

## Hydrogenation of $\alpha,\beta$ -unsaturated aldehydes over Ru/Al<sub>2</sub>O<sub>3</sub> catalysts

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### Abstract

The hydrogenation of citral and cinnamaldehyde has been investigated over Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. The effect of metal particle size on the catalytic activity and selectivity has been studied by using catalysts having a metal dispersion ranging from 0.05 to 0.88. It has been observed that the overall rate of hydrogenation of both the unsaturated aldehydes is not influenced by the Ru particle size. In the hydrogenation of cinnamaldehyde a higher selectivity to cinnamyl alcohol has been observed on catalysts with larger metal particle size. No variations have been found in the hydrogenation of citral. It is suggested that steric effects do not influence significantly the product selectivity. A repulsive interaction between the aromatic ring and the catalyst surface would explain the higher selectivity to cinnamyl alcohol. On all the investigated catalysts the isolated C=C double bond of citral shows a low reactivity. It is suggested that the unsaturated aldehyde is adsorbed through the carbonyl group. This strong adsorption prevents the hydrogenation of the isolated olefinic bond which is located far away from the adsorption centers.

**Keywords:** Hydrogenation; Unsaturated aldehydes; Ruthenium; Particle size effect

### 1. Introduction

The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to the corresponding unsaturated alcohols is a reaction of great importance in the synthesis of fine chemicals. So far, the stoichiometric reduction with NaBH<sub>4</sub> has been the most commonly used synthetic route due the difficulty to preparing an heterogeneous catalyst able to perform the hydrogenation reaction with high selectivity. In the last decade much research effort has been devoted to improve the selectivity of heterogeneous supported metal catalysts and high yields to unsaturated alcohols have been obtained

on Group VIII metal catalysts by addition of promoters [1–11]. Among the parameters influencing the catalytic activity and selectivity of this reaction, the variation of the catalytic properties with the metal particle size has been widely investigated [3–10]. Both electronic and geometric effects have been invoked to explain the observed changes in selectivity.

Metal particles size is known to determine the relative proportion of atoms on the corner, edges and planes of the crystallites. Atoms in a different crystallographic position can have different catalytic properties as a result of a different electronic and/or geometric structure. The structure of the reactant molecule and its interaction with the metal active sites are also important [2]. Cinnamal-

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maldehyde has been reported to show a significant variation of the selectivity with the metal particle size [3–6], whereas controversial results have been reported on aliphatic  $\alpha,\beta$ -unsaturated aldehydes [6–9]. It has been suggested that the presence of a large substituent on the  $\beta$ -carbon decreases, through a steric effect, the reactivity of the C=C double thus increasing the selectivity to unsaturated alcohols.

In this paper we report a study carried out on well characterized Ru–Al<sub>2</sub>O<sub>3</sub> catalysts with the aim of studying the influence of the Ru particle size on the activity and selectivity of the liquid-phase hydrogenation of cinnamaldehyde and citral. Citral has been chosen since it is an aliphatic unsaturated aldehyde with a bulky substituent on the  $\beta$ -carbon. Moreover citral and its hydrogenation products are important chemicals used in the perfumery industry. In a previous paper carried out on Ru/C, we have found that citral hydrogenation can be regarded as a ‘structure insensitive’ reaction in the range of dispersion between 0.1–0.4 [9]. In the present paper we have extended our study to catalysts supported on  $\gamma$ -alumina and with a wider range of dispersion.

## 2. Experimental

### 2.1. Preparation of the catalysts

The catalysts were prepared by using ruthenium acetylacetonate (Ru(acac)<sub>3</sub>, Heraeus) or Ru nitrosyl nitrate (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, Johnson Matthey) as precursors. Samples obtained from Ru(acac)<sub>3</sub> were prepared by contacting a toluene solution of the precursor with the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Rhone Poulenc, BET 220 m<sup>2</sup> g<sup>-1</sup>) for many hours. After this step the catalysts were filtered, dried at 333 K under vacuum, treated under a nitrogen stream at 523 K for 2 h and then reduced in flowing H<sub>2</sub>. Sample RuEC2(O/HTR) was obtained by treatment of the RuEC2 sample at 623 K for 1 h in air, cooling to room temperature, reduction at 753 K for 4 h under flowing hydrogen. Samples obtained from Ru(NO)(NO<sub>3</sub>)<sub>3</sub> were

prepared by contacting an aqueous solution of the precursor with the support. The amount of solution used was slightly greater than the pore volume of the Al<sub>2</sub>O<sub>3</sub>. After drying for 2 h at 393 K in air, the solids were reduced in H<sub>2</sub> at 623 K for 3 h.

