



Citral hydrogenation over Rh and Pt catalysts supported on TiO₂: Influence of the preparation and activation protocols of the catalysts

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ABSTRACT

During citral hydrogenation, the products distribution obtained on Rh/TiO₂ and Pt/TiO₂ catalysts depends on their preparation and activation protocols: (i) the unsaturated alcohols (the intended products) are formed in higher quantity on samples reduced at 500 °C and more notably with Pt/TiO₂ catalyst; (ii) samples prepared by impregnation of the metallic precursor salt in HCl medium and activated at 300 °C are the only ones to lead to the formation of isopulegol as by-product. On the catalysts activated at 500 °C, these results can be explained by the presence of the SMSI effect beneficial to hydrogenate selectively the C=O bond of citral towards unsaturated alcohols.

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1. Introduction

Selective hydrogenation of organic substrates containing several unsaturated functional group is an important step in the preparation of various fine chemical products [1–3]. Particularly, the preparation of unsaturated alcohols by selective hydrogenation of the corresponding α , β -unsaturated aldehydes has a great industrial importance and constitutes a challenging task, since the hydrogenation of the C=C bond is thermodynamically favoured over the hydrogenation of the carbonyl group. In the present work, the liquid-phase hydrogenation of citral (3,7-dimethyl-2,6-octadienal) was studied, this molecule and its unsaturated alcohols being of considerable interest in the perfumery industry [4,5]. Citral is an α , β -unsaturated aldehyde including conjugated C=O and C=C bonds as well as an isolated C=C bond [6]. Heterogeneous catalysts for the hydrogenation of α , β -unsaturated aldehydes are mostly based on supported noble metals (Pt, Ru, Rh, Pd) [6–18]. In the case of these metals are deposited on reducible support as TiO₂, the hydrogenation of the carbonyl bond can be promoted due to the presence of partially reduced species generated upon reduc-

tion at high temperature (i.e. “strong metal-support interaction” or SMSI effect) [19]. In the present paper, we examine the influence of the preparation and activation protocols (nature of the impregnation medium of the precursor salt and reduction temperature) of Rh/TiO₂ and Pt/TiO₂ catalysts on their performances for selective hydrogenation of citral towards unsaturated alcohols.

2. Experimental

2.1. Catalyst preparation

The TiO₂ support (Degussa P25, surface area = 50 m² g⁻¹) was ground and then sieved to retain particles with sizes between 0.10 and 0.04 mm. After calcination of the support in flowing air for 4 h at 500 °C, 1.0 wt%Rh_{NH₃}/TiO₂, 1.0 wt%Rh_{HCl}/TiO₂ and 1.0 wt%Pt_{HCl}/TiO₂ monometallic catalysts were prepared by impregnation using a limpid aqueous solution of RhCl₃ and H₂PtCl₆, respectively, in the presence of either HCl (pH 1) or NH₃ (pH 11) medium. Catalysts were dried at 120 °C overnight, followed by a calcination in flowing air for 4 h at 300 °C for Rh samples and 400 °C for Pt ones, then reduced in flowing pure hydrogen at 300 °C or 500 °C. After preparation, the chlorine content on each catalyst was determined by means of potentiometry at the “Service central d’analyse” of the CNRS.

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Table 1
Characteristics of the 1.0 wt%Rh/TiO₂ and 1.0 wt%Pt/TiO₂ monometallic catalysts.

Catalyst/TiO ₂	Impregnation medium	T _{reduction} (°C)	Cl (wt%)	Average particle size (nm)
Rh _{NH₃} (300)	NH ₃	300	0.5	2.3
Rh _{NH₃} (500)	NH ₃	500	≤0.2	2.3
Rh _{HCl} (300)	HCl	300	0.8	2.3
Rh _{HCl} (500)	HCl	500	≤0.2	2.2
Pt _{HCl} (300)	HCl	300	0.5	1.9
Pt _{HCl} (500)	HCl	500	≤0.2	2.0

2.2. Transmission electron microscopy (TEM)

TEM analysis was performed on a Philips CM 120 instrument operating at 120 kV. Samples were embedded in a polymeric resin and cut into a section as small as 40 nm with an ultramicrotome fitted with a diamond knife. Cuts were then deposited on an Al grid previously covered with a thin layer of carbon. Average particle sizes were determined by measuring at least hundred particles for each sample analyzed, from at least five different micrographs.

