



## Preparation of silica-supported cobalt catalysts from water-in-oil microemulsion for selective hydrogenation of citral

K. Kouachi<sup>a,b</sup>, G. Lafaye<sup>a</sup>, C. Especel<sup>a,\*</sup>, O. Cherifi<sup>b</sup>, P. Marécot<sup>a</sup>

<sup>a</sup> Université de Poitiers, Laboratoire de Catalyse en Chimie Organique, UMR 6503, 82022 Poitiers, France

<sup>b</sup> Laboratoire de Chimie de Gaz Naturel, Faculté de Chimie, USTHB, BP 32, 16111 El Alia, Bab Ezzouar, Algeria

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### ABSTRACT

Silica-supported Co catalysts with different metal loadings were prepared by water-in-oil (w/o) microemulsion (ME) and tested for the selective hydrogenation of citral. The performances of the ME samples were compared to those of previously studied Co impregnated catalysts. Compared to impregnated Co catalysts, ME samples show more homogeneously dispersed Co particles, the crystallite mean size increasing with the Co content. For the ME samples, the selectivity to unsaturated alcohols (i.e. nerol and geraniol) increases with the metal content then reaches a plateau from approximately 15 wt% Co, suggesting that particles of large enough size are required to optimize the C=O group activation. Above 15 wt% Co content, the selectivity is markedly higher on the ME catalysts compared to the impregnated ones (90% versus 45–65% depending on the nature of the support). This result can be directly related to the higher proportion of  $\beta$  H–Co species detected by temperature-programmed desorption of hydrogen ( $H_2$ -TPD) on these ME samples.

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### 1. Introduction

$\alpha,\beta$ -Unsaturated aldehydes are a broad class of significant compounds that are useful in fine chemical industries. The selective hydrogenation of these compounds is one of the most important industrial reactions, and has been the subject of many studies [1–9]. In this field, the hydrogenation of citral, along with crotonaldehyde and cinnamaldehyde, towards unsaturated alcohols (UA) is important, since these compounds are of great interest in the perfumery industry.

In a previous work [10], we studied the effects of support and metal loading on the characteristics of Co-based catalysts for selective hydrogenation of citral. The Co catalysts were prepared by wet-impregnation of four different supports:  $SiO_2$  with low or high surface area,  $\gamma-Al_2O_3$  and  $TiO_2$ . We observed that whatever the nature of the support, the highest UA selectivities (around 65%) were observed on catalysts presenting Co large particles with  $Co^0$  hexagonal phase and particular H–Co species (labelled  $\beta$ ) detected by temperature programmed desorption of hydrogen. Following this study, a new preparation method of Co supported catalysts was performed, in order to provide further insight into this structure–selectivity relationship. The retained preparation method is a water-in-oil (w/o) or reverse microemulsion. In fact,

w/o microemulsions appear as an attractive route to prepare materials with applications in a wide range of disciplines, such as optics, magnetism, electrochemistry and heterogeneous catalysis [11–13]. A microemulsion is defined as a system of water, oil and amphiphile (surfactant). At macroscopic scale, a microemulsion looks like a homogeneous solution but at molecular scale, it appears to be heterogeneous. The internal structure of a microemulsion, at a given temperature, is determined by the ratio of its constituents.

Only few publications stated the use of the microemulsion method to synthesize Co-based catalysts, for a main application in the Fischer–Tropsch synthesis [14,15]. To our knowledge, this is the first time that Co microemulsion-derived catalysts were used for the selective hydrogenation of citral. So, the aim of the present paper was: (i) to control the preparation of silica-supported cobalt catalysts by this original preparation method, and (ii) to compare the catalytic performances for citral hydrogenation of these catalysts with those of their counterparts previously synthesized by classical impregnation [10].

### 2. Experimental

#### 2.1. Catalyst preparation

Silica-supported Co catalysts with different expected Co loadings (denoted  $x_0$  wt%) were prepared by using microemulsion

\* Corresponding author. Tel.: +335 49 45 39 94; fax: +335 49 45 37 41.  
E-mail address: [catherine.especel@univ-poitiers.fr](mailto:catherine.especel@univ-poitiers.fr) (C. Especel).