The amount of ruthenium on the catalysts was varied from 1 to 4 wt%. Table 1 reports the chemical composition and the main characteristics of all samples.

Hydrogen chemisorption measurements were carried out using a static volumetric apparatus. The hydrogen adsorption isotherms were carried out in the pressure range 50–400 Torr at a temperature of 373 K. The H/Ru ratio was used to measure the Ru dispersion (Ru surface atoms/Ru total atoms). The average ruthenium particle size was calculated (assuming a spherical geometry) from the equation:  $d$  (nm) =  $6V/S$ , where  $V$  is the ruthenium volume and  $S$  the ruthenium surface area. Metal surface area was measured assuming a stoichiometry H/Ru = 1 and a Ru surface density of  $1.63 \times 10^{19}$  atoms m<sup>-2</sup> [12].

Analyses by TEM were performed using a JEOL 100 CX apparatus following the extractive replica technique [13].

EXAFS (extended X-ray absorption fine structure) analysis was performed using the beam line at the LURE (Orsay) synchrotron radiation. The samples were reduced in situ by hydrogen flow, following a programmed heating/cooling cycle. More details on the preparation of the catalysts and their characterization are reported elsewhere [13].

### 2.2. Catalytic experiments

The hydrogenation reactions were carried out in a 100 ml four-necked flask fitted with a reflux condenser, a thermocouple, a dropping funnel and a stirred head. Before catalytic measurements the catalysts were reduced for 2 h at 623 K. After cooling at room temperature the catalyst was transferred into the reactor and added to 25 ml of ethanol and treated at 343 K under flowing H<sub>2</sub> for one hour at atmospheric pressure. It has been previously demonstrated [13] that, due the slow oxi-

Table 1  
Characterization of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts

Catalysts observation	Ruthenium		H/Ru	<i>d</i> (nm) <sup>a</sup>	<i>N</i> <sup>b</sup>	TEM
	Precursor	Ru (wt %)				
RuEC1	Ru(acac) <sub>3</sub>	0.97	0.88	1.5	3.81 <sup>c</sup>	0.8–1.5 nm narrow distribution
RuEC2	Ru(acac) <sub>3</sub>	2.5	0.44	3.0	7.40	bimodal distribution around 1 nm and 6 nm
RuEC2 (O/HTR)	Ru(acac) <sub>3</sub>	2.5	0.05	27	n.a.	n.a.
RuEC3	Ru(acac) <sub>3</sub>	4	0.25	5.4	9.92	1–10 nm; wide distribution
RuNI1	Ru(NO)(NO <sub>3</sub> ) <sub>3</sub>	0.92	0.23	5.9	9.18	1–10 nm bimodal distribution
RuNI2	Ru(NO)(NO <sub>3</sub> ) <sub>3</sub>	2.23	0.23	5.9	10.92	n.a.

<sup>a</sup> Average particle size calculated from H<sub>2</sub> chemisorption.

<sup>b</sup> Average coordination number measured by EXAFS.

<sup>c</sup> For this sample Ru<sup>6+</sup> (*N*=0.54) and O (*N*=0.28) were observed in the first coordination shell.

n.a. = not available.

dation of Ru, catalysts reduced at 623 K can suffer short exposure to air, and can be easily reactivated at low temperature in H<sub>2</sub>. After this step, the reactor temperature is lowered to 333 K and 0.1 ml of substrate is injected through one arm of the flask. The progress of the reaction is followed by analyzing a sufficient number of microsamples. Substrates and solvent are commercial analytical grade products and were used without further purification. Chemical analysis is performed with a gas chromatograph HP (model 5890) equipped with a flame ionization detector and a wide-bore capillary column (Supelcowax, 30 m, 0.53 mm i.d.). Quantitative analysis is carried out calculating the area of the chromatographic peaks using an electron integrator. Catalytic activity was measured in terms of initial turnover rates and calculated from the slope of the curves conversion versus time (*t*) at *t*=0. Selectivities were calculated by the expression  $S_i = C_i / \sum C_p$ , where *C<sub>i</sub>* is the concentration of product *i* and *C<sub>p</sub>* the total concentration of the products.

