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Crotonaldehyde Hydrogenation on Rh/TiO$_2$ catalysts.
***In situ* DRIFTS studies.**

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ABSTRACT

The surface and catalytic properties in the vapor-phase hydrogenation of crotonaldehyde on Rh/TiO$_2$ has been studied. It was found that a partial reduction of the support produces a surface decoration of the metal component. Thus, interfacial sites are created, which are responsible of an increase in the selectivity to crotyl alcohol, via enhancement of the polarization of the C=O bond. Photoelectron spectra revelead that rhodium is in different oxidation states, with a contribution of ca. 20 % Rhd $^+$ and 80 % Rhº species for LTR catalyst and only a slight increase of Rhd $^+$ for HTR catalyst. TEM studies revelead that Rh has metal particle size close 3 nm with small increases in the catalyst reduced at high temperature. DRIFTS essayed carried out under reaction conditions allowed to identify crotonaldehyde species strongly adsorbed through the C=C bond and weakly coordinated through both the C=C and C=O bonds. After reduction at 723 K an increase in the peak at 1660 cm^{-1} ascribed to an interaction between the carbonyl group and the surface, was observed. This peak seems to be stabilized at interfacial Rh/TiO$_x$ sites The deactivation in crotyl alcohol formation can be ascribed to the generation of strongly chemisorbed asymmetric carboxylate species detected by band at 1740 cm^{-1}. This band grows at expense of crotonaldehyde O s - bonded intermediate chemisorbed on coordinatively unsaturated sites (Lewis acid sites) responsible of the crotyl alcohol obtaintion (detected by a band at 1653 cm^{-1}). Additionally, a small band at 2068 cm^{-1} assigned to CO adsorbed on transition metals, which increases with time on-stream may explain the deactivation of the catalysts in flow systems.

Keywords : Rh/TiO$_2$, crotonaldehyde hydrogenation , DRIFTS

RESUMEN

Se estudiaron las propiedades superficiales y catalíticas en la hidrogenación de crotonaldehído en fase vapor de catalizadores Rh/TiO$_2$. Se encontró que una parcial reducción del soporte, inducida por una reducción a alta temperatura produce una decoración superficial del componente metálico. Los sitios interfaciales creados son los responsables de un incremento en la selectividad hacia el alcohol crotílico a través de un aumento en la polarización del enlace C=O. La espectroscopía fotoelectrónica de rayos X, XPS, reveló que el rodio se encontraba en diferentes estados de oxidación, con una contribución cercana a 20% de especies Rhd $^+$ y 80 % de especies Rhº para catalizadores reducido a a baja temperatura, LTR, y sólo un ligero aumento adicional de la proporción de Rhd $^+$ para catalizadores reducidos a alta temperatura, HTR. Estudios por microscopía electrónica de transmisión,TEM, mostraron que los cristalitos de Rh tenían un tamaño cercano a 3 nm , detectandosé sólo un ligero incremento en el tamaño de cristal en el catalizador HTR. Los estudios mediante DRIFTS se efectuaron en condiciones de reacción y permitieron identificar especies crotonaldehído fuertemente adsorbidas a través del enlace C=C y débilmente coordinada a través de ambos enlaces C=C y C=O. El catalizador reducido a alta temperatura, 723 K, muestró un incremento en la banda a 1660 cm^{-1} atribuído a interacción entre el grupo carbonílico y la superficie. Esta banda parece ser estabilizada en los sitios interfaciales Rh/TiO$_x$ .La desactivación

observada en la hidrogenación del alcohol crotílico puede atribuírse a la generación de especies carboxilato asimétricas fuertemente quimisorbidas, que aparece como una banda a 1740 cm^{-1}. Esta banda crece a expensas del intermediario de crotonaldehído con enlace O s - quimisorbido coordinativamente sobre sitios insaturados (sitios ácidos Lewis) responsables de la formación del alcohol crotílico (detectado por una banda a 1653 cm^{-1}). Adicionalmente, se observa una pequeña banda a 2068 cm^{-1}, la cual es asignada a CO adsorbido sobre metales de transición, la cual crece con el tiempo de reacción, puede explicar la desactivación observada en los catalizadores que operan en reactores de flujo contínuo.

Palabras claves *: R*h/TiO$_2$, crotonaldehído, hidrogenación , DRIFTS.