2.3. Temperature-programmed reduction (TPR)

TPR experiments were aimed to investigate the H₂ consumption during the reduction of the Rh/TiO₂ and Pt/TiO₂ monometallic catalysts. They were done with a 1.0 vol%H₂/Ar gas mixture. The temperature range was 25–500 °C with a ramp of 5 °C min⁻¹ and then maintained at 500 °C for 1 h. The hydrogen uptake was monitored by a thermal conductivity detector.

2.4. Citral hydrogenation

The citral hydrogenation was performed in liquid phase in a 300 mL stirred autoclave (Autoclave Engineers, fitted with a system for liquid sampling), at 70 °C and at constant pressure of 7 MPa. Prereduced catalysts (400 mg) were immersed into 90 mL of solvent (isopropanol, 99%) without exposure to air before introduction into the autoclave. After a first flush with nitrogen and a second with hydrogen, the temperature was raised to 70 °C under 3 MPa of hydrogen. Then, a mixture of substrate (3 mL of citral, i.e. 17.6 mmol) and of isopropanol (10 mL) was loaded into the autoclave through a cylinder under a 7 MPa hydrogen pressure. Zero time was taken at this moment and stirring was switched on. Liquid samples were analyzed by gas chromatography on a Thermofinnigan chromatograph equipped with a flame ionization detector and a capillary column DB-WAX (J&W, 30 m, 0.53 mm i.d.) using nitrogen as carrier gas. Preliminary runs carried out at different stirring conditions, loadings and catalyst grain sizes have demonstrated the absence of external and internal diffusional limitations.

3. Results and discussion

3.1. Characterizations of the Rh/TiO₂ and Pt/TiO₂ catalysts

The prepared catalysts and their characteristics are listed in Table 1 with their code name, depending on their impregnation medium (HCl or NH₃) and their reduction temperature (300 °C or 500 °C). For each catalyst, TEM image analysis reveals small and well-dispersed particles on the TiO₂ surface and a narrow particle size distribution. Examples of characteristic TEM images are given in Fig. 1 for Pt_{HCl}/TiO₂ catalyst. TEM results in Table 1 indicate that the average particle size of the Rh/TiO₂ samples is independent of the impregnation medium since all the Rh-based catalysts present particle size around 2.2–2.3 nm. Moreover, whatever the monometallic catalyst, the reduction temperature (300 °C

or 500 °C) has no effect on the particle size distribution and then on the mean particle size (Table 1).

Rh_{NH₃}/TiO₂ and Pt_{HCl}/TiO₂ monometallic catalysts were characterized by TPR after being pretreated *in situ* under oxygen for 30 min at 300 °C or 400 °C, respectively, and cooled down to room temperature. The TPR profiles (Fig. 2) show that the reduction of oxidized rhodium and platinum starts from the ambient temperature. For the 1.0 wt%Rh_{NH₃}/TiO₂ catalyst, the main H₂ consumption is located around 100 °C, followed by a broader and smaller peak from 200 °C to 500 °C. For the 1.0 wt%Pt_{HCl}/TiO₂ catalyst, the main peak presents a maximum below 100 °C and a second larger peak appears from 250 °C to 500 °C. Previous results obtained on Rh/Al₂O₃ and Pt/Al₂O₃ catalysts showed that the rhodium and platinum oxides are generally reduced before 250–300 °C [20]. Thus the H₂ consumption obtained at higher temperature for our samples can be attributed to the partial reduction of the TiO₂ support, i.e. the SMSI effect which induces TiO_{2-x} species (x < 2). Indeed, the total hydrogen consumptions deduced from the TPR profiles are 189 μmol g_{catalyst}⁻¹ for 1.0 wt%Rh/TiO₂ and 171 μmol g_{catalyst}⁻¹ for 1.0 wt%Pt/TiO₂, whereas the theoretical values for the reduction of Rh₂O₃ and PtO₂ are 146 and 102 μmol g_{catalyst}⁻¹, respectively. The vertical dotted lines in Fig. 2 indicate when the H₂ consumptions reach these theoretical values. If we admit that all the Rh and Pt atoms are reduced before the support, the indexed temperature would then correspond to the beginning of the partial reduction of TiO₂.

3.2. Citral hydrogenation over Rh/TiO₂ and Pt/TiO₂ catalysts

Fig. 3 presents the main reaction pathways that occur during citral hydrogenation. The reduction of citral can lead to a variety of products. A first step is the reduction of either the C=O or the conjugated C=C bond to produce geraniol and nerol (unsaturated alcohols) or citronellal, respectively. Consecutive hydrogenation leads to citronellol and finally to 3,7-dimethyl octanol. Beside these reactions, processes of cyclization or of reaction with the solvent (alcohol) can lead to other by-products like isopulegol or acetals, respectively.