(denoted ME). The following standard protocol (denoted protocol ME-I) was established in order to prepare 2 g of Co/SiO<sub>2</sub> sample. Firstly, 8 g of CTAB (cetyltrimethylammonium bromide) used as surfactant was dissolved in 75 mL of hexan-1-ol at 40 °C. 5 mL of an aqueous solution containing various amounts of the Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O precursor salt was added at ambient temperature to the previous organic solution under vigorous stirring to form reverse micelles (water-in-oil microemulsion). Then, a volume *V* of trimethylamine equal to 1.5 mL was added to the microemulsion as precipitating agent of the Co ions. Secondly, an oil-in-water microemulsion was prepared with 8 mL of tetraethylorthosilicate (TEOS) and 27 mL of water (corresponding to a water-to-surfactant ratio  $\omega = 12.3$ ). This microemulsion was added to the w/o microemulsion, the resulting mixture was stirred for 1 h at 50 °C, then filtered and washed with 95% ethanol. The obtained samples were dried for 48 h at 120 °C, and reduced at 450 °C in flowing pure hydrogen for 12 h (heating rate = 2 °C min<sup>-1</sup>).

Afterwards, some experimental parameters (stirring procedure, volume of hexanol, volume *V* of added amine) were modified in the standard protocol ME-I, leading to a new protocol denoted ME-II. The details of this protocol will be given in "Section 3".

The Co weight loading in each reduced sample (denoted *x* wt%) was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after digestion in an acid solution and dilution.

All the prepared catalysts are listed in Table 1, with the following code name: *x*Co(*x*<sub>0</sub>)-ME-*i*-*V*, where *x* and *x*<sub>0</sub> are the experimental and theoretical Co content (wt%), ME-*i* the corresponding protocol used for the preparation (ME-I or ME-II), and *V* the volume of amine (expressed in mL).

## 2.2. Transmission electron microscopy (TEM) and electron diffraction

The morphology of the catalysts was studied by transmission electron microscopy (TEM) and by electronic diffraction to examine the Co particle shape and the phase composition, respectively.

Transmission electron microscopy studies were performed on a Philips CM 120 instrument operating at 120 kV. All the samples were ultrasonically dispersed in an ethanol/water mixture and the suspension was brought onto a copper grid with a carbon support film.

Electron diffraction patterns were obtained in the same electron microscope. Interreticular distances *d*<sub>hkl</sub> as well as lattice parameters were calculated from the distances between the spots and the angles formed by the lines passing through these spots. A program [16] allows one to check the calculated values by drawing the theo-

retical pattern along the same zone axis and by comparing it to the experimental pattern.

## 2.3. Gas-phase reaction

Cyclohexane dehydrogenation reaction was carried out under atmospheric pressure in a continuous flow reactor at 300 °C. Injection of cyclohexane was made using a calibrated motor-driven syringe. The partial pressures were 97 and 3 kPa for hydrogen and cyclohexane, respectively. All measurements were performed with a total flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>. Analysis of the reaction products was performed by gas chromatography with a flame ionization detector (Varian 3400X) on a HP-PLOT Al<sub>2</sub>O<sub>3</sub> "KCl" column.

## 2.4. XRD measurements

Powder X-ray diffraction (XRD) patterns of various samples were recorded on a Siemens D-500 diffractometer. The diffractograms were performed with Cu K $\alpha$  radiation ( $\lambda = 1.5404 \text{ \AA}$ ) over a range of  $2\theta$  from 20° to 80° with a 0.04° step size. Crystalline phases were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files.