INTRODUCTION

There is an increased interest in the use of heterogeneous catalysts for the synthesis of fine chemicals. Hydrogenation reactions of a , b unsaturated aldehydes to produce unsaturated alcohol are of great importance in the field of fine chemistry. One kind of reactions lead to two primary reaction products, the saturated aldehyde and the unsaturated alcohol (see Fig. 1). For small molecules, like acrolein and crotonaldehyde the hydrogenation of C=C bond is favored both by kinetics and thermodynamics considerations [1-3], while for larger α ,β - unsaturated aldehydes, steric restrictions imposed by the substituents on the C=C double bond might influence the products selectivity. Therefore, it is desirable to find catalysts, which may control the intramolecular selectivity by preferentially hydrogenation of the C=O group while keeping the olefinic double bond intact (Fig. 1, reaction 1 vs 2). Additionally, in order to prevent consecutive hydrogenation towards the saturated alcohol (reaction 3 and 4) and the isomerization of the allylic alcohol (reaction 5), the catalyst has to suppress these reaction pathways. Different metals and supports have been used to study the selective hydrogenation of these kind of unsaturated compounds.
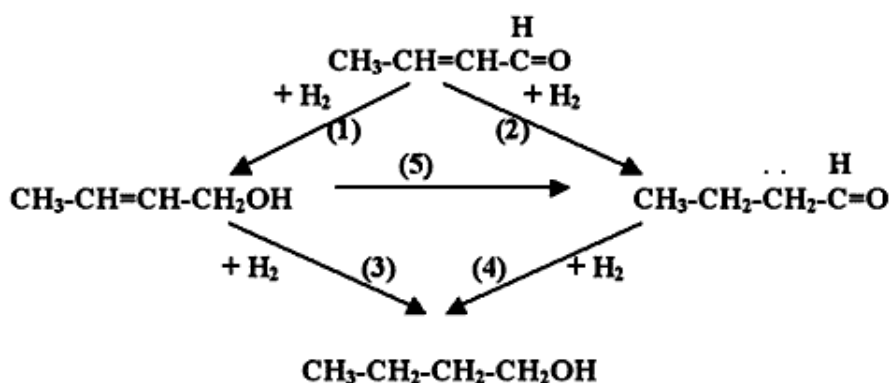

Fig. 1. Reaction network of the hydrogenation of crotonaldehyde.

Catalysts used in this type reaction contain a group VIII hydrogenation component(Pt, Rh, Co, Ru, Ir etc.) showing great differences in activity and selectivity. Catalysts modified by the addition of a second metal have been prepared by different ways: alloying [1,2], by adding promoters [3,4], by using strong interactive support [5-8], by inducing electronic effects and by providing appropriate morphologies to the active sites[9-10]. Eventhough the number of investigations carried out in this field, there is not an agreement in which effect may have a more significant impact on the selectivity towards the unsaturated alcohol, because usually two or more effects are acting simultaneously.

Particularly important seems to be the catalytic behavior exhibited by catalysts supported on reducible oxides, responsible of the strong metal support interaction (SMSI) effect. Vannice et.al [11] have reported significant differences in both activity and selectivity to crotyl alcohol during hydrogenation of crotonaldehyde on Pt supported catalysts. In fact, catalysts in which little or not metal-support interactions should exist, specific activities show similar values. Conversely, Pt/TiO$_2$ catalysts reduced at high temperature, HTR, which exhibit the SMSI effect, show much higher selectivities to the crotyl alcohol. Due to the characteristics of this state, a decrease in H$_2$ chemisorption capacity produced by physical blockage of the metal surface caused by the migration of TiO$_x$ species during the HTR step [12-14]. Besides the differences in activity even more critical is the change in selectivity. Thus, the selectivity to crotyl alcohol increases from zero over Pt/SiO$_2$ and Pt/h -Al$_2$O$_3$ to 37 % over Pt/TiO$_2$. In all of these samples, the metal was highly dispersed. If the reaction is performed on poorly disperse catalysts, the selectivity to the unsaturated alcohol may reach higher values [8,15].

The aim of the present work, is to study the hydrogenation of crotonaldehyde over Rh/TiO$_2$ catalysts, after high and low temperature reduction (LTR and HTR) in order to change the surface decoration. The catalysts have been characterized by nitrogen adsorption at 77 K, H$_2$ chemisorption measurements, TEM studies for particle size evaluation, XPS experiments to estimate surface composition and in situ DRIFTS studies during of adsorbed

crotonaldehyde hydrogenation to add further information dealing with possible reaction intermediates were also performed. Additionally, catalytic hydrogenation of crotonaldehyde was also carried out by pulse method at 373 K.

