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SYNTHESIS, CHARACTERIZATION AND CATALYTIC BEHAVIOR OF THE Ir/Nb_2O_5/SiO_2 SYSTEM IN THE CITRONELLAL HYDROGENATION

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ABSTRACT

The citronellal hydrogenation was studied on Ir/Nb_2O_5-SiO_2 catalysts. A series of catalysts was synthesized with different niobia contents (Ir/N1 1.10%; Ir/N2 2.54%; Ir/N3 3.25%; Ir/N4 5.30%wt%) using the wet impregnation method. These catalysts were reduced in hydrogen atmosphere at low or high temperatures, 473K (LTR) or 773K respectively. Their structural and surface properties were investigated by XRD, TEM, XPS, DTP, FTIR, H_2 chemisorption at 298 K and surface specific area by using the BET method. The X ray diffraction studies revealed only the peaks due to niobia, mainly in those with higher niobia loading. No diffraction lines due to Ir were observed due to its lower content and/or to its high dispersion. The catalytic tests in the hydrogenation of citronellal were carried out in a batch reactor operated at 6.2 bar of H_2 and 343 K. All catalysts showed higher selectivity to isopulegol and to their products due to the cyclization of the citronellal molecule.

Keywords: Ir/Nb_2O_5/SiO_2 Catalysts, citronellal hydrogenation, cyclization, isopulegol

INTRODUCTION

An important property of niobia, such as acidity and geometry has been reported in the literature for catalysts with low niobia content as well as stability and the support metal strong interaction effect (SMSI) [1]. Mixed oxides with niobium and niobium oxide supported over other oxides also show the above effect [2]. Niobia reduction is very important for SMSI effect but it has been less studied in the literature [3]. It is very known that SMSI effect is characterized for the suppression of the chemisorption ability of H_2 and CO over supported noble metals on reducible oxides such as TiO_2, CeO_2, and Nb_2O_5 after a reduction procedure at high temperature (approximately 773 K). It was also demonstrated that this interaction can affect the activity and selectivity of noble metals in different reactions, involving molecules with carbonyl bonds. Ziolek et al [4,5] studied the reducibility with several catalysts containing niobia using temperature programmed reduction (H_2-TPR) at high (HT), and low temperature (LT). In LT catalyst an increased of hydrogen consumption was showed with a maximum peak between 870 K and 930 K. When the silica is used as support of niobia, the TPR profile presents a wide peak with a maximum of 910 K covering a wide range of temperatures and it could be due to the reduction of several niobia species presenting various oxidation states [4]. The system noble metal/Nb_2O_5 showed the SMSI effect, where the catalytic properties of the particles of the noble metal on Nb_2O_5 are highly modified by reduction with H_2 at high temperature such as 773 K [6]. Reyes et al [7,8,9] found that Ir supported catalysts used in aldehyde hydrogenation are very active and selective towards the hydrogenation of carbonyl bond and exhibited a high selectivity towards the unsaturated alcohols. This fact may be attributed to the use of reducible supports which develop the SMSI effect. Marzialetti et al [10] indicate that in Ir catalysts in which the metal component is present as $Ir^{\delta+}$ species, the reaction rates increase as a consequence of the polarization of the carbonyl bond. This species may be generated due the high temperature reduction, in the case of a partially reducible support or by the addition of promoter oxides [10].

The main use of mixed oxides containing niobium or niobia supported on other oxides such as silica [6] is the catalytic application of their redox properties in acid catalyzed reactions, such as alcohols dehydration, esterification [11], etherification and alkylbencenes dealkylation [12]. Lewis acidity was found in all the systems of supported niobium oxides, whereas the Brönsted acid sites (BAS) were only detected in niobia supported on alumina and silica [11]. The high surface acidity is probably the most important property in niobium oxides compounds [11], niobia sulphates and niobia phosphates [13]. Studies show that the niobium oxides supported on silica catalyze the propene photoxidation to produce propanal or propene oxide and the selectivity is affected by the local structure of the species of niobium oxide [14]. The structure has been discussed in the literature and it exhibits different forms, as monomers, dymers or polymeric species of NbOx anchored to SiO_2 surface. The catalytic behavior changes depending on the structure [15]. Asakura et al [16], has reported that a monolayer of niobia is strongly formed on the SiO_2 by a simple impregnation. The preparation of niobium oxide supported on silica or alumina has been described in the literature by different methods, such as: (i) wet impregnation of ammonium oxaloniobate or oxaloniobic acid [17]; (ii) impregnation with niobium ethoxide using organic solvents [18] (iii) chemical vapor deposition of niobium ethoxide [19,20]. Ko et al. reported that a Ni/Nb_2O_5 catalyst shows a higher selectivity toward the olefinic hydrocarbons compared with a Ni/SiO_2 catalyst which is attributed to the strong metal-support interaction (SMSI) effect between that of Nb_2O_5 and the metallic Ni [21].