Preliminary tests, with different catalyst amount, grain size and stirring rate, were carried out in order to ascertain the absence of diffusional limitations.

### 3. Results

The catalytic hydrogenations of citral and cinnamaldehyde have been investigated over a series

of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts having a different metal dispersion and obtained from different metal precursors. Catalyst samples have been characterized by several physico-chemical techniques and the most pertinent results regarding this communication are reported in Table 1. More details on the characterization results and on the experimental procedures used are reported elsewhere [13].

Table 1 summarizes the results of H<sub>2</sub> chemisorption reported either in terms of the H/Ru ratio and of the calculated average Ru particle size. Moreover the average coordination number of the Ru atoms, as determined by EXAFS, has been reported together with the main results of the TEM observations carried out on the examined samples.

The results reported in Table 1 show that the size and distribution of the Ru particles depend on

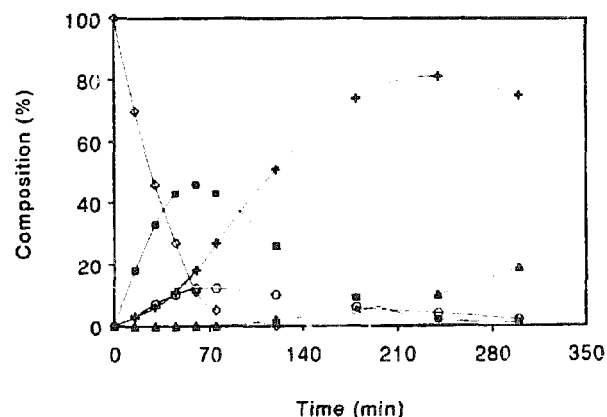
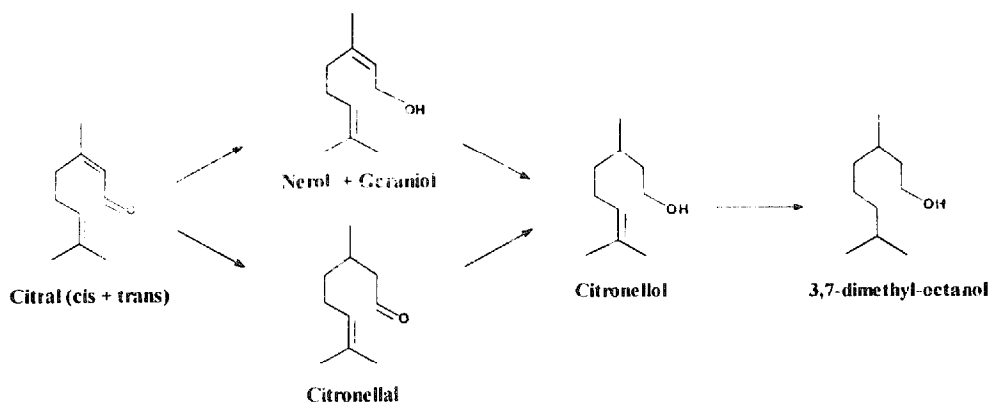


Fig. 1. Hydrogenation of citral over Ru/Al<sub>2</sub>O<sub>3</sub> (◇) citral, (■) citronellal, (○) geraniol + nerol, (+) citronellol, (▲) 3,7-dimethyl-octanol.