EXPERIMENTAL

Rh/TiO_2 catalysts were prepared by impregnation of TiO_2 (P25 -DEGUSSA, S_{BET} =72 m^2/g) at 398 K with the appropriate amount of aqueous solution of $RhCl_3$ to get 0.5 wt % of the metal. Then, the samples were dried at 383 K for 24 h and calcined at 673 K for 4 h. Prior to their characterization or catalytic use the solids were reduced in situ in flowing H_2 at 473 K (LTR) or 723 K (HTR) for 2 h. These samples were labelled as Rh/TiO_2 LTR or HTR respectively. To evaluate specific surface area, pore volume and average pore diameter, nitrogen adsorption isotherms at 77 K in the relative pressure range 0.05 to 0.0995 were carried out in a Micromeritics Gemini 2370 apparatus. Hydrogen chemisorption at 298 K was carried out in a volumetric system to evaluate the H_2 uptake and H/Rh ratio. Prior the chemisorption experiments, the samples were reduced in situ at 723 K (HTR) or 473 K (LTR) for 2 h and then outgassed for 4 h at 773 K.

Transmission electron microscopy (TEM) was used for the observation of supported rhodium particles these experiment were performed in JEOL JEM-1200 EX II System. the samples were prepared by the extractive replica procedure. Powder X-ray diffraction (XRD patterns) were performed in a Rigaku diffractometer using a Nickel filtered CuKa radiation.

Diffuse-reflectance infrared spectra, DRIFTS, (256 scans) were collected on a Nicolet-510 FTIR spectrophotometer working at a resolution of 4 cm^{-1} using a Harrick HVC-DRP environmentally-controlled cell. About 50 mg of the powdered sample was packed in a sample holder and different gases were passed through the sample . First of all sample was reduced in 50 mL min^{-1} of pure H_2 at 723 K (HTR) or 473 K (LTR) for 2 h (heating rate 5 K/min). Then, it was cooled down in H_2 a 373 K. Subsequently, He flow was switched to 50 mL.min^{-1} and DRIFT spectrum of sample was recorded as background. All the following recorded spectra were referred to this background. Then, flow is switched to the reaction mixture and DRIFT spectrum of sample under reaction conditions and after different time on-stream was recorded. Reaction mixture was obtained by bubbling H_2 through a saturator containing crotonaldehyde and maintained in an ice bath 273 K. A number of spectra were recorded after different time under reaction conditions. After some time on-stream, reaction mixture was switched again and He flowed through the sample. Several spectra at different time and temperature under He flow were then collected.

Photoelectron spectra (XPS) were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer, operated in a constant pass energy mode and unmonochromatized Mg Ka , X- ray radiation (hn =1253.6 eV), working at 120 watts. The surface Rh/Ti were estimated from the integrated intensities of Rh 3 d $_{5/2}$ and Ti 2 p $_{3/2}$ lines after background subtraction and corrected by the atomic sensitivity factors [16] . The C1s line at 284.9 e V was used as an internal standard . Rhodium were decomposed into several components assuming that the peaks had Gaussian -Lorentzian shapes.

Catalytic experiments were carried out in a pulse reactor with an on line GC. This procedure was chosen because steady-state measurements could not be reached due to the strong catalyst deactivation. This deactivation process has been observed in other catalysts as it has been well documented[17]. In each experiments, 50 mg of catalyst was reduced in situ in flowing of hydrogen (20 mL.min-1) in a programmed mode at 10 K.min^{-1} up to 723 K (HTR) or 573 K (LTR) for 2 h. Then, the sample was cooled down till the reaction temperature. The catalytic activity was measured by injecting 1.0 m L of the organic reactant . Blank experiment showed no catalytic activity due to the support in these conditions.