3.2.1. Influence of the impregnation method of monometallic Rh/TiO₂ catalyst

The hydrogenating properties of Rh_{HCl}/TiO₂ and Rh_{NH₃}/TiO₂ catalysts prepared by impregnation of the rhodium salt on the support, either in HCl (pH 1) or NH₃ (pH 11) medium, and both activated at 300 °C were compared. Fig. 4 presents the temporal concentration profile of the reactant and the main products during citral hydrogenation on these catalysts.

Citronellal is the main product formed over the Rh_{NH₃}/TiO₂ catalyst under our experimental conditions. The formation of citronellol and 3,7-dimethyloctanol (listed as “others products”) is also observed at longer reaction times. The formation of the intended products (i.e. the unsaturated alcohols) remains rather low indicating that the C=C/C=O adsorption competition of the citral molecules is mainly in favor of the C=C bond on this catalyst. On Rh_{HCl} catalyst, citronellal is rapidly formed and then for the biggest part converted into isopulegol. It becomes the main product on this sample, reaching 50 mol%, whereas it was not detected on Rh_{NH₃} catalyst. Once citral is totally converted, isopulegol is then hydrogenated into menthol (listed as “others products”).

The different reaction pathways observed on these two catalysts presenting the same particle size are bound to be due to their preparation procedure, i.e. their impregnation medium. In fact, isopulegol is a by-product of citral hydrogenation resulting from the isomerisation of citronellal in protonic medium [21,22] and generally favoured in hydrophobic solvents [23,24]. Then, Rh_{HCl}/TiO₂ catalyst prepared in HCl medium possesses acid sites