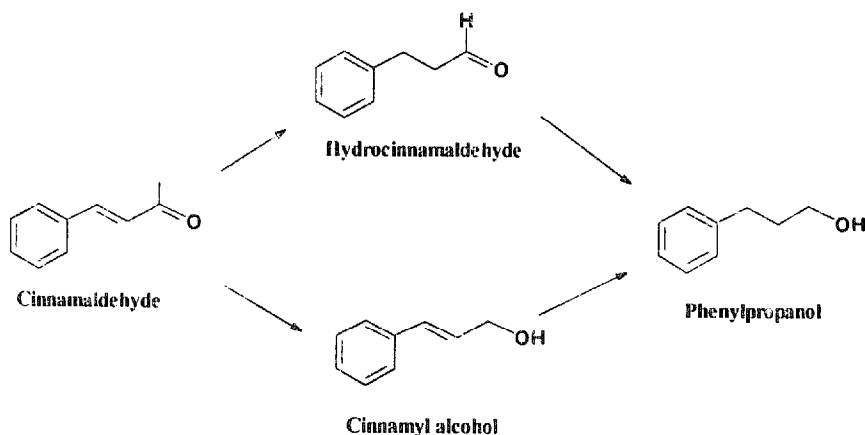
Scheme 1.

the preparation method used and on the metal loading. On the samples prepared from  $\text{Ru}(\text{acac})_3$ , the H/Ru ratio was found to decrease with the Ru loading. This is in agreement with the larger Ru particles observed by TEM. All the samples obtained from  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  show instead, regardless of the Ru loading, a similar H/Ru ratio (0.23–0.26) and a less homogeneous distribution of the Ru particles. The EXAFS investigation at the Ru K-edge has given results which are in agreement with TEM and chemisorption results. The coordination number,  $N$ , was found to increase with decreasing the H/Ru ratio. On all but the RuEC1 sample, only EXAFS peaks related to Ru–Ru bonds were observed. On the RuEC1 sample instead, the presence of  $\text{Ru}^{\delta+}-\text{O}$  species was also observed. This was taken as an indication of a less efficient reduction of this catalyst likely due to its small particles which lead to a strong interaction with the support. The amount of  $\text{Ru}^{\delta+}$  species has been estimated to be below

10% of the total Ru content. A  $\text{Ru}/\text{Al}_2\text{O}_3$  sample (RuEC2(O/HTR)) having large metal particles (27 nm) was obtained from the RuEC2 catalyst by oxidation in air at 623 K followed by reduction at 753 K.

In order to avoid interference of residual chloride ions on the catalytic performance, all the catalysts investigated were prepared by using precursors which do not contain chlorine.

Fig. 1 shows a typical product distribution as a function of the reaction time obtained during the hydrogenation of citral. Since a mixture of the isomers *E* and *Z* of citral has been used the corresponding isomeric α,β-unsaturated alcohols (geraniol and nerol) were obtained through the hydrogenation of the carbonyl group. In the first stages, the reaction was found to proceed through two parallel routes leading to citronellal and α,β-unsaturated alcohols. Citronellol and the fully saturated alcohol (3,7-dimethyl-octanol) were formed at higher reaction times according to



Scheme 2.

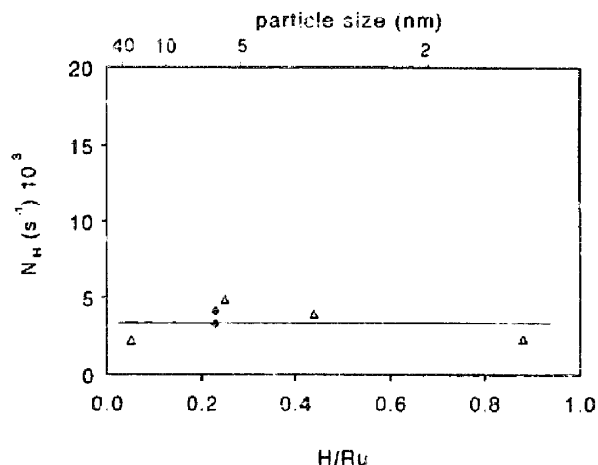


Fig. 2. Influence of Ru dispersion ( $H/Ru$ ) on the rate of hydrogenation of citral.  $N_H$ , ( $\Delta$ ) RuEC series, ( $\blacklozenge$ ) RuNI series.