The isopulegol, a monoterpenic alcohol, is widely used in flavors and perfums industry for the production of fragrances and to manufacture menthol that is an important ingredient of cosmetics, pharmaceutical products and other special products [22]. In this field, one of the most competitive industrial processes is the Takasago process in which the (-) menthol is produced by the hydrogenation of (-) isopulegol, obtained from the (+) citronellal through a catalyzed acid cyclization [23,24]. Among the eight forms of sterioisomers of menthol, only the (-) menthol possesses a characteristic scent and it produces a refreshing physiologic effect. Milone et al [25], reported the (+) citronellal isomerisation with Zn(II) supported over SiO_2-TiO_2, SiO_2-Al_2O_3, SiO_2-ZrO_2 catalysts and Cu supported over mixed oxides. The (+) citronellal isomerisation is an acid catalyzed reaction and is a synthetic route for the production of (-) isopulegol. It has been suggested that the Lewis sites are active and stereoselectives to (-) isopulegol. The stereoselectivity values were reported between 63 and 74%. Kropp et al [26], have studied the (+) citronellal isomerisation over silica and silica supported catalysts. They reported a stereoselectivity toward (-) isopulegol of 80%. The high stereoselectivity values toward (-) isopulegol reported on silica is remarkable. Other authors have reported 62% of stereoselectivity toward (-) isopulegol when a high surface area silica (600m^2/g) is used [22]. On the other hand, they found 60% of stereoselectivity toward (-) isopulegol using silica with a surface area of 330 m^2/g [27].

In this study, citronellal is hydrogenated over Ir/Nb_2O_5-SiO_2 catalysts to obtain an unsaturated alcohol, isopulegol. The catalysts were reduced to 473K or 773 K, in order to analyze the effect of the partially reducible support. The characterization of the catalysts was performed by XRD, H_2 chemisorption at 298 K, surface acidity measurements by TPD of ammonia and determination of the surface area by the BET method. The catalytic tests were carried out in a reactor batch at 0.62 MPa of H_2 and 343 K. The obtained products were analyzed by GC-MS.

EXPERIMENTAL

Catalysts preparation

Niobium Ethoxide (Aldrich, reagent grade) (0.05 mmolg^{-1} of silica) was dispersed in toluene (150 mL) and added to an aerosil silica (Syloid-266-Grace Davidson, S_{BET} = 295 m^2g^{-1}) which was activated at 423 K under vacuum. The resultant mixture was stirred for 16 h under inert atmosphere at the solvent

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reflux temperature. Then, the modified silica was filtered, washed with toluene, ethyl ether and deionized water. The resulting solid N1 was dried for 5 h under vacuum at 423 K. One aliquot of this material (N1) was impregnated with an aqueous solution of H_2IrCl_6 to give an Ir loading of 1 wt.%. The impregnated solid was dried at 343 K for 6h, calcined in air at 673 K for 4 h and reduced at 473 K (LT) and 773 K (HT) for 2 h, obtaining Ir/N1 LT and Ir/N1 HT, respectively. A second aliquot of the solid N1 was enriched with Nb-(O-Et)$_5$ to obtain N2 support, following the same procedure of reflux, dried, and calcination described for the synthesis of N1. A portion of the obtained solid N2 was impregnated with H_2IrCl_6 to obtain Ir/N2 catalysts following the same preparation procedure described previously for Ir/N1 obtaining the Ir/N2 HT and Ir/N2 LT. Similar procedure was used for samples with higher Nb loading, referred as N3 and N4 as supports and Ir/N3 LT, Ir/N3 HT, Ir/N4 LT and Ir/N4 HT as catalysts. The theoretical contents of niobia are showed in table 1.

Table 1. Theoretical content of Nb_2O_5 and Ir.

Catalysts	Nb_2O_5 loading, wt%	Ir loading, wt.%
Ir/N1	1.12	1.0
Ir/N2	2.54	1.0
Ir/N3	3.25	1.0
Ir/N4	5.30	1.0

2.2 Characterization and Catalytic Evaluation

Nitrogen physisorption at 77 K and hydrogen chemisorption at 298 K were carried out in a Micromeritics ASAP 2010 apparatus, , profiles TPD/TPR were obtained in TPD/TPR Micromeritics 2900, TEM micrographs were obtained in JEOL Model JEM -1200 EXII System and XRD in a Rigaku apparatus. FTIR spectra of the samples were recorded on Nicolet 550 FTIR spectrometer at room temperature with 64 scans and a resolution of 4 cm^{-1} on sample wafers consisting of 150 mg dry KBr and about 1.5 mg sample. Photoelectron spectra (XPS) were recorded using an Escalab 200 R spectrometer provided with a hemispherical analyzer, and using non-monochromatic Mg K$_\alpha$ X-ray radiation source.