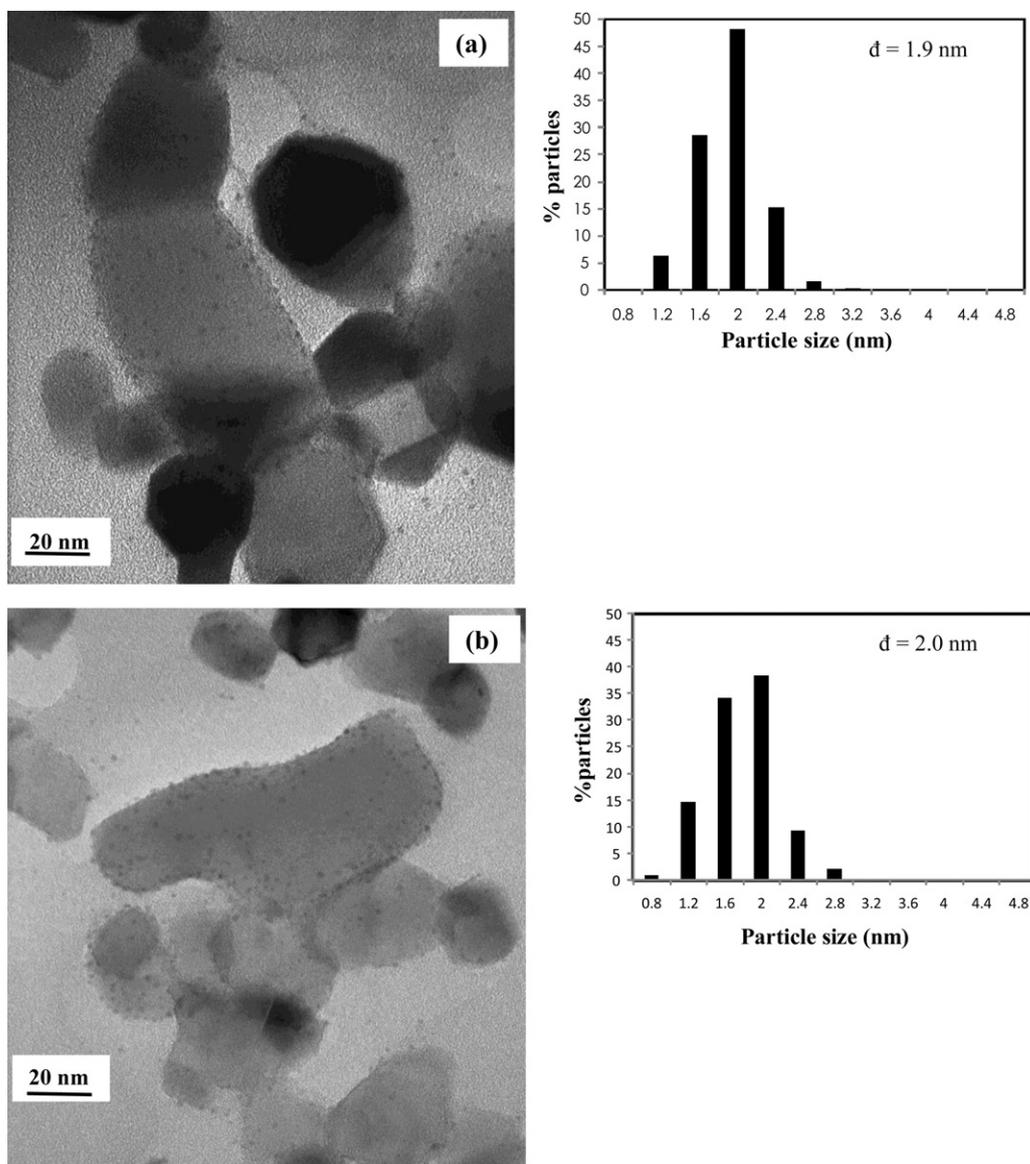


Fig. 1. TEM images and metal particle size distributions of 1.0 wt%Pt_{HCl}/TiO₂ catalyst reduced at (a) 300 °C and (b) 500 °C.

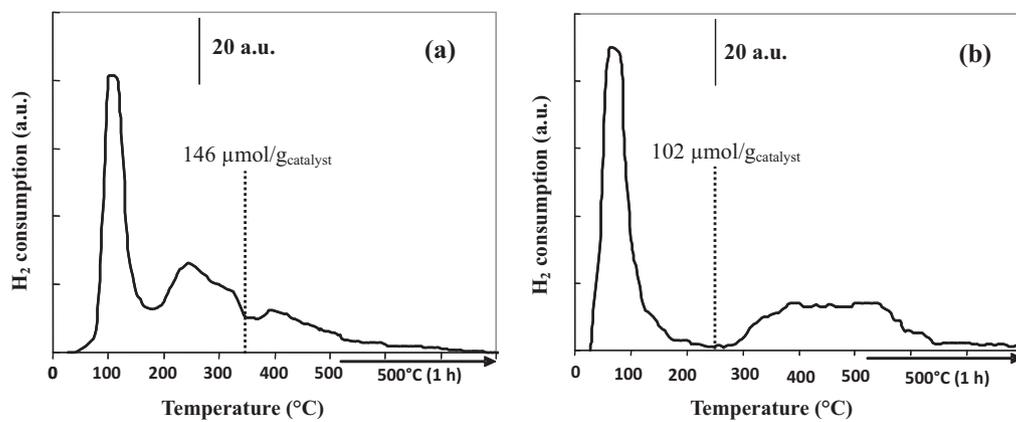


Fig. 2. TPR profiles of (a) 1.0 wt%RhNH₃/TiO₂ and (b) 1.0 wt%Pt_{HCl}/TiO₂ catalysts.