## 2.5. Temperature-programmed desorption of hydrogen (H<sub>2</sub>-TPD) experiments

The temperature-programmed desorption of hydrogen (H<sub>2</sub>-TPD) experiments were carried out using an U-shaped quartz reactor connected to a thermal conductivity detector. First, the samples were reduced in a 1.0 vol.% H<sub>2</sub>/Ar gas mixture at 450 °C (heating rate = 5 °C min<sup>-1</sup>) for 1 h. Once the catalysts were cooled down to room temperature, the surface was purged by flowing Ar for 1 h. Subsequently, temperature was linearly increased from room temperature to 350 °C at 5 °C min<sup>-1</sup>, following the hydrogen desorption with the thermal conductivity detector. The amount of H-Co species was calculated from desorption peaks area obtained by Gaussian deconvolution of H<sub>2</sub>-TPD spectra.

## 2.6. Citral hydrogenation

The liquid-phase hydrogenation of citral was carried out in a 300 mL stirred autoclave (Autoclave Engineers, fitted with a system for liquid sampling) at 90 °C and at constant pressure of 7 MPa. Before each catalytic experiment, the catalyst (400 mg) was reduced at the desired temperature for 1 h, then immersed into 90 mL of solvent (isopropanol 99%) without exposure to air before the transfer towards the autoclave. After a first flush with nitrogen and a second with hydrogen, the temperature was raised to 90 °C under 3 MPa of hydrogen. Then a mixture of substrate (3 mL of citral) and isopropanol (10 mL) was loaded into the autoclave through a cylinder under 7 MPa hydrogen pressure. Zero time was taken at this moment and stirring was switched on.

Liquid samples were analysed by gas chromatography on a Thermofinnigan chromatograph provided with a FID detector and a capillary column DB-WAX (J&W, 30 m, 0.53 mm i.d.) using nitrogen as carrier gas.

## 3. Results and discussion

### 3.1. Study of various parameters in the microemulsion preparation protocol

#### 3.1.1. ME-I and ME-II protocols

The primary goal of this work was to prepare 2 g of *x*<sub>0</sub> wt% Co/SiO<sub>2</sub> catalysts with *x*<sub>0</sub> = 2, 3.5 and 5 from the standard proto-

**Table 1**

Co/SiO<sub>2</sub> catalysts prepared by microemulsion: code name, synthesis yield and nominal Co content (*x* wt%) determined by ICP-OES on reduced samples.

Entry	Catalyst	Synthesis yield (%)	<i>x</i> wt% Co
1	<i>x</i> Co(2)-ME-I-1.5	30	5.9
2	<i>x</i> Co(3.5)-ME-I-1.5	21	14.7
3	<i>x</i> Co(5)-ME-I-1.5	16	27.3
4	<i>x</i> Co(3.5)-ME-II-1.5	55	5.6
5	<i>x</i> Co(3.5)-ME-II-5	92	3.3
6	<i>x</i> Co(10)-ME-II-5	61	14.4
7	<i>x</i> Co(10)-ME-II-14	93	9.4
8	<i>x</i> Co(16)-ME-II-7	33	44.0
9	<i>x</i> Co(16)-ME-II-10	56	25.0
10	<i>x</i> Co(16)-ME-II-15	90	15.3
11	<i>x</i> Co(23)-ME-II-26	95	21.4
12	<i>x</i> Co(28)-ME-II-32	91	26.5

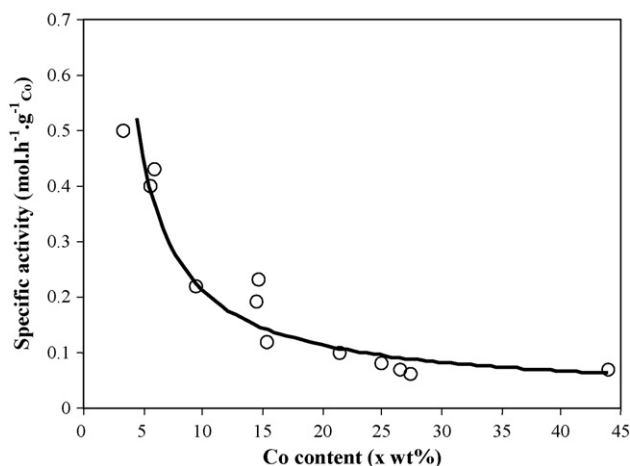


Fig. 1. Specific activity of the Co/SiO<sub>2</sub> catalysts prepared by w/o microemulsion for cyclohexane dehydrogenation at 300 °C versus Co content.