RESULTS AND DISCUSSION

Table I summarizes the H/Rh atomic ratio and metal particle size obtained from TEM. The H/Rh values are higher for the catalysts reduced at lower temperatures (LTR), which indicates a higher metal exposure and it is not related to changes in metal dispersion. The particle size values of the LTR catalysts are close to those reported previously for Rh/TiO_2 catalysts prepared under comparable conditions [18]. However , TEM analysis revealed only a slight increase in the catalysts reduced at higher temperature. This apparent discrepancy is explained on the basis of the significant decrease in the hydrogen uptake observed in the catalysts reduced at higher temperature (HTR). This fact, first identified by Tauster at al [19] is a distinctive feature of the so called SMSI catalysts. Nowadays, it is well established that the chemisorption suppression after high temperature reduction, is a common feature of all group VIII metals supported catalysts on partial reducible support such as TiO_2. The extent of suppression is usually taken as an indication of the extent of metal-support interaction and described as decoration of metal particles by TiO_x species generated upon reduction process. Obviously, it is expected that this process will occur in a higher extension as temperature increases. The presence of chlorine ions may also produce a slight suppression in the hydrogen uptake. Similar behavior reported previously by Van der Boogert et al [20] and Orita et al[21], responsible of decrease in CO hydrogenation activity on Rh/TiO_2 and it has been ascribed in terms of a chloride-assisted TiO_x migration.

X-ray diffractogram of Degussa P25 TiO_2 used as support, shows the expected lines attributed to rutile and anatase, having approximately 85 % of anatase and 15 % of rutile . This latter is the most stable and the complete transformation anatase to rutile takes place at about 1300 K. However, in the presence of foreign atoms which can catalize this transformation, it may occur at lower temperatures [18,22]. Both rhodium HTR and LTR catalysts shown no changes in crystallinity in agreement with previous findings which have shown that for Rh/TiO_2 a 2 wt % Rh is the minimum required to enhance the anatase to rutile transformation [22].

Table I.H/Rh ratio obtained from chemisorption data, particle size evaluated by chemisorption and TEM, binding energies (eV) of Rh 3 d $_{5/2}$ core level, Rh/Ti atomic ratios evaluated from XPS for 0.5wt % Rh/TiO_2 catalysts.

Catalysts	H/Rh	d,nm		Rh $3d_{5/2}$B.E(eV)	(Rh/Ti)s
		Chem	TEM		
Rh/TiO_2-HTR	0.10	9.0	3.0	307.1 (78) 308.8 (22)	0.010
Rh/TiO_2-LTR	0.49	1.8	2.8	307.3 (80) 308.8 (20)	0.012

The chemical state of rhodium for both catalysts has been studied by XPS. Fig. 2 displays Rh 3d core level for Rh/TiO_2 catalysts. Table I also gives the Rh/Ti surface ratio obtained from XPS. The B.E of the Rh $3d_{5/2}$ peak are ca. 307.2 and 308.7 by Rhº and Rh δ $^+$, respectively. For the reduced samples the XP spectra of Rh 3d core levels showed the 3d doublet having a broadening indicative of Rh in different oxidation states. After curves deconvolution, a contribution of approximately 80 and 20 % of Rhº and Rhδ $^+$ species respectively were found. Only a slight increase in the extent of Rhd $^+$ species were found in those catalysts reduced at higher temperatures (HTR). At low temperatures, the small metal particles are in intimate contact with the TiO_2 being possible to produce electronic transfer between the support and the metal, generating Mδ $^+$ species. These species seems to be responsible in the increase in selectivity to crotyl alcohol discussed below, due to an enhancement in the polarization of the carbonyl group.