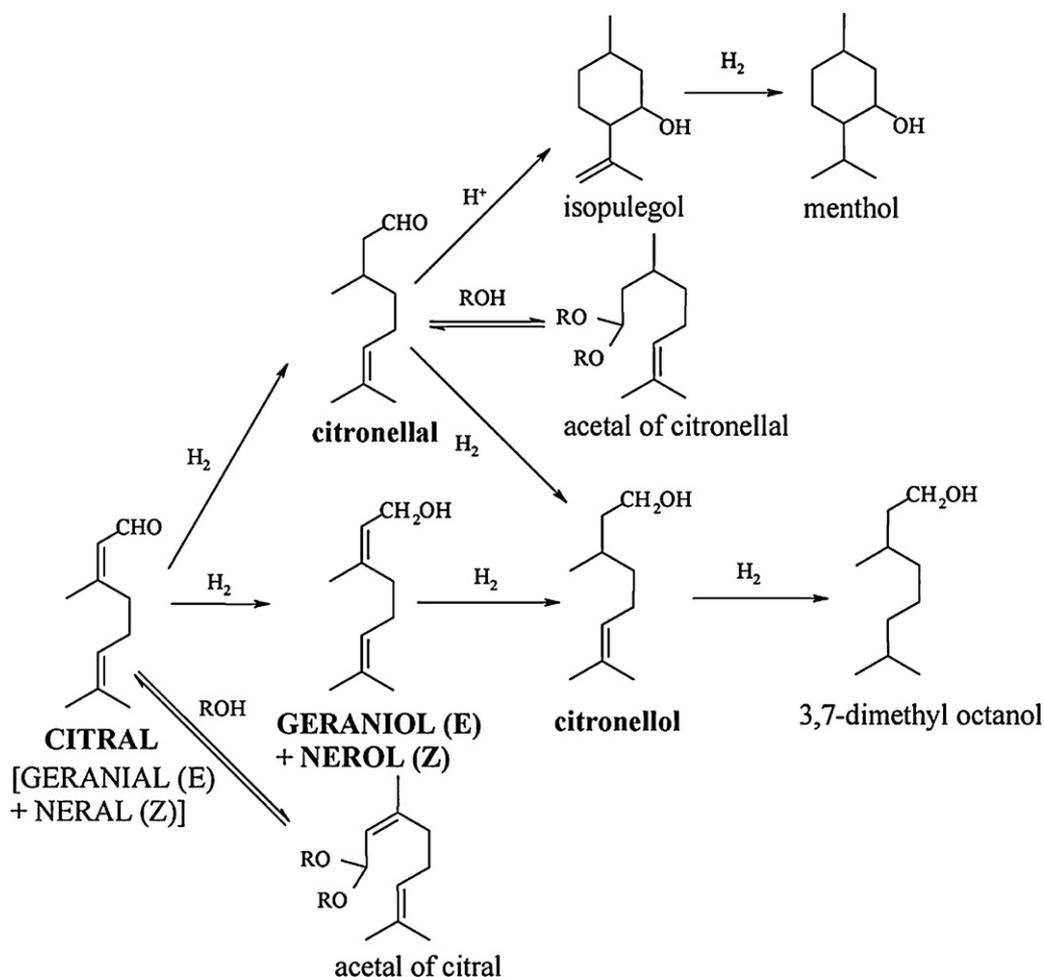


Fig. 3. Reaction scheme for citral hydrogenation.

necessary for the isopulegol formation. Conversely, the impregnation of $RhCl_3$ salt in NH_3 medium followed by a reduction at $300^\circ C$ allows one to synthesize Rh/TiO_2 catalyst without such acid sites. Previous studies have reported that the acidity was induced by the presence of remaining chlorine on the catalyst surface [23]. In fact, by inductive effect, the presence of chlorine ions allows decreasing the electronic density of the metal particles and its close vicinity, and consequently increasing the acidic character of the catalyst.

This is consistent with the fact that Rh_{HCl}/TiO_2 catalyst leads to isopulegol since it presents higher chlorine content than Rh_{NH_3}/TiO_2 after reduction at $300^\circ C$ (Table 1).

3.2.2. Influence of the reduction temperature of monometallic Rh/TiO_2 catalysts

The results stated above showed that both Rh_{HCl}/TiO_2 and Rh_{NH_3}/TiO_2 monometallic catalysts after reduction at $300^\circ C$ pos-

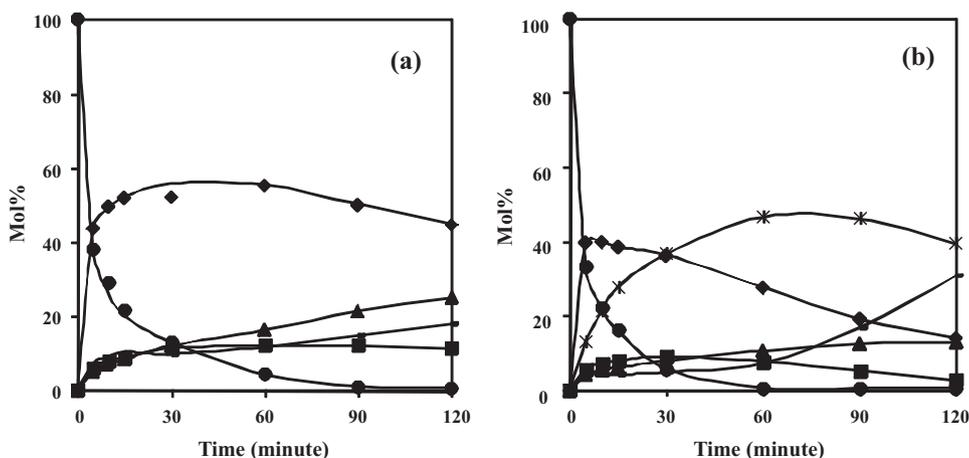


Fig. 4. Citral hydrogenation on 1.0 wt% Rh/TiO_2 catalysts reduced at $300^\circ C$ prepared in (a) NH_3 and (b) HCl medium: (●) citral; (◆) citronellal; (▲) citronellol; (■) unsaturated alcohols; (*) isopulegol; and (—) others products.