col ME-I described in Section 2. The results of Table 1 show that the contents of these three catalysts (entries 1–3 in Table 1, respectively) are three to five times higher than the expected ones. These high cobalt loadings must be related to the poor synthesis yields. Since no Co trace was detected by ICP in the filtrates at the end of the catalysts preparation, we can consider that all the introduced metal has precipitated on the substrate. So, these low synthesis yields were probably due to a partial hydrolysis of TEOS and thus to the loss of a part of the silica support. In order to improve the TEOS hydrolysis and thus to increase the synthesis yield of the catalysts, various parameters of the ME-I preparation protocol were modified thereafter.

The key factor of a microemulsion is the stirring system since this one determines the degree of dispersion of the water droplets in the organic phase. In the ME-II protocol, a stirring system with magnetic drive (antivortex) was then used in order to improve the effectiveness of the stirring. Moreover, the organic phase volume was increased in order to improve the diffusion of the TEOS towards the aqueous droplets of the w/o microemulsion. 15 mL of hexanol was then added to the TEOS/H<sub>2</sub>O mixture. The comparison of the Co(3.5)-ME-I-1.5 and Co(3.5)-ME-II-1.5 catalysts (entries 2 and 4, respectively) shows that this new experimental protocol is beneficial since the synthesis yield is twice higher for the ME-II sample. Nevertheless, although the ME-II protocol allows

one to improve the synthesis yield, the TEOS hydrolysis is still not total since the cobalt content of the Co(3.5)-ME-II-1.5 catalyst is higher than the theoretical value, i.e. 5.6 wt% instead of 3.5 wt%.

Until now, the volume of amine (precipitating agent) was maintained to 1.5 mL. In the continuation of this work, variable quantities of the amine were added to optimize the TEOS hydrolysis.

### 3.1.2. ME-II protocol with variable volumes of amine

First, 5 mL of amine was introduced to synthesize the Co(3.5)-ME-II-5 catalyst (entry 5 in Table 1). The obtained Co content corresponds to that expected (3.3 wt% versus 3.5 wt%), contrary to the result obtained with 1.5 mL of amine (entry 4, 5.6 wt% Co). Thus, the quantity of precipitating agent plays a determining role, a basic medium supporting the TEOS hydrolysis as reported in the literature [17,18].

Afterwards, different amounts of amine were used to prepare Co catalysts with higher metallic contents (10, 16, 23 and 28 wt%, respectively) in order to obtain the desired metallic loadings (entries 6–12). Finally, volumes of 14, 15, 26 and 32 mL were necessary to synthesize these respective samples, with in each case a synthesis yield equal or higher than 90%.

## 3.2. Catalyst characterizations

The different Co/SiO<sub>2</sub> catalysts prepared by microemulsion were tested for cyclohexane dehydrogenation at 300 °C under atmospheric pressure. This structure insensitive reaction [19–21] was used in order to appreciate the evolution of the metal accessibility of the catalysts with the cobalt content. The samples prerduced at 450 °C are reduced again at the same temperature during 1 h in the dehydrogenation reactor, then cooled down to 300 °C. The specific activities are reported in Fig. 1 as a function of the cobalt loading. The shape of the curve shows that the activity decreases as the cobalt content increases. This observation indicates a decrease of the metallic accessibility, which means that either the average particle size increases with the cobalt loading of the catalysts, or an encapsulation phenomenon of Co particles in SiO<sub>2</sub> occurs during the microemulsion preparation [13,22]. To conclude on these first results, some Co/SiO<sub>2</sub> catalysts were characterized by TEM after reduction at 450 °C. The comparison of the TEM images of the 15.3Co(16)-ME-II-15 and 44Co(16)-ME-II-7 catalysts (Fig. 2) clearly shows that the metal particle size is larger for the sample with the highest metal content. This observation proves that, when the Co content increases, the loss of metallic accessibility deduced from