Fig. 2. XP spectra by reduced Rh/TiO_2 catalysts , Rh 3d core level .
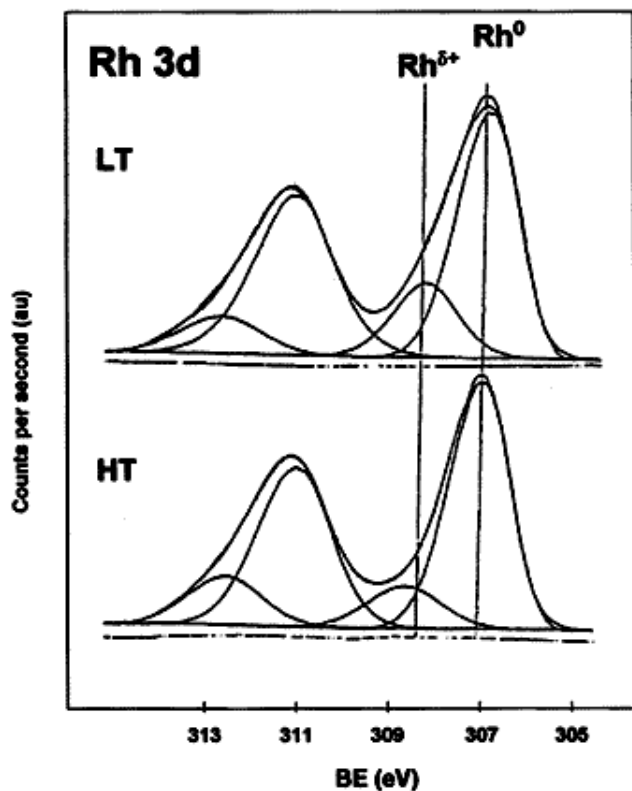
Hydrogenation crotonaldehyde was carried out in a pulse reactor at 373 K. This procedure is extremely useful in reaction in which deactivation takes place, avoiding interference due to the deactivation process. The obtained products were mainly crotyl alcohol (CROL), butyraldehyde (BUHO), butylalcohol (BUOH), CO and products of hydrogenolysis and polymerization. Table II summarizes the activity and selectivity of the Rh/TiO$_2$ catalysts. It can be seen that the activity, expressed as m mole converted per second per gram of catalyst, in LTR catalyst was approximately half of that observed for the HTR counterpart. Selectivity to different products expressed, as % does not change significantely. Converserly, activity per site, TOF, displays values 10 times higher for the catalyst reduced at high temperature (values between brackets in table II). This behavior may be understood considering that, in spite of a low extent of metal surface is exposed to the reactant molecules, Rh/TiO$_x$ interfacial sites having improved characteristic are involved. As Vannice has pointed out[23], the creation of the new active sites in the interfacial region may explain not only the change in activity, but also the change in selectivity. In fact, these sites, which implies partially reduced TiO$_x$ species (or oxygen vacancies) decorating Rh crystallites, can coordinate the oxygen atom in the C=O group to account a more selective activation of these organic molecule[8,23]. Further support to this theory is supplied by the DRIFT experiments showed below. Only small changes in selectivity (mole %) were observed. However, considering that the activity, expressed as m mole of crotonaldehyde converted per second per gram of catalysts, exhibit by HTR catalyst is almost twice to that of LTR state, the yield to CROL is larger in the former state. This indicates that a higher proportion of sites for selective hydrogenation of C=O bond are present at HTR state. Eventhough the selectivity towards crotyl alcohol is low -close to 10 %- it is considerable better than Rh metal catalysts supported on non-SMSI catalysts for which the selectivity to the unsaturated alcohol is almost zero. In all rhodium catalysts, the saturated aldehyde is the main product (selectivity higher than 50 %) indicating that the reaction path 2 in fig.1 is more favorable.

Table II. Catalytic activity (m mole/s gcat) and TOF (S-1) at 373 K and selectivity (mole%) in brackets as (m mole/s gcat) to products in crotonaldehyde hydrogenation.

Catalysts	Activity μ mole/s gcat	TOF s^{-1}	Selectivity,mole% (umole/s gcat)		
			CROL	BUOH	BUHO
Rh/TiO$_2$-HTR	6.0	1.24	10(0.60)	70(4.20)	20(1.20)
Rh/TiO$_2$-LTR	3.1	0.13	12(0.37)	54 (1.67)	34 (1.05)

, shows the DRIFT spectra obtained under reaction and after switching to He flow by Rh/TiO$_2$-HTR. , displays the result of subtracting the DRIFT spectrum of the sample after 5 min under reaction mixture to the spectra of sample after more than 5 min on-stream. This figure is very helpful in order to see new intermittent bands under reaction mixture. At the C-H stretching vibration region, bands at 2959, 2930, 2876, 2718, 1695, 1653, 1541, 1458 and 1400 cm^{-1} were clearly visible. The 2718 cm^{-1} bands is assigned to n (C-H) of aldehydic group, which suggests that adsorbate containing aldehyde functional group is present at the surface of the catalysts. They can not be assigned neither to reaction intermediate at the catalysts surface nor to reaction product at the gas phase since bands intensity remains when reaction mixture is swichted to He flow. They must arise from side-products or spectators of the reaction which are strongly chemisorbed at the catalyst surface (their intensity is not much altered after flowing He at 473 K). Actually, their concentration at the catalyst surface increase with time on-stream. This means that the surface is progressively covered by such compounds. The 2805 cm^{-1} bands can also be assigned to C-H aldehydic groups [24].
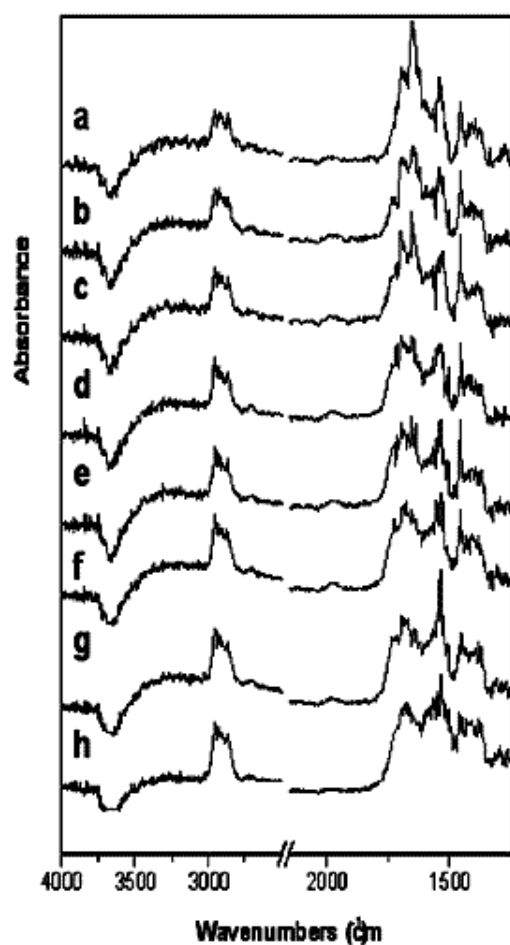