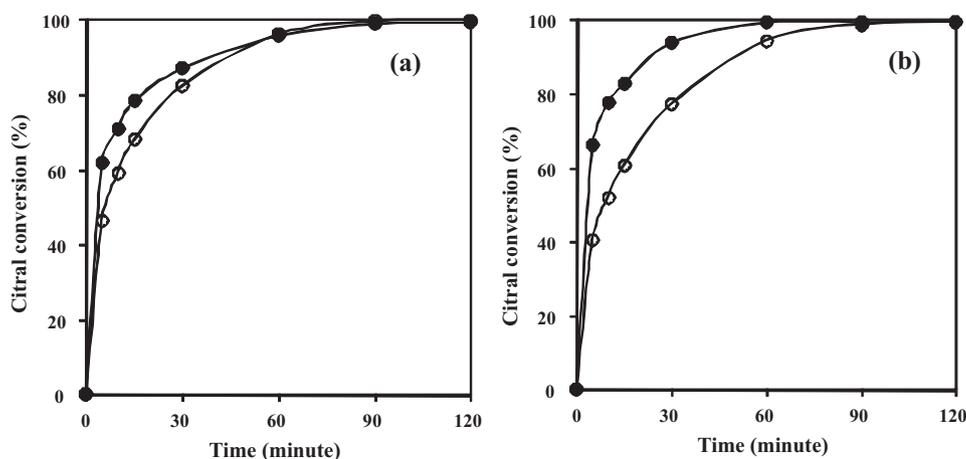


Fig. 5. Citral conversion as function of time on 1.0 wt%Rh/TiO₂ catalysts prepared in (a) NH₃ and (b) HCl medium: reduced at (●) 300 °C and (○) 500 °C.

sess sites able to hydrogenate C=O and C=C double bonds of citral and of its secondary products. Besides, a competitive adsorption must exist between the α,β -unsaturated aldehyde and its secondary products. The effect of the reduction temperature of both catalysts on their catalytic properties was investigated. They were reduced at 500 °C with the aim of favoring the C=O hydrogenation of citral.

Fig. 5 displays the citral conversion as function of time for both catalysts reduced at 300 °C and 500 °C. First, a deactivation of the catalysts occurs during the first few minutes, explained either by a polymerization of carbonaceous species, or by a decarbonylation of citral and/or unsaturated alcohols leading in both cases to a poisoning of the active sites [25–30]. For both Rh_{HCl}/TiO₂ and Rh_{NH₃}/TiO₂ catalysts, whatever the reduction temperature, citral is totally converted after 90 min reaction time. However, the samples reduced at 500 °C are fewer active than their counterparts reduced at 300 °C, particularly for the Rh_{HCl}/TiO₂ catalyst (Fig. 5b). This phenomenon is explained by the presence of partially reduced support species (TiO_(2-x) ($x < 2$)) generated after reduction at high temperature, which can cover part of the metallic surface. For the Rh_{NH₃}/TiO₂ monometallic catalyst, an increase of the reduction temperature from 300 °C to 500 °C involves an increase of the unsaturated alcohols and citronellol formation (Fig. 6a compared to Fig. 4a). This phenomenon is linked to the use of the TiO₂ support since the selectivity to unsaturated alcohols of previously studied Rh/Al₂O₃ catalysts was proved to be independent of the reduction temperature, remaining in all cases rather low (1–2%) [25]. In the case

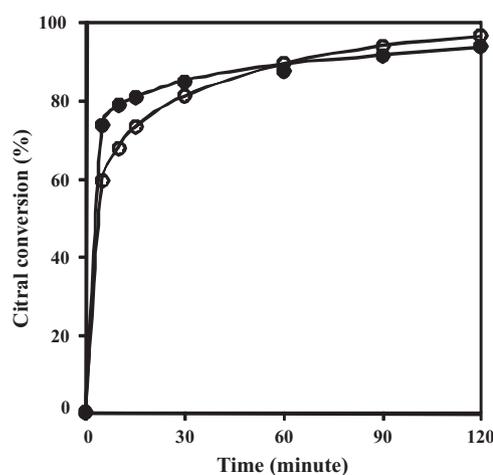


Fig. 7. Citral conversion as function of time on 1.0 wt%Pt_{HCl}/TiO₂ catalysts reduced at (●) 300 °C and (○) 500 °C.

of the Rh_{HCl}/TiO₂ sample, citronellal and citronellol are formed in larger extent after reduction at 500 °C to the detriment of isopulegol (Fig. 6b compared to Fig. 4b). This phenomenon cannot be explained by an evolution of the metal particle size since both samples present similar average particle diameters (Table 1). The drop of isopulegol formation after reduction at high temperature can be