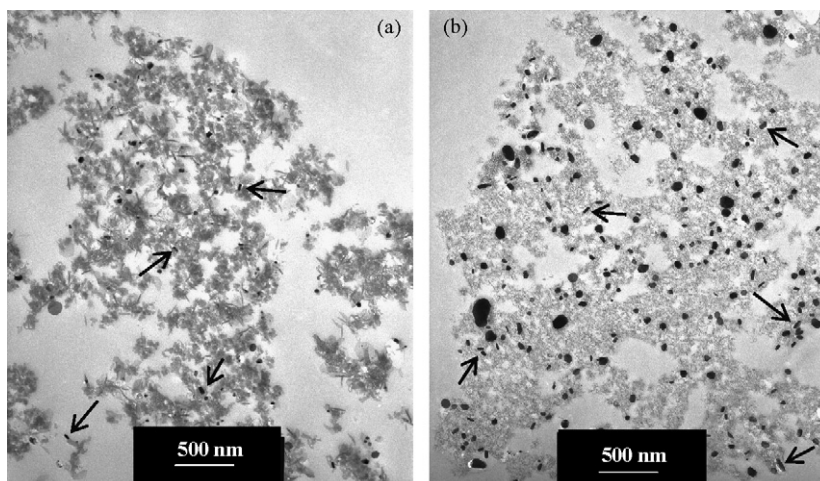


Fig. 2. TEM images of (a) 15.3Co(16)-ME-II-15 and (b) 44Co(16)-ME-II-7.

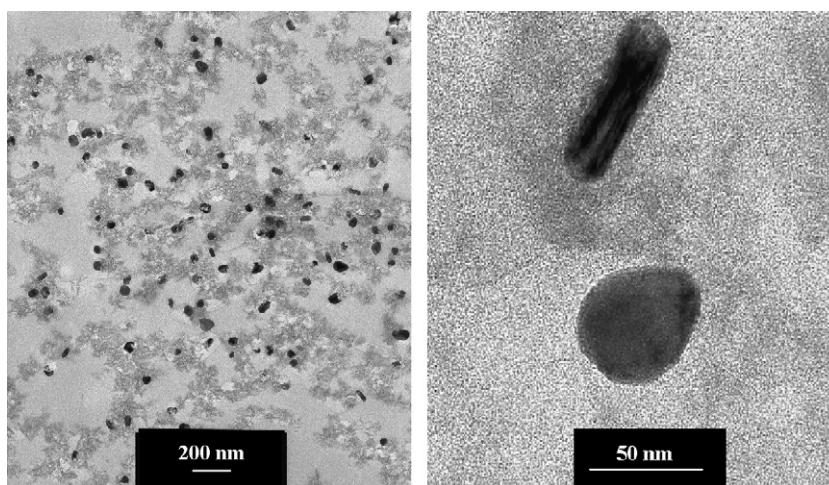


Fig. 3. TEM images of 27.3Co(5)-ME-I-1.5.

cyclohexane dehydrogenation is mainly due to an increase of the average particle size. Moreover, compared to previously studied Co/SiO<sub>2</sub> catalysts prepared by impregnation [10], the TEM images in Fig. 2 highlight a noticeable homogeneity of the ME systems. Nevertheless, the particle size distribution remains a delicate task since the structure of the metallic particles presents two shapes: spherical and cylindrical (announced by arrows in Fig. 2). The presence of the cylinders can be explained by a two-dimensional growth of the particles. This phenomenon is independent of the ME preparation protocol used since TEM images of the 27.3Co(5)-ME-I-1.5 catalyst also reveal the presence of cylinders (Fig. 3). Pileni et al. [23,24] have already observed the formation of cylinders of Cu, Co and Cd nanocrystals prepared by microemulsion using AOT (Aerosol OT, sodium bis(2-ethylhexyl)sulfosuccinate) as surfactant. They demonstrated that according to the water content, some spherical water-in-oil droplets can turn into cylinders.