Fig. 3. DRIFT spectra of Rh/TiO$_2$ HT during crotonaldehyde hydrogenation at 373 K after 5 min on stream. b) 15 min. c) 30 min. d) 60 min. e) 90min. f) after 15 min under helium flow at 373 K. g) 30 min under helium flow at 373 K. h) after 15 min under helium flow at 473 k.
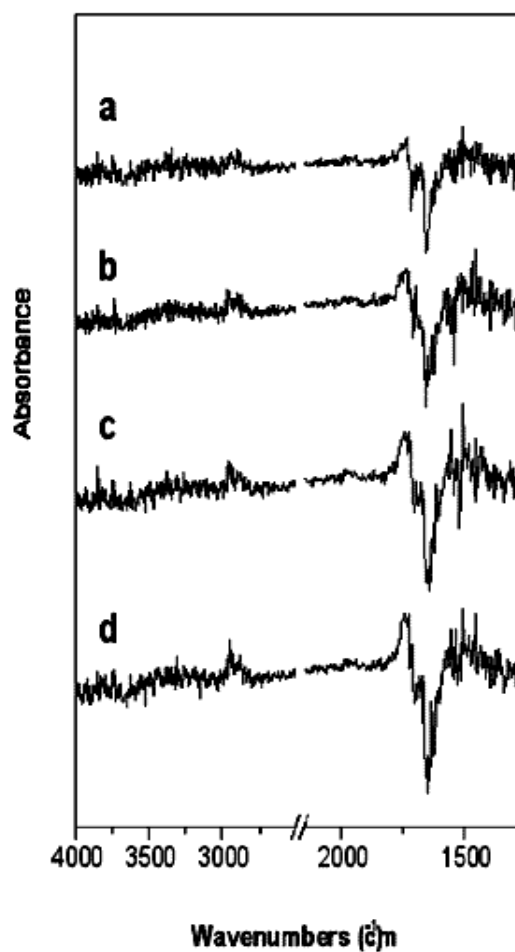
Fig. 4. DRIFT spectra of Rh/TiO$_2$ HT during crotonaldehyde hydrogenation at 373 K after subtraction of 5 min on stream spectrum to a) 15 min, b) 30 min, 60min, d) 90min.

CO displacement by adsorption of products on the Rh particles was also evidenced by feature at 1977 cm^{-1} band. Among the more remarkable complexes detected by the DRIFT spectra are: O s bonded aldehyde to cationic sites (1653 cm^{-1}), carbonyl group interacting with OH forming asymmetric and symmetric carboxylates (1541 and 1458 cm^{-1}). The strong band at 1653 cm^{-1} is believed to arise from crotonaldehyde O s -bonded to coordinatively unsaturated metal cations in metal oxide surfaces. The s complex is formed between the unshared electron pair on the antibonding n(s) orbital localized on the oxygen atom of the carbonyl group and the metal cation[25] . This adsorption mode has also been described a donating -on-top h $_1$ adsorbed species[26, 27] . Such interaction results in a 50-70 cm^{-1} red shift of ν (C=O) frequency with respect to gas phase crotonaldehyde. This band has been observed in crotonaldehyde interacting with Ni/TiO$_2$ and Pt/TiO$_2$ reduced at high temperature [11]. TiOx moities covering the metal particles and originated while reduction at high temperature supplies the cationic metal sites