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 100 mg, 25 ml of a 0.10 M solution of citronellal in n-heptane (Aldrich) and reaction temperature of 343 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 minutes. Prior the experiment, all catalysts were reduced *in situ* under hydrogen flow of 20 cm^{3}min^{-1} at atmospheric pressure and temperature of 343 K. In all reaction internal diffusion limitations were also shown to be absent by applying the Weisz-Prater parameter, which gave a value maximum of 0.19. Blank experiment showed no catalytic activity due to the supports under these conditions. Reaction products were analyzed in a GC Varian 3400 furnished with an HP Wax column of 30 m and 0.53 mm ID. The GC analysis was performed using a flame ionization detector, using *He* as carrier, and the column was kept at a constant temperature of 393 K.

RESULTS AND DISCUSSION

Catalysts Characterization

XRD and IR of absorbed species.

The difractograms of the catalysts reduced at high temperature (HT) are showed in figure 1. No diffraction lines due to iridium is observed which is attributed to the low Ir content (1 wt%). The figure 1a showed the XRD patterns for Ir/SiO$_2$ which corresponds to a solid in amorphous phase. The observed diffraction lines corresponding to 22.5º, 28.5º, 37º and 46º are characteristic of the crystalline niobia (figure 1f).

For the Ir/N1(figure 1b), Ir/N2 (figure 1c), Ir/N3 (figure 1d) and Ir/N4 (figure 1e) catalysts, the XRD patterns correspond to solids with an amorphous phase, indicating that the Nb_2O_5 is highly dispersed on the surface of the silica, suggesting a coverage of patches of monolayer of Nb_2O_5 on the support, as it has been described by Asakura et al. and Schmal et al.[16, 28]. This fact was also verified by studying the IR bands characteristic of the silanols groups in the region close to 3400 cm^{-1}. As can be observed in figure 2, a decrease of this band with the niobia loading is indicative that the surface becomes covered by niobia suggesting a strong interaction of the niobia with the OH$^-$ groups of the silica surface.

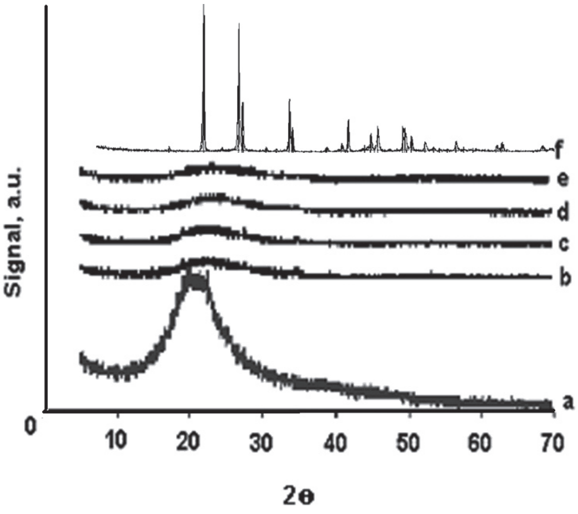

Figure 1: XRD patterns of HT catalysts: (a). Ir/SiO$_2$. (b). Ir/N$_1$ (c).Ir/N$_2$ (d).Ir/N$_3$ (e). Ir/N$_4$ (f). Ir/Nb$_2$O$_5$.

3.1.2 Surface area, H$_2$ chemisorption and TEM.

Table 2 displays the values of Nb_2O_5 content, the specific surface, the atomic H/Ir ratio and the metal particle size obtained by TEM. It is possible to observe that the Ir/SiO$_2$ catalyst possesses the highest surface area (290 m^{2}g^{-1}), close to the area of the support (295 m^{2}g^{-1}). As niobia loading increases a slight decrease in the surface area takes place due to a surface coverage of the support by niobia due to a strong interaction between both oxides. In fact, the catalysts with highest niobia loading (5.3 wt.%) display a decreases in the area close to one third of the starting value. No significant differences occurs is the catalysts are reduced at high or low temperature, indicating that almost no sintering of the niobia species takes place as a consequence of H$_2$ treatment al high temperatures. On the other hand, the niobia posses a low surface area (8.1 m^{2}g^{-1}) in agreement with its high crystallinity and absence of meso and micropores.

Table 2. Theoretical content of Nb_2O_5, the specific surface, the atomic H/Ir ratio and the metal particle size obtained by TEM.

