomic ratios of Ir-supported catalysts

Catalyst	Ir/M	Fe/M	Ge/M
Ir/TiO ₂ -LTR	0.0242	–	–
Ir-Fe/TiO ₂ -LTR	0.0200	0.115	–
Ir-Ge/TiO ₂ -LTR	0.0228	–	0.047
Ir/SiO ₂ -HTR	0.0026	–	–
Ir-Fe/SiO ₂ -HTR	0.0075	0.094	–
Ir-Ge/SiO ₂ -HTR	0.0026	–	0.008
Ir/TiO ₂ -HTR	0.0271	–	–
Ir-Fe/TiO ₂ -HTR	0.0194	0.125	–
Ir-Ge/TiO ₂ -HTR	0.0203	–	0.0057

migration of TiO_x moieties on the Ir particles. The observed trends on Ir/SiO₂ samples are expected taking into account the differences in specific area and on basis of the previous explanation. For the Fe and Ge-promoted titania-supported Ir catalysts, partial reduction of Fe₂O₃ and GeO₂ additives is inferred as judging from the binding energies of Fe 2p_{3/2} and Ge 3d_{5/2} levels, which are lower than that measured on their silica-supported counterparts.

Fig. 3 shows the evolution of the conversion level with time at 343 K in citral hydrogenation over Ir/TiO₂-HTR unpromoted and promoted (with Fe and Ge ions) catalysts. It can be seen that the reaction rate is higher at short reaction times (below 1 h) and

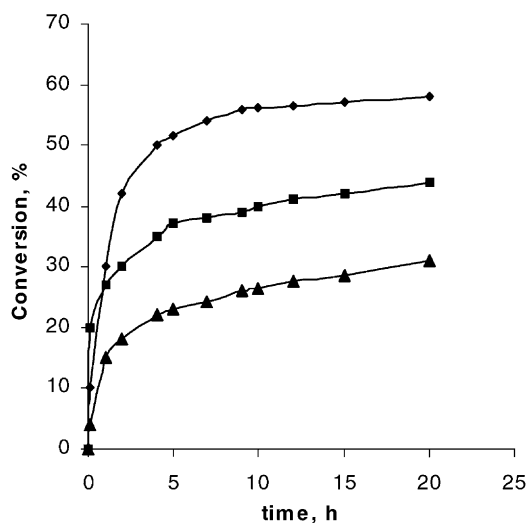


Fig. 3. Hydrogenation of citral at 343 K. Conversion level as a function of time for Ir/TiO₂-HTR catalysts: (◆) Ir/TiO₂-HTR; (■) Ir-Ge/TiO₂-HTR; (▲) Ir-Fe/TiO₂-HTR.

almost a steady state is reached around 10 h on-stream. On the other hand, when silica-supported catalysts are used, the steady state is obtained a lower reaction times (around 2–3 h). Table 4 summarises the conversion level at the same reaction time (4 h) as well as the initial activity for citral hydrogenation, expressed as micromole converted per second per gram of catalysts and the initial turnover frequency, evaluated by means of the average of TOF during first 30 min of reaction, obtained from the plot conversion vs. time. The addition of Fe or Ge to inactive Ir/SiO₂ and Ir/TiO₂-LTR catalysts produces a significant increase in both the activity and the TOF of the catalysts. This feature may be attributed to a modification of the nature of the metallic sites by Fe or Ge ionic species. On the other hand, the behaviour is different for Ir/TiO₂-HTR catalyst, being their activity higher than that exhibited by the non-promoted catalyst. This may be explained considering that, in this case, two effects are involved: the presence of Ir⁰-(Fe³⁺ or Ge⁴⁺) sites and the iridium particles covered by TiO_x moieties developed during the reduction of catalysts at high temperature (SMSI effect). The lower activity observed for Ir-Fe/TiO₂-HTR and Ir-Ge/TiO₂-HTR compared with the unpromoted Ir/TiO₂-HTR would indicate that when the active sites are developed at the metal-support interface, only a small fraction of Fe₂O₃ and GeO₂ promoters is deposited on the Ir particles. Support to this interpretation is provided by quantitative XPS data and also from H₂ chemisorption data. Additionally, there is a dramatic enhancement in the initial TOF of the promoted catalysts, which show a TOF three or five times higher than the unpromoted Ir/TiO₂-HTR catalyst. This can be explained on a basis of lower exposed iridium surface atoms in the former catalysts.