for the s bond. The same phenomenon was also observed for the other α,β unsaturated aldehydes contacting Co/SiO$_2$ [28]. Cationic cobalt species, remaining due to an incomplete reduction of Co oxide supplies the Lewis acid sites for the C=O donating-on -top η_1 crotonaldehyde adsorption. Figure 4, shows that as the catalysts is under reaction conditions, the 1653 cm^{-1} band is weakened as a band at 1740 cm^{-1}, no clearly visible in figure 3 develops. This effect, explained by the formation of asymmetric carboxylate at expenses of the active intermediate (O -σ bonded aldehyde). Several authors have reported similar results: The O -σ bonded of carbonyl group is transformed to an asymmetric surface carboxylate complex when heated or increasing the aldehyde-metal oxide surface contact time[25, 29]. Therefore, it can be proposed that the drops in the yield to crotyl alcohol must be related with the transformation of the active intermediate into inactive and strongly chemisorbed surface asymmetric carboxylate spectator, while catalysts is under reaction conditions. When reaction mixture flow swichted to He flow, after 5min of inert gas flush, the band at 1653 cm^{-1} has almost disappeared which demonstrates that this adsorbate is only present when crotonaldehyde is flowing. This fact gives additional support to the assumption that the s complex is an intermediate of crotyl alcohol formation.

The band at 1720 cm^{-1} is in the region of carbonyl frequency, which indicates that it arises from a carbonyl group containing compound. It is strongly adsorbed at the surface because it also remains adsorbed after He flow at 474 K. A band 1725 cm^{-1} was detected by Trifiro at al [30] after adsorbing acrolein on silica at high temperatures and they suggest that it arises from acrolein oligomerization leading to polymeric acrolein. It is reasonable that the carbonyl group are weakly affected by the surface and the vibration frequency is close to 1720 cm^{-1}, frequency at which C=O group of gas phase acrolein vibrates. Falconer et al.[31] showed that acetaldehyde undergoes aldol condensation on TiO$_2$ producing crotonaldehyde which again oligomerizes leading to heavier products containing carbonyl group with conjugated C=C bonds only removable by H$_2$ reduction or oxidation and higher temperatures. Crotonaldehyde can undergoes similar aldol condensation and oligomerization processes on the Rh/TiO$_2$ surface catalysts, leaving heavy residues containing C=O and C=C functional groups on the catalysts surface, which must be taken into account also as a source of deactivation.

The 1545 and 1454 cm^{-1} bands can be ascribed to carboxylate (crotonoates or butanoates) complexes ($\nu_{asym.}$ and n$_{sym.}$ of CO$_2^-$ carboxylate group)[25,29,32]. They are definitively different in nature to the species described above as asymmetric carboxylate complexes even if they are related with the metal oxide support: The former are bonded to metal cations to lattice oxygen. However, it must be taken into account that symmetric carboxylates have been shown to arise from the conversion of asymmetric carboxylates complexes[25,29]. It has been suggested that symmetric complexes are related with the lack of crotyl alcohol formation while on-stream [28], but since the observed weakening of the 1653 cm^{-1} band is not related with any change in the n$_{as}$ and n$_s$ of CO$_2^-$ carboxylate group frequencies such involvement can be discarded. Other features suggest a non involvement of the symmetric carboxylate complexes in the reaction, such as: i) their intensities do not change significantly with time on stream and ii) these species are strongly chemisorbed to surface and they remain on He flow and even after heating under He at 473 K, the intensities are maintained.