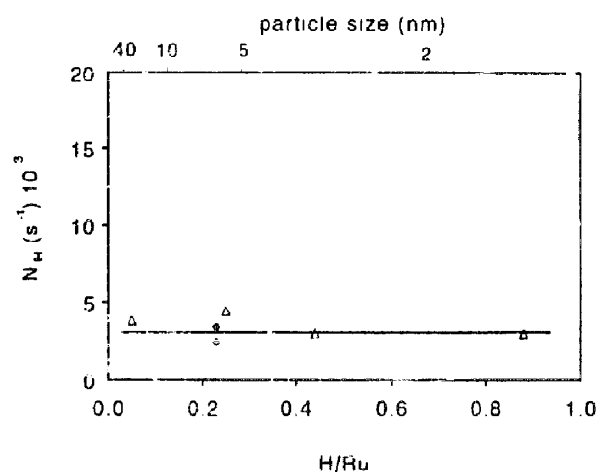


Fig. 3. Influence of Ru dispersion ( $H/Ru$ ) on the rate of hydrogenation of cinnamaldehyde.  $N_H$ , ( $\Delta$ ) RuEC series, ( $\blacklozenge$ ) RuNI series.

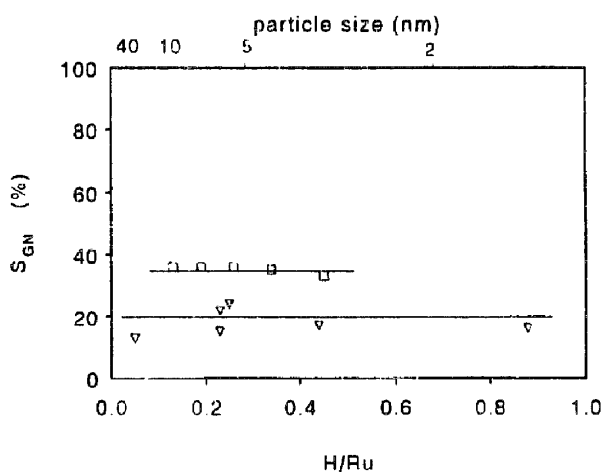


Fig. 4. Hydrogenation of citral: Influence of Ru dispersion ( $H/Ru$ ) on the selectivity to unsaturated alcohols,  $S_{GN}$ , ( $\square$ ) Ru/C, ( $\nabla$ ) Ru/ $Al_2O_3$ .

Scheme 1. A detailed discussion of the mechanism of hydrogenation of citral over Ru supported catalysts is reported elsewhere [14]. It is interesting to note that the addition of  $H_2$  to the isolated  $C=C$  double bond occurs only after the  $C=O$  group has been hydrogenated.

Under the same experimental conditions, hydrogenation of cinnamaldehyde proceeds through a reaction mechanism (Scheme 2) similar to that described for the hydrogenation of citral.

The effect of the Ru dispersion (measured by the  $H/Ru$  ratio) on the initial rate of hydrogenation of citral and cinnamaldehyde is reported in Fig. 2 and Fig. 3, respectively. Even though it is not possible to derive a mean particle size in the case of bimodal distribution, as there is from TEM in a number of cases (Table 1), all the characterization results (TEM, EXAFS, chemisorption) are consistent with an increase of Ru particle size with decreasing the  $H/Ru$  ratio. We have therefore reported in Fig. 2 and Fig. 3 the corresponding Ru particle size calculated by  $H_2$  chemisorption. Of course the derived conclusions have to be interpreted with appropriate caution. The initial turnover rates ( $N_H$ ) are based on hydrogen chemisorption and expressed as molecules of substrate reacting per ruthenium surface atom per second. For both reactions the initial turnover rate was found almost constant in all range of dispersion investigated. Samples prepared from