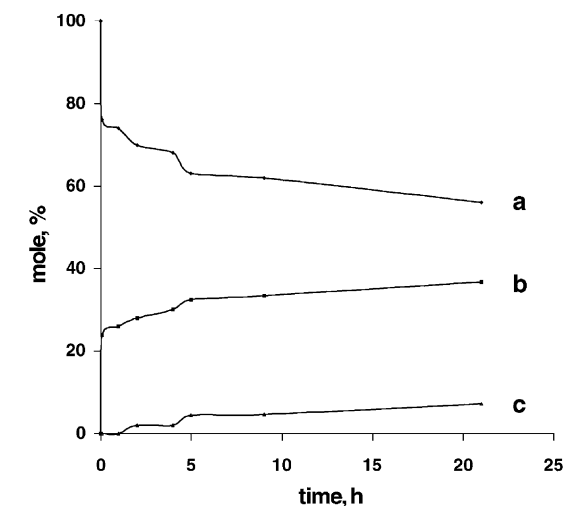


Fig. 4. Hydrogenation of citral at 343 K. Selectivity of the reaction as a function of time for Ir-Ge/TiO₂-HTR catalysts. (a) Citral; (b) geraniol; (c) nerol.

moted Ir/TiO₂-HTR catalyst. This can be explained on a basis of lower exposed iridium surface atoms in the former catalysts.

The highest activities exhibited by the TiO₂-HTR catalysts might result from the development of a high proportion of Ir-TiO_x interfacial sites. On the contrary, when the required dual sites are not developed as in the Ir/SiO₂ and Ir/TiO₂-LTR catalysts, the activities and turnover frequencies are extremely low. With regard to the selectivity, Fig. 4 displays the evolution of the molar concentration of the reactant and products during citral hydrogenation at 343 K on the Ir-Ge/TiO₂-HTR catalyst. It can be seen that in

Table 4

Catalytic activity in citral hydrogenation at 343 K and 60 psi, expressed as conversion at 4 h, initial activity and TOF and selectivity at 10% conversion

Catalyst	Total, X (%)	Initial activity ($\mu\text{mol/s g}_{\text{cat}}$)	TOF (s^{-1})	Selectivities (%)		
				Geraniol	Nerol	Citronellal
Ir/TiO ₂ -LTR ^a	3	0.13	9.8×10^{-3}	0	100	0
Ir-Fe/TiO ₂ -LTR	18	0.95	0.35	82	16	2
Ir-Ge/TiO ₂ -LTR	14	0.85	0.23	76	12	12
Ir/SiO ₂ -HTR ^a	0.2	0.02	1.4×10^{-3}	70	30	0
Ir-Fe/SiO ₂ -HTR	28	3.51	1.18	95	5	0
Ir-Ge/SiO ₂ -HTR	8	7.65	1.52	73	27	0
Ir/TiO ₂ -HTR	55	7.80	0.92	64	35	1
Ir-Fe/TiO ₂ -HTR	23	2.82	2.66	79	21	0
Ir-Ge/TiO ₂ -HTR	37	5.08	4.79	100	0	0

^a Conversion at 20 h of reaction (10% of conversion was not reached).

the range 2–20 h on-stream, only small changes are produced indicating that the selectivity remains virtually unchanged along this time. The selectivity to the hydrogenation of the carbonyl bond was very high (88–100%), with geraniol being the main product. A summary of the selectivities obtained at 10% conversion level is also shown in Table 4. The increase in TOF values in the catalysts promoted by Fe or Ge ions or in catalysts having the SMSI effect is evident. This is a consequence of the modification of metal sites either through the SMSI effect or by deliberately incorporating Fe₂O₃ or GeO₂ oxides, which develop the dual functionality, required for the selective hydrogenation of the carbonyl bond.

4. Conclusions

The results obtained allow one to conclude that iridium-supported catalysts can be very selective towards the hydrogenation of the carbonyl bond during citral hydrogenation. Significant enhancement in selectivity can be obtained due to the creation of new active sites, upon the addition of Fe or Ge as promoters due to the presence of metal ions (Lewis sites) or by using reducible supports such as TiO₂, which develop an SMSI effect; reduction at high temperature leads to surface decoration of the iridium metal crystallites by TiO_x moieties. Both MO_x (M: Fe, Ge) oxides or the TiO_x species contribute to the polarisation of the carbonyl group, thus enhancing the reactivity towards hydrogenation of the unsaturated alcohol (geraniol or nerol). The characterisation results supported the previous explanation.

Acknowledgements

The authors thank MIDEPLAN, Grants Milenio ICM P99-92 for their financial support.

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