CATALYST	% Nb_2O_5		S_{BET} m^{2}g^{-1}		H/Ir		TEM, nm	
	LT	HT	LT	HT	LT	HT	LT	HT
Ir/SiO$_2$	-	-	290	290	0.038	0.034	4.5	4.7
Ir/N1	1,12	1,12	262	262	0.086	0.034	3.0	3.0
Ir/N2	2,54	2,54	241	238	0.052	0.038	2.8	2.8
Ir/N3	3,25	3,25	216	222	0.016	0.007	2.9	2.9
Ir/N4	5,30	5,30	209	214	0.010	0.008	2.9	2.8
Ir/Nb$_2$O$_5$	99	99	8,1	8,3	0,078	0.031	8.5	8.7

The Ir/SiO$_2$ catalysts shows similar chemisorption values when it is reduced at low or high temperatures, as expected because under this temperature range 473 –773 K, almost not sintering of Ir crystallites can be expected and also due to the inert characteristic of the support. The chemisorption values of Ir/Nb$_2$O$_5$ HT catalyst and Ir/N HT catalysts series are lower compared to the LT counterpart. This behaviour is explained by the SMSI effect. This occurs because niobia is a partially reducible oxide and at high temperature reduction a slight reduction may takes place leading to partially reduced species (Nb$_2$O$_{5-x}$) which can easily migrate over small metal particles. In the series Ir/N HT and LT catalysts, the chemisorption values are similar for those catalysts with lower Nb content, but at niobia loadings >2.54% the chemisorption value decrease for both LT and HT catalysts. This fact is due to at lower niobia content, a strong interaction between OH groups of the support exists which lead to a monolayer strongly bond to the support that cannot be reduced and neither migrate. At higher Nb content, the thickness slightly increases allowing a partial reduction when it is treated at high temperature, leading to a migration of Nb_2O_{5-x} species on the Ir crystallites and therefore a drop in the H/Ir ratio should occurs. The decreases in that ratio can not be attributed to sintering of the metal crystals as TEM results have shown.

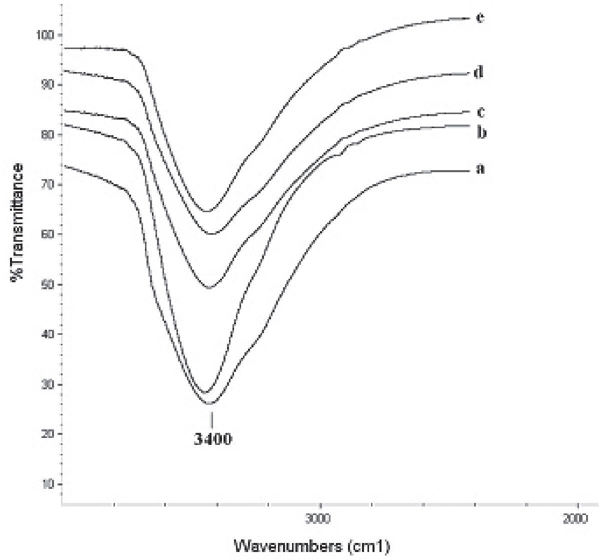

Figure 2: Infrared Spectra of the HT Ir catalysts in the region 2000- 4000 cm^{-1}.(a) Ir/SiO_2 (b)Ir/N1 (c) Ir/N2 (d) Ir/N3 and (e).Ir/N4.

TPR and TPD

Figure 3 shows the TPR profiles of the studied samples in an oxidized state. The temperature programmed reduction of the calcined samples revealed that the reduction of iridium oxide species takes place in two regions, being complete at temperatures lower than 500°C, as can be demonstrated by integration of the H_2 consumption during TPR experiments. The TPR profile of the catalyst supported on niobia apart from the two peaks already described, exhibits a continuous increases in the baseline at temperatures higher than 500°C which can be ascribed to a partial reduction of the support.

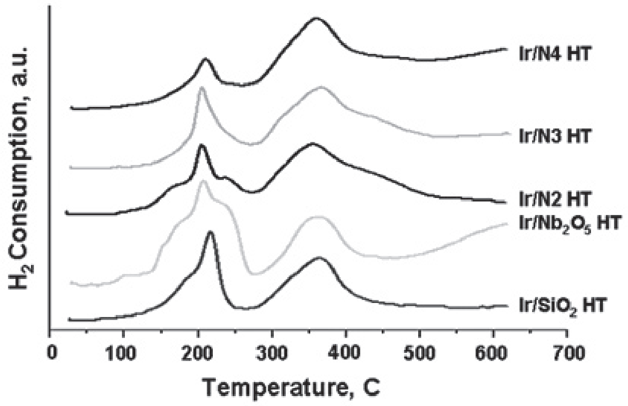

Figure 3: The TPR profiles of the studied samples in an oxidized state.