Spectra features in figure 5. DRIFT spectrum by Rh/TiO$_2$-LTR after 5 min on-stream (bands at 2950 , 2932, 2882, 2802, 2706, 1722, 1656, 1535, 1464, 1381 and 1255 cm^{-1}) can also be discussed according to the assignation already presented for previous spectra. It is noteworthy that 1535 and 1464 cm^{-1}, ascribable to symmetric carboxylate complexes are rather weak as compared with the intensity in HTR Rh catalyst. The 1656 cm^{-1} band (O σ bonded to cationic sites) is quite weak after 5 min on-stream. Considering that it has been proposed to be the intermediate of the crotyl alcohol formation, its low intensity explains the lower yield to crotyl alcohol of these catalysts. The removal of CO adsorbed on Rh particles by new crotonaldehdye derived adsorbates explains the negative peaks at 2056 cm^{-1} and positive peak at 2006 cm^{-1}. A new peak at ca. 1800 cm^{-1} never seen in previous experiments, are due to bridged CO chemisorbed on Rh particles [33]. It is unlikely that it comes from displacement of initially adsorbed CO. It is reasonable to assign this band to the decarbonylation of crotonaldehydewhich supplies additional CO that ends up chemisorbed on Rh-TiO$_x$ patches. The more remarkable changes in the spectra when catalyst is maintained under reaction stream is that the intensity of the bands at 1722 and 1656 cm^{-1} decrease significantly. After switching to He flow the band at 1690 cm^{-1} dominate in ν (C=O) frequency region, whereas the 1722 cm^{-1} band significantly faded and 1653 cm^{-1} peak vanished.
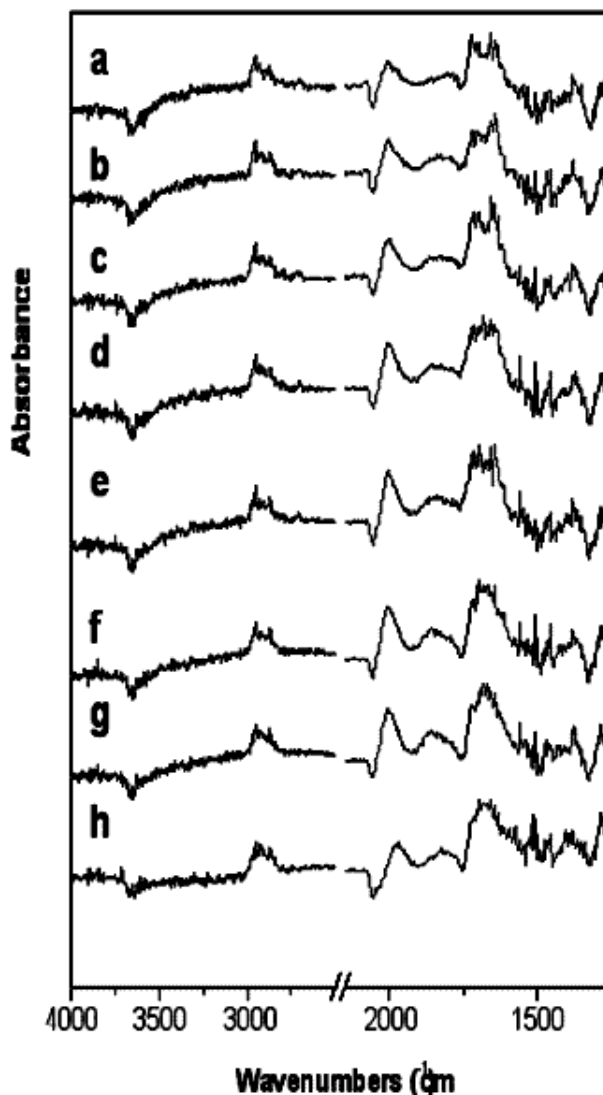
Fig. 5. DRIFT spectra of Rh/TiO$_2$ LT during crotonaldehyde hydrogenation at 373 K after 5min on stream , b) 15 min, c) 30 min , d) 60 min , e) 90 min , f) after 15 min under helium flow at 373 K, g) 30 min under helium flow at K , h) after 15 min under helium flow at 473 K.

CONCLUSIONS

A kinetic and DRIFTS study of crotonaldehyde hydrogenation was carried out over Rh/TiO$_2$ catalysts. The influence of the reduction temperature on the surface and catalytic properties was also analyzed. It was found that partial reduction of the support produce a surface decoration of the metal component, generating interfacial sites responsible of an increase in the selectivity to crotyl alcohol, allowing an enhancement in the polarization of the C=O bond as a result of surface decoration of the metal component. The presence of chlorine ions in the metal-support interfacial region also allows, in a certain extension, a polarization of the carbonyl bond. DRIFT studies carried out under reaction condition allowed to identify an adsorbed species responsible to the obtaintion of crotyl alcohol. This characteristic band appears at 1653 cm^{-1} and it is ascribed to an interaction between the carbonyl group and the surface, which is likely to be, stabilized at interfacial Rh/TiO$_2$ sites. Additionally, a small band at 2068 cm^{-1} assigned to a CO adsorbed on transition metals, which increase with time on stream may also explain the deactivation of the catalysts in flow systems.

ACKNOWLEDGMENTS

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