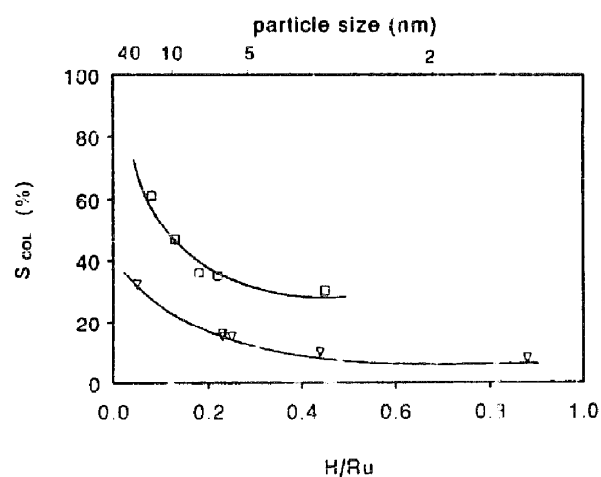


Fig. 5. Hydrogenation of cinnamaldehyde: Influence of Ru dispersion ( $H/Ru$ ) on the selectivity to unsaturated alcohols,  $S_{COI}$ , ( $\square$ ) Ru/C, ( $\nabla$ ) Ru/ $Al_2O_3$ .

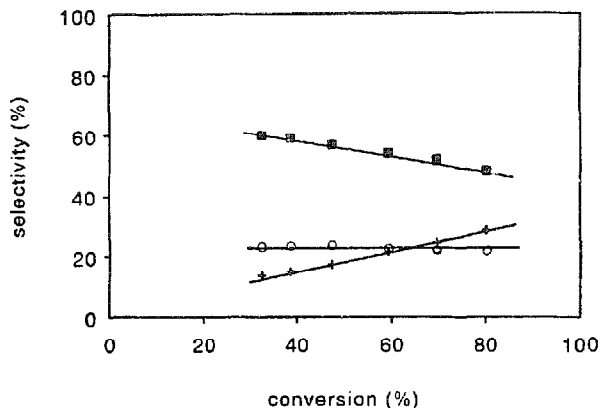


Fig. 6. Hydrogenation of citral: Selectivity to reaction products as a function of conversion. Catalyst: RuNI<sub>2</sub>. (■), citronellal, (○), geraniol + nerol, (+), citronellol.

Ru(acac)<sub>3</sub> and Ru(NO)(NO<sub>3</sub>)<sub>3</sub> gave similar results.

The effect of the H/Ru ratio on the selectivity to unsaturated alcohols is reported in Fig. 4 and Fig. 5 for the hydrogenation of citral and cinnamaldehyde, respectively. The selectivity values reported in Fig. 4 and Fig. 5 have been measured at 50% conversion. It should be however noted that the same results are found in a large range of conversion. The selectivity to unsaturated alcohols is scarcely influenced by the level of conversion. The selectivity to citronellal was instead found to decrease with increasing conversion with a corresponding increase in the selectivity to citronellol. Results on the influence of the conversion levels on the product selectivity is reported in Fig. 6.

Fig. 4 shows that in the hydrogenation of citral, the selectivity to unsaturated alcohols remains almost constant regardless of the Ru dispersion. Fig. 5 shows instead that in the hydrogenation of cinnamaldehyde a larger amount of unsaturated alcohols is obtained on the catalyst samples having a lower H/Ru ratio.

In Fig. 4 and Fig. 5 are also reported, for comparison, the results previously obtained on Ru/C [5,9] which show that the effect of Ru particle size on the hydrogenation of citral and cinnamaldehyde is similar regardless of the support used. However, on the Ru/C samples a shift (20%) to a higher selectivity to unsaturated alcohols has been observed.

#### 4. Discussion

The results reported in the previous section show the following main features:

1. On Ru/Al<sub>2</sub>O<sub>3</sub> hydrogenation of citral and cinnamaldehyde occur with a similar turnover rate. In both cases the rate of reaction is independent on the Ru dispersion.
2. Addition of hydrogen to citral takes place exclusively on the carbonyl group and on the conjugated C=C double bond. The hydrogenation of the isolated C=C double bond starts only after the aldehydes (citral and citronellal) have been transformed to alcohols.
3. The Ru dispersion plays a different role in the hydrogenation of the two investigated molecules. In the hydrogenation of citral the selectivity to unsaturated alcohols remains constant in all range of H/Ru ratios investigated. A higher selectivity to cinnamyl alcohol is instead observed in the hydrogenation of cinnamaldehyde on the samples showing a lower H/Ru ratio.