Figure 4 shows the TPD profiles of the studied samples. Table 3 shows the acidity surface of the studied samples. TPD of ammonia was used to evaluate the surface acidity of the catalysts. The profiles show a small and wide desorption peak in the range 200- 400°C for iridium supported on silica and niobia, whereas in those supported on the mixed Nb_2O_5- SiO_2 oxides a significant enhancement in the evolved ammonia takes place (figure 4). This process occur in the same temperature range and the amount of desorbed ammonia reach a maximum for the catalyst with 2.54 wt % of Nb (Ir/N2), and decreases slightly at higher Nb content. This fact can be explained considering that the acid sites may be attribute to Si-O-Nb sites and, as was described previously, the strong interaction between niobia and silica is reached for a niobia loading of 2.54 wt %, At higher Nb content apart from an increases in the layer thickness and surface coverage, a decreases in the surface area takes place.

Table 3. Surface acidity NH_3 (mmol g^{-1}) of the studied samples..

Catalysts	TPD, NH_3 mmol g^{-1}	
	LT	HT
Ir/SiO_2	71	71
Ir/Nb_2O_5	40	40
Ir/N1	103	109
Ir/N2	340	359
Ir/N3	334	340
Ir/N4	280	309

XPS studies were performed in order to get information dealing with the surface composition and the oxidation state of the iridium species. Table 4 summarizes the binding energy of Ir $4f_{7/2}$ core level and the Nb/Si and Ir/Nb+Si bulk and surface atomic ratios of the studied Ir catalysts. The B.E of Ir $4f_{7/2}$ displays a value of 60.2 eV for the Ir/SiO_2 catalyst and slightly higher BE values for the catalysts supported on niobia or mixed oxides. This behavior can be explained on the basis of the electron metal deficient species, as $Ir^{\delta+}$ generated in the Ir/niobia interphase. On the other hand, the Nb/Si atomic ratios increases almost four times as the Nb loading change from 1.12 to 5.3 wt %, which may indicate that Nb dispersion remains almost constant on the silica surface, which does not agree with previous results (XRD and TPR) and may be understood considering that this techniques allow the analysis of more than one layer thickness and if the patches of niobia deposited on silica are enough thin, they may be detected as being in the surface. The same explanation can be given for the Ir/Si+Nb, in which rather stable atomic ratio were found in both catalysts serie. The fact that the Ir/Si+Nb surface atomic ratio, does not change significantly with Nb loading suggests similar metal dispersion or Ir particle size in line with TEM results.

Table 4. Binding energy of Ir $4f_{7/2}$, Nb/Si and Ir/Nb+Si bulk and surface atomic ratios of Ir/Nb_2O_5-SiO_2 Catalysts.

Catalysts	Binding Energy Ir $4f_{7/2}$ eV	Atomic ratios Nb/Si		Atomic ratios Ir/ Nb/Si	
		Bulk	Surface	Bulk	Surface
Ir/SiO_2 LT	60.2	-	-	0.0032	0.0018
Ir/N1 LT	60.3	0.005	0.007	0.0031	0.0023
Ir/N2 LT	60.4	0.012	0.015	0.0032	0.0022
Ir/N3 LT	60.4	0.015	0.022	0.0032	0.0024
Ir/N4 LT	60.5	0.018	0.030	0.0033	0.0025
Ir/Nb_2O_5 LT	60.4	-	--	0.0741	0.0050
Ir/SiO_2 HT	60.2	-	-	0.0032	0.0014
Ir/N1 HT	60.5	0.005	0.008	0.0031	0.0020
Ir/N2 HT	60.6	0.012	0.017	0.0032	0.0019
Ir/N3 HT	60.6	0.015	0.023	0.0032	0.0021
Ir/N4 HT	60.7	0.018	0.033	0.0033	0.0022
Ir/Nb_2O_5 HT	60.6	-	-	0.0741	0.0045

Catalytic activity

The catalytic activity in the hydrogenation of citronellal on the Ir catalysts were carried out at 343 K and 0.62 MPa and the reaction products were: (-) isopulegol, (+)isopulegol and citronellol. The conversion levels at 5 h of reaction, the initial activity and the activity per site (TOF) at 10 % of conversion over Ir catalysts are showed in the table 5. The evolution of the conversion level showed by all catalysts are displayed in figures 5 and 6 whereas the evolution of the citronellal concentration as function of time for Ir/N4 catalyst is showed in the figure 7 and the selectivity to isopulegol at 20% of conversion is showed in figure 8. The selectivity at isopulegols and citronellol at 20% of conversion is showed in the table 6.