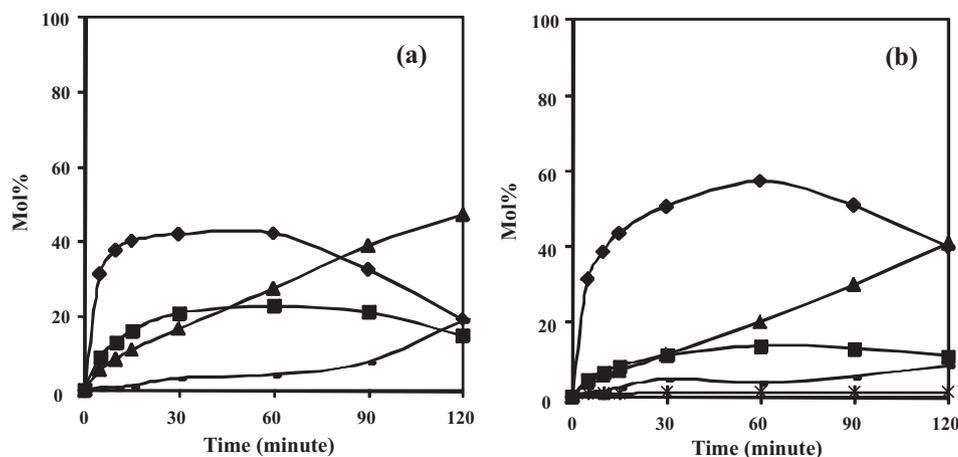


Fig. 6. Citral hydrogenation on 1.0 wt%Rh/TiO₂ catalysts reduced at 500 °C prepared in (a) NH₃ and (b) HCl medium: (◆) citronellal; (▲) citronellol; (■) unsaturated alcohols; (*) isopulegol; and (—) others products.

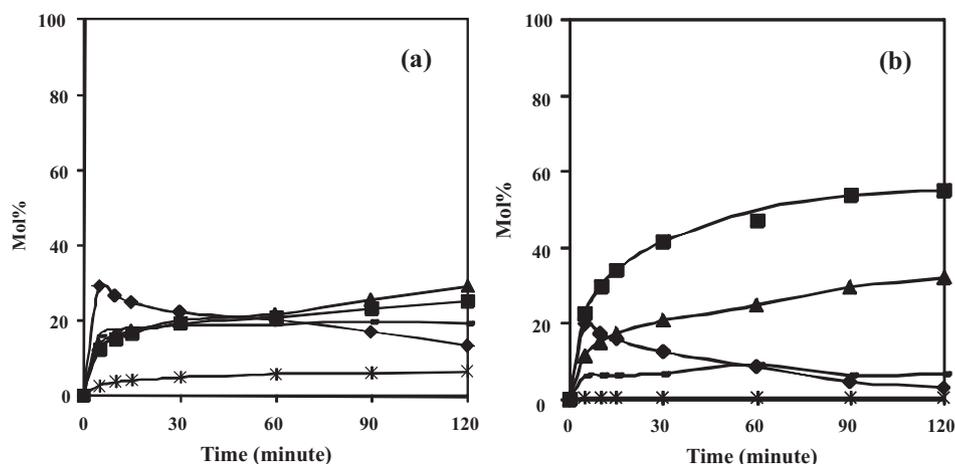


Fig. 8. Citral hydrogenation on 1.0 wt%Pt_{HCl}/TiO₂ catalysts reduced at (a) 300 °C and (b) 500 °C: (◆) citronellal; (▲) citronellol; (■) unsaturated alcohols; (*) isopulegol; and (—) others products.

explained by the removal of chloride ions (Table 1) that means the elimination of acid sites on the catalyst surface.

Finally, on both Rh/TiO₂ monometallic catalysts, the SMSI effect is slightly beneficial on the unsaturated alcohols formation. Nevertheless, once the citral conversion reaches 100%, the unsaturated alcohols keep being hydrogenated. Thus, the presence of TiO_(2-x) species does not poison the C=C hydrogenation sites, but modifies the C=C/C=O adsorption competition by enhancing the activation of the oxygen electronic doublet of the carbonyl function [31–33].