On all Ru samples (Fig. 2 and Fig. 3) the rate of hydrogenation is independent on the H/Ru ratio. The same turnover rate has also been observed on the RuEC1 sample notwithstanding that on this catalyst a fraction of the Ru atoms is not completely reduced. The EXAFS measurements have shown that on this sample a fraction of the metal atoms are in the form of Ru<sup>δ+</sup> even after in situ treatment at 400°C. This seems to suggest that the same amount of atoms which are counted by chemisorption are responsible for the catalytic hydrogenation of the aldehydes. It is likely that the 'unreduced' ruthenium does not chemisorb hydrogen and does not participate to the catalytic hydrogenation. However it should be noted that the amount of Ru<sup>δ+</sup> estimated by EXFAS is less than 10% of the total Ru content and therefore variation of the catalytic activity due to the presence of Ru<sup>δ+</sup> can be accounted within the experimental error.

In the hydrogenation of citral it has been observed that the addition of hydrogen to the

isolated C=C double bond does not occur until molecules containing carbonyl groups are present in the reaction mixture. In order to check the reactivity of a simple olefin and to rule out the presence of some steric effect, the hydrogenation of 3,7-dimethyl-1-octene has been investigated. At 333 K the reaction was very fast and it was necessary to run the hydrogenation at lower temperature in order to avoid the influence of mass transfer limitations. At 283 K the turnover rate of the hydrogenation of 3,7-dimethyl-1-octene was about one order of magnitude faster than the turnover rates measured at 333 K on the unsaturated aldehydes. These results suggest that the aldehydes are adsorbed on the Ru surface through the carbonyl or the conjugated C=C–C=O group, the strong adsorption of which prevents the hydrogenation of the isolated C=C double bond which is located far away from the adsorption centers.

Fig. 4 shows the influence of the Ru dispersion on the selectivity to geraniol + nerol,  $S_{GN}$ . For comparison the results previously obtained on Ru/C (taken from ref. [9]) have been also reported. In all range of Ru dispersion investigated  $S_{GN}$  remains constant (about 15% on Ru/Al<sub>2</sub>O<sub>3</sub> and about 35% on Ru/C). Notwithstanding the limitations, evidenced in the results section, in deriving a mean particle size from the H/Ru ratio, it should be pointed out that all the characterization results obtained on the investigated samples are consistent with an increase in the number of metal particles having a larger size with decreasing the H/Ru ratio. A direct correlation can be in fact observed between the average particle size derived from the chemisorption experiments and the average coordination number measured by EXAFS. Therefore it can be concluded that selectivity to geraniol,  $S_{GN}$ , remains constant regardless of the Ru particle size.

Increasing the metal particle size the fraction of Ru surface atoms at the edge and corner sites decreases whereas the fraction of Ru

atoms located on flat planes increases. The absence of an effect of particle size on the product selectivity suggests that the geometry and the coordination number of the Ru sites are not important factors in the hydrogenation of citral to citronellal or to unsaturated alcohols.

The lower selectivity obtained on Ru/Al<sub>2</sub>O<sub>3</sub> compared to the values previously reported on Ru/C is likely due to the presence of impurities (mainly Fe) on the surface of the carbon support. Fe is known to act as promoter for selective hydrogenation of unsaturated aldehydes [15,16]. Moreover it has been suggested that an electron transfer from the support to metal can decrease the probability of the activation of the C=C bond [17].