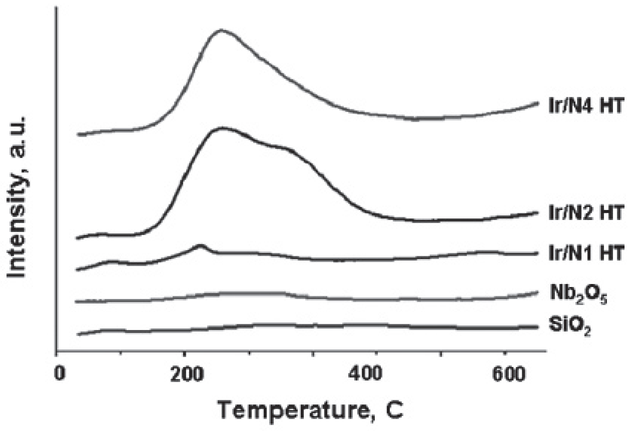

Figure 4: The TPD of ammonia for the Ir catalysts.

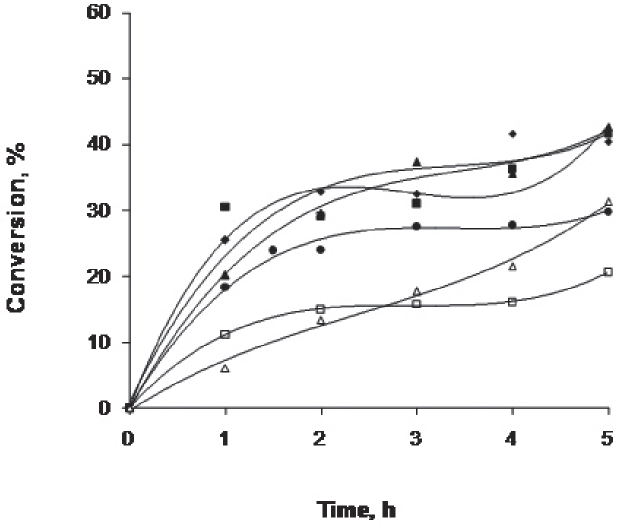

Figure 5: Citronellal hydrogenation at 343 K and 0.62 MPa. Conversion Level in function of time. LTR series. ((●) Ir/SiO_2; (Δ) Ir/Nb_2O_5; (♦) Ir/N1; (■) Ir/N2; (▲) Ir/N3 e (□) Ir/N4.

The Ir/SiO_2 LT and HT catalysts, show similar conversion values, as well as initial activities and TOF. The Ir/SiO_2 LT and Ir/SiO_2 HT catalysts are highly selective to citronellol due C=O bond hydrogenation. This behaviour can be attributed to the low acidity of these samples. the acidity of the Ir/SiO_2 is low and the main product is the formed on metallic sites, that is citronellol (a hydrogenation product).

The conversion of citronellal on Ir/SiO_2 and Ir/Nb_2O_5 catalysts is lower compared with those obtained on Ir supported on mixed oxides catalysts. In mixed oxides catalysts the conversion values increase until Ir/N2 but at niobia loading the conversion decrease for the Ir/N3 and Ir/N4 catalysts suggesting that at niobia loading affect the conversion and activity for a decrease at surface area and a decrease surface acidity. This fact is related with the modification in the surface properties. In those supported on mixed oxides (Ir/Nb_2O_5/SiO_2) which posses much higher surface acidity, such as Ir/N2, the reaction takes place over metallic and acid sites (bifunctional catalysts), changing the product distribution and affecting strongly the catalytic activity.

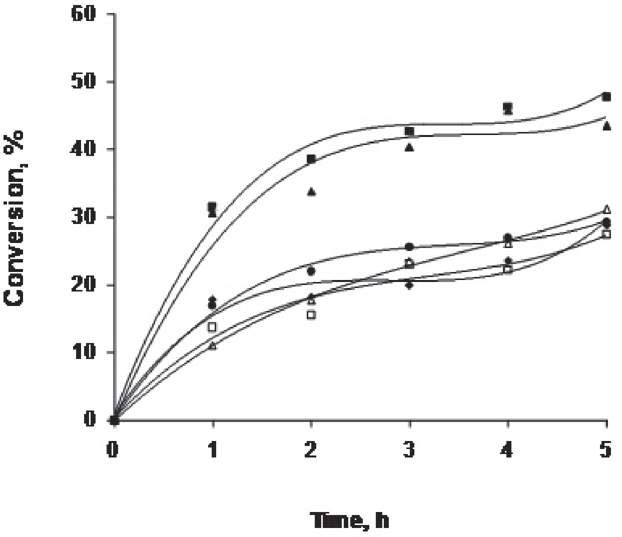

Figure 6: Citronellal hydrogenation at 343 K and 0.62 MPa. Conversion Level in function of time. HTR series. (●) Ir/SiO_2; (Δ) Ir/Nb_2O_5; (♦) Ir/N1; (■) Ir/N2; (▲) Ir/N3 e (□) Ir/N4.