3.2.3. Influence of the reduction temperature of monometallic Pt_{HCl}/TiO₂ catalyst

Fig. 7 shows the evolution of the citral conversion as function of time for the 1.0 wt%Pt_{HCl}/TiO₂ catalyst reduced at 300 °C and 500 °C. As observed for Rh/TiO₂ catalysts, the sample reduced at 300 °C is more active than the one reduced at 500 °C, but both are rapidly deactivated. The deactivation process is then independent of the metal nature (Rh or Pt). The curves reported in Fig. 8 indicate that the increase of reduction temperature from 300 °C to 500 °C allows one to double the amount of unsaturated alcohols, while this phenomenon is not observed by using a classical support as alumina for example. The opposite behavior is observed for the hydrogenation of the conjugated C=C double bond leading to citronellal formation. For both reduction temperatures, citronellol increases as function of time, indicating the hydrogenation of the carbonyl function of citronellal. Moreover, isopulegol is obtained in noticeable quantity on the Pt/TiO₂ after reduction at 300 °C, whereas reducing the catalyst at 500 °C leads almost to its disappearance. This phenomenon was previously observed on

Rh_{HCl}/TiO₂ catalyst and explained by the acidity decrease after high reduction temperature (500 °C). Nevertheless, it should be noticed that isopulegol formation is rather limited on Pt_{HCl}/TiO₂ catalyst reduced at 300 °C compared to the Rh_{HCl}/TiO₂ sample prepared and activated in the same conditions (Fig. 8a vs Fig. 4b).

Finally, as with Rh/TiO₂ catalysts, the high temperature reduction generates TiO_(2-x) ($x < 2$) moieties on Pt_{HCl}/TiO₂ sample, which activate the C=O bond of citral. However, the SMSI effect is more marked in the case of Pt after reduction at 500 °C since more than 50 mol% of unsaturated alcohols are obtained after 1 h reaction time. In fact, the beneficial effect of the SMSI phenomenon on the unsaturated alcohols selectivity is known to be more important on Pt or Ir-based catalysts [12,34,35]. Moreover, in a previous study concerning the preparation and characterization of bimetallic Rh–Ge and Pt–Ge catalysts supported on TiO₂ [20], we tested the catalytic performances of the samples for the cyclohexane dehydrogenation, a structure insensitive reaction, under atmospheric pressure and at 270 °C. The catalytic activities of the monometallic Rh and Pt catalysts measured before their modification by Ge addition indicated lower values for all catalysts reduced at 500 °C compared to 300 °C. These results evidenced the SMSI effect developed by TiO_{2-x} species covering one part of the metallic active surface of the samples reduced at high temperature. Moreover, we observed that the decrease of activity was more pronounced with Pt than with Rh catalysts, suggesting that Pt is more sensitive than Rh to the SMSI effect. According to Herrmann [36], the sensitivity to the SMSI effect which varies with the nature of the metal in the order Pt > Rh, is explained by a greater number of unfilled *d*-orbitals per metal atoms in the case of Rh.

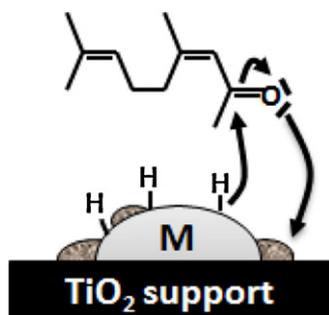


Fig. 9. Schematic representation of the adsorption mode of citral on M/TiO₂ catalyst reduced at high temperature (500 °C): (●) support in a partially reduced state TiO_(2-x) ($x < 2$).

4. Conclusion

Rh and Pt monometallic catalysts supported on titania oxide were prepared by impregnation of precursor salt in various media (NH₃ or HCl), and reduced either at 300 °C or at 500 °C (high temperature required to generate SMSI effect). Whatever the preparation and activation protocols, TEM analysis revealed small (1.9–2.3 nm) well-dispersed particles of Rh and Pt on the support. TPR experiments highlighted the partial reduction of TiO₂ species above 300 °C as reduction temperature. Selective hydrogenation of citral was performed at 70 °C on all samples and under 7 MPa hydrogen pressure. When Rh and Pt salts are impregnated in HCl medium, reducing the resulting catalysts at low temperature (300 °C) leads mainly to citral cyclization towards isopulegol, due to the presence of acidic sites induced by chloride species. A reduction of these cat-

alysts at high temperature (500 °C) allows one to decrease chlorine content and consequently isopulegol formation. For all catalysts, the presence of $\text{TiO}_{(2-x)}$ moieties ($x < 2$) on the Rh and Pt active surface after reduction at 500 °C involves a slight decrease of the citral conversion. Nevertheless, the SMSI effect promotes the formation of unsaturated alcohols (intended products), this effect being more pronounced with Pt/ TiO_2 catalyst. The $\text{TiO}_{(2-x)}$ species are responsible for the activation of the C=O group of citral according to the schematic representation proposed in Fig. 9.

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