The effect of particle size on the hydrogenation of unsaturated aldehydes is a controversial issue. Literature data have shown that the selectivity to unsaturated alcohols may depend on the substituents R and R' present on the  $\beta$ -carbon and on the morphology of the active sites [7–9,18]. Bircherm et al. [19] have pointed out that in the gas-phase hydrogenation of methylcrotonaldehyde (R = CH<sub>3</sub>, R' = CH<sub>3</sub>) carried out on single crystal Pt(111) the activation of the C=C bond is difficult because the accommodation of the two methyl groups is hindered by the three-fold symmetry of the flat Pt(111) plane. This interpretation takes into account the higher selectivity to unsaturated alcohol observed in the hydrogenation of 3-methylcrotonaldehyde with respect to crotonaldehyde. On the highly unsaturated surface atoms of the Pt(100) planes the accommodation of the methyl groups is instead easier because of the fourfold symmetry of the Pt(100) [20]. This has been shown to result in a lower selectivity to unsaturated alcohols. From these model studies, a structure sensitivity is to be expected when bulky substituents are presents on the  $\beta$ -carbon of the substrate.

In accord with this hypothesis, Coq et al. [7] have reported that in the gas-phase hydro-

genation of acrolein ( $R=H$ ,  $R'=H$ ) the selectivity to allyl alcohol does not change much with Ru particle size. In a recent paper, Marinelli et al. [18] have reported that in the gas phase hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes the selectivity to unsaturated alcohols increases with increasing substitution on the terminal olefinic carbon atoms.

Investigations on the effect of the metal particle size on the hydrogenation of aliphatic  $\alpha,\beta$ -unsaturated aldehydes have been carried mostly on aldehydes containing relatively small groups ( $-H$  and  $-CH_3$ ) as substituents on the  $\beta$ -carbon. Citral is an aldehyde with a very bulky aliphatic substituent in the  $\beta$ -carbon position, so it is more suitable to probe any steric effect. The results of Fig. 4 show the absence of any variation in the selectivity with changing the Ru particle size. This indicates that in the conditions used in this work steric effects are not very important. It should be noted however that in our case the reaction was carried out in the presence of ethanol. It is known that the solvent molecules may interact with the metal surface by changing the adsorption mode of substrate [21].

Nitta et al. [6,8] have reported, that when ethanol is used as solvent, in the liquid-phase reduction of acrolein and crotonaldehyde over  $Co/Al_2O_3$ , the selectivity to the unsaturated alcohols increases for both substrates with the size of the Co crystallites. The higher selectivity observed in the hydrogenation of crotonaldehyde with respect to acrolein has been suggested to depend largely on the steric effect of the methyl group on  $\beta$ -carbon of the substrate which inhibits the hydrogenation of the  $C=C$  double bond. Such an effect is emphasized by the presence of residual chlorine on the surface. Due to the absence of steric effects on the acrolein, it was proposed that some electronic effect must be responsible for the higher selectivity to unsaturated alcohols on the larger Co crystallites [8].

In the hydrogenation of cinnamaldehyde the influence of the Ru dispersion on the selec-

tivity to cinnamyl alcohol shows two regions (Fig. 5). At  $H/Ru$  values higher than 0.2 the selectivity increases only slightly with decreasing the Ru dispersion. At  $H/Ru$  values lower than 0.2 a sharp increase in the selectivity is instead observed. The same behaviour is found on  $Ru/Al_2O_3$  and on  $Ru/C$ . The observation that the largest variation is observed at low Ru dispersion rules out the possibility that the higher selectivity is due to a change in the coordination number of the Ru surface atoms. It is known that the largest variation in the fraction of metal sites located at the edges or corners with respect to those located on the flat planes is more evident for small particle (1–5 nm which correspond to variation in the  $H/Ru$  ratio of about 1–0.3). Moreover the results of the hydrogenation of citral show out that a simple steric effect cannot account for the observed changes.

For the hydrogenation of cinnamaldehyde the higher selectivity to cinnamyl alcohol observed on the largest metal particles is in agreement with previous observations on other metal catalysts [6,22]. These results have been explained by Gallezot et al. [4] by considering that on the flat metal surface of a large particle, the unsaturated aldehyde is tilted out from the surface owing to a repulsive interaction occurring between the aromatic ring and the metal which protect the  $C=C$  double bond from hydrogenation.

In conclusion, the results reported in the present paper while confirming the positive effect of the metal particle size on the formation of cinnamyl alcohol in the hydrogenation of cinnamaldehyde have ruled out the presence of a steric effect on the hydrogenation of a bulky aldehyde such as citral.

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