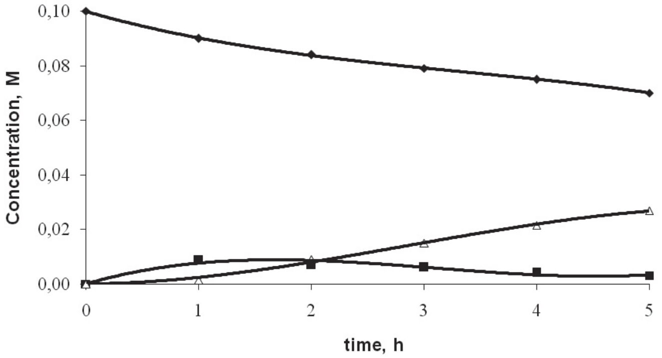

Figure 7: Citronellal hydrogenation at 343 K and 0.62 MPa. Citronellal concentration as a function of time. Ir/N4. (♦) Citronellal. (■) Citronellol. (Δ) Isopulegols.

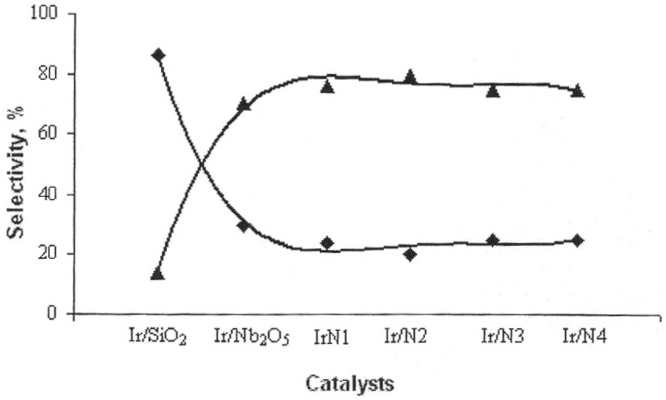

Figure 8: Citronellal hydrogenation at 343 K and 0.62 MPa. Selectivity to isopulegol at 20% of conversion for the Ir catalyst: (▲) Isopulegol; (■) Citronellol.*F*

Table 5. Conversion at 5 h of reaction, initial activity, TOF at conversion 10 %, for the Citronellal hydrogenation at 363 K and 0.62 MPa over Ir supported catalysts.

Catalyst	Conversion, %		Initial Activity (μmol $s^{-1}g^{-1}$)		TOF (s^{-1})	
	LT	HT	LT	HT	LT	HT
Ir/SiO_2	36	32	1.25	1.19	1.032	1.273
Ir/N1	29	35	1.24	1.73	0.278	0.972
Ir/N2	48	45	1.38	1.54	0.519	1.14
Ir/N3	44	43	1.19	1.28	1.481	3.191
Ir/N4	30	31	0.99	1.4	1.852	3.457
Ir/Nb_2O_5	28	34	1.11	1.13	0.562	1.05

Even though differences in the activity in the studied catalyst exist, as can be observed if the conversion level at the same reaction time is compared, the initial activity for the Ir/N LT and HT series does not show significant changes. However, the Ir/N2 catalyst shows a maximum at conversion and surface acidity and a niobia loading for Ir/N3 and Ir/N4 catalysts the conversion and activity decrease, this fact is due probably for a surface area and surface acidity decrease for coverage the niobia over silica. However, the TOF values are increases with Nb loading. The catalysts of the HT series display the highest TOF value compared to the LT counterpart, which may be explained considering that in the former, there are acidic sites provided by the interaction between niobia and silica and Ir sites, which exists in these catalysts as Ir° and $Ir^{\delta+}$, being the Ir crystals partially covered by slightly reduced niobium oxide species. Therefore, the characteristic of the metallic sites is different compared to the LT series which is mainly in a zero valent state, and therefore it should be expected differences in the activity per site values. Due to the surface acidity of LT and HT series are similar; almost no changes in selectivity are expected, in agreement with the obtained results. In a previous study of the hydrogenation of α, β unsaturated aldehydes on Co/TiO_2 catalysts it has also been shown that surface and morphological changes affects significantly both, the activity and the selectivity of the reactions [29]

Table 6. Selectivity at isopulegols and citronellol at 20% of Conversion.

Catalysts	Selectivity, %					
	Citronellol		(+)Isopulegol		(-)Isopulegol	
	LT	HT	LT	HT	LT	HT
Ir/SiO_2	68	63	4	9	30	28
Ir/N1	24	24	23	24	53	52
Ir/N2	24	20	26	28	50	52
Ir/N3	27	25	20	20	53	55
Ir/N4	36	24	24	21	40	55
Ir/Nb_2O_5	20	22	25	20	55	58

The surface acidity of the HT and LT catalysts increases with the addition of niobia due the presence of Si-O-Nb bonds. It is well known that Lewis acid sites are the most active and stereoselectives to isopulegol [25], therefore it should be expected that in these catalysts the selectivity to isopulegols during the citronellal hydrogenation be very high and it can not be neglected that a cyclization of citronellal takes place leading to isopulegol stereoisomers.

CONCLUSIONS

The results have shown that the Ir supported on SiO_2-Nb_2O_5 mixed oxides are bifunctional catalysts. Their acidity depends on the niobia loading and the catalytic activity and selectivity in the hydrogenation of citronellal is highly dependent on the balance between metallic and acid sites. Low surface acidity produces mainly hydrogenation product (citronellol), whereas as the catalyst become more acidic, the formation of isopulegols is favoured.

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REFERENCES

1. J.M Jehng, I.E Wachs. A. Chem. Soc. Miami Beach Meeting, 10–15 September, 546, (1989)
2. K Tanabe. *J. Mol. Catal. A: Chem.* **199**, 3, (2003).
3. D.A.G, Aranda, M. Schmal, *J. Catal.* **171**, 398, (1997).
4. M Ziolek, I. Sobezac, A. Lewandowska, M.Renn, M. Nowa, I.P. Decyk and B. Jankowska. *Catal. Today*. **70**, 169, (2001)
5. M. Ziolek. *Catal. Today*. **78**, 47, (2003)
6. M. Ziolek, A. Lewandowska, M. Renn, I. Nowak, P. Decyk and J. Kujawa. *Stud. Surf.*
7. P. Reyes, H. Rojas, and J.L.G. Fierro. *Appl. Catal. A.*, **248**, 59, (2003)
8. P. Reyes, H. Rojas, H. and J.L.G Fierro. *J. Mol. Catal. A: Chem.* **203**, 203, (2003)
9. P. Reyes and H. Rojas. *React. Kinetic. Catal. Lett.* **88**, 363, (2006)
10. T. Marzialetti, J.L.G . Fierro and P. Reyes. *Catal. Today.* **107-108**, 235, (2005)
11. T. Iizuka, K. Ogasawara, K. Tanabe. *Bull. Chem. Soc. Jpn.* **56**, 2927, (1983)
12. A.C.B. Dos Santos, W.B. Kover and A.C. Faro. *Appl. Catal. A.* **153**, 83, (1997)
13. M. Danot, J.C. Afonso, M. Breysse and T. Courieres. *Catal. Today* **10**, 629, (1991)
14. S. Yoshida, Y. Nishimura, T. Tanaka, H. Kanai and T. Funabiki. *Catal. Today.* **8**, 67, (1990)
15. Y. Iwasawa. 11th Int. Congr. on Catalysis. 101, 21, (1996)
16. K. Asakura and Y. Iwasawa. *J. Phys. Chem*. **95**, 1711, 8, (1991)
17. J.M. Jheng, E.I. Wachs. *Catal. Today*. **8**, 37, (1990)
18. P.A. Burke, E.I. Ko. *J. Catal.* **129**, 38, (1991)
19. C.L. Tavares, V.L.L. Camorim, J.L. Zotin, M.L.R.Duarte and A.C. Faro. *Catal. Today.* **57**, 209, (2000)
20. M. Fuentes, D.L.P.J. Magraner, J.C.R Roque-Malherbe, J.P.Pariente and A. Corma. *Appl. Catal.* **47**, 367, (1989)
21. E.I. Ko, J.M. Hupp and N.J. Wagner. *J. Chem. Soc. Chem. Commun*. **94**, (1983)
22. N. Ravasio, M. Antenori, F. Babudri, M. Gargano. *Stud. Surf. Sci. Catal.* **108**, 625, (1997)
23. D.H. Pybus and C.S. Sell. The Chemistry of Fragrances. ISBN:9780854045280. Springer Verlag. Cambridge, UK. (2004)
24. P.M.Arvela, N. Kumar, V. Nieminen, R. Sjoholm, T. Salmi and D.Y. Murzin. *J. Catal.* **225**, 155, (2004)
25. C. Milone, A. Perri, A. Pistone, G. Neri and S. Calvagno. *Appl. Catal..* **233**, 151, (2002)
26. P.J. Kropp, W. Breton, S.L. Craif, S.D. Crawford, W.F. Durland, J.E. Jones, J.S. Raleigh. *J. Org. Chem.* **60**, 4146, (1995)
27. C. Milone, C.Gangemi, G. Neri, A. Pistone and S. Galvagno. *Appl. Catal. A: Gen.* **199**, 239, (2000)
28. E.B. Pereira, M. M. Pereira, Y.I. Lam, C.A.C. Perez and M. Schmal. *Appl. Catal*. **1997**, 99, (2000)
29. M. C. Aguirre , G. Santori , O. Ferretti, J. L. G. Fierro , P. Reyes, *J. Chil. Chem. Soc.* **51**, 791-799, (2006).