X-ray diffraction experiments were performed on some samples prepared from protocols I and II and reduced at 450 °C. The diffractograms are reported in Fig. 4. For the three  $x\text{Co}(x_0)$ -ME-I-1.5 catalysts, the XRD analysis reveals the presence of a single phase corresponding to the hexagonal metallic cobalt structure (Fig. 4A). In the case of the  $x\text{Co}(x_0)$ -ME-II-V samples, the Co<sup>0</sup> hexagonal phase coexists with the Co<sup>0</sup> cubic structure (Fig. 4B). In order to determine which parameter leads to the appearance of the Co<sup>0</sup> cubic

phase between the two protocols ME-I and ME-II (i.e. the addition of a higher quantity of hexanol or amine), the 5.6Co(3.5)-ME-II-1.5 sample was also analysed by XRD. Since the Co<sup>0</sup> cubic phase was also observed on this catalyst, it means that the higher quantity of hexanol in the organic phase would be then responsible for the formation of this crystalline structure. All results were confirmed by electron diffraction analysis performed during the TEM measurements. It should be pointed out that all the samples consist only of metallic cobalt phases, regardless of Co content and preparation protocol used. No cobalt silicate was observed on the various samples, in accordance with the formation of these species which can be observed only for reduction temperature higher than 500 °C [25,26].

Various catalysts were finally characterized by TPD of hydrogen from ambient temperature to 350 °C. Examples of H<sub>2</sub>-TPD profiles are reported in Fig. 5. The decomposition of these profiles reveals the presence of four peaks located around 50, 100, 120–160 and 160–300 °C, attributed to four different H-Co surface sites, labelled  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\sigma$ , respectively [27–29]. Table 2 summarizes the relative amount of these various H-Co species, calculated by Gaussian deconvolution. It appears that the distribution of the different H-Co sites depends on the Co loading of the catalysts. In fact, an increase of the Co content induces a noticeable increase of the H-Co  $\beta$  species, from 36% (9.4 wt% Co) until around 70% (wt% Co  $\geq$  15.3).

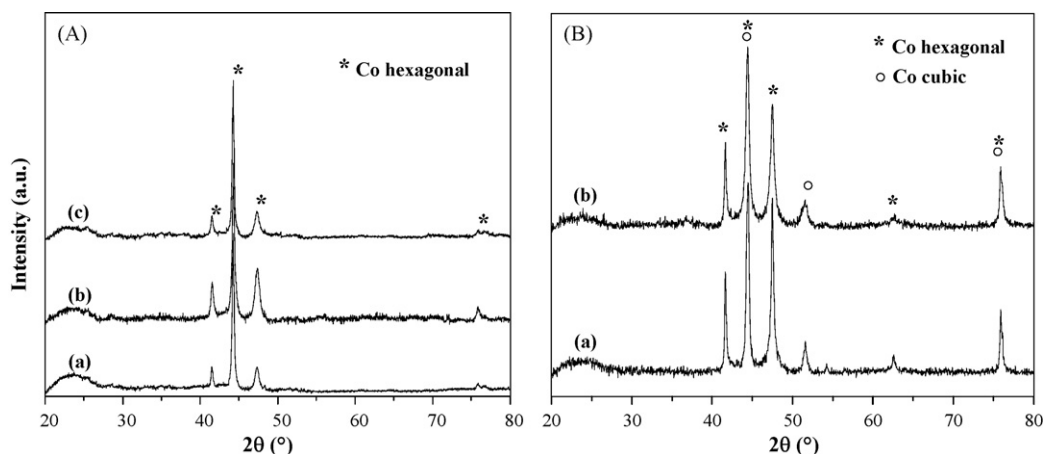


Fig. 4. Diffractograms of Co/SiO<sub>2</sub> catalysts prepared by protocol (A) ME-I and (B) ME-II. (A) (a) 5.9Co(2)-ME-I-1.5; (b) 14.7Co(3.5)-ME-I-1.5; (c) 27.3Co(5)-ME-I-1.5. (B) (a) 15.3Co(16)-ME-II-15; (b) 26.5Co(23)-ME-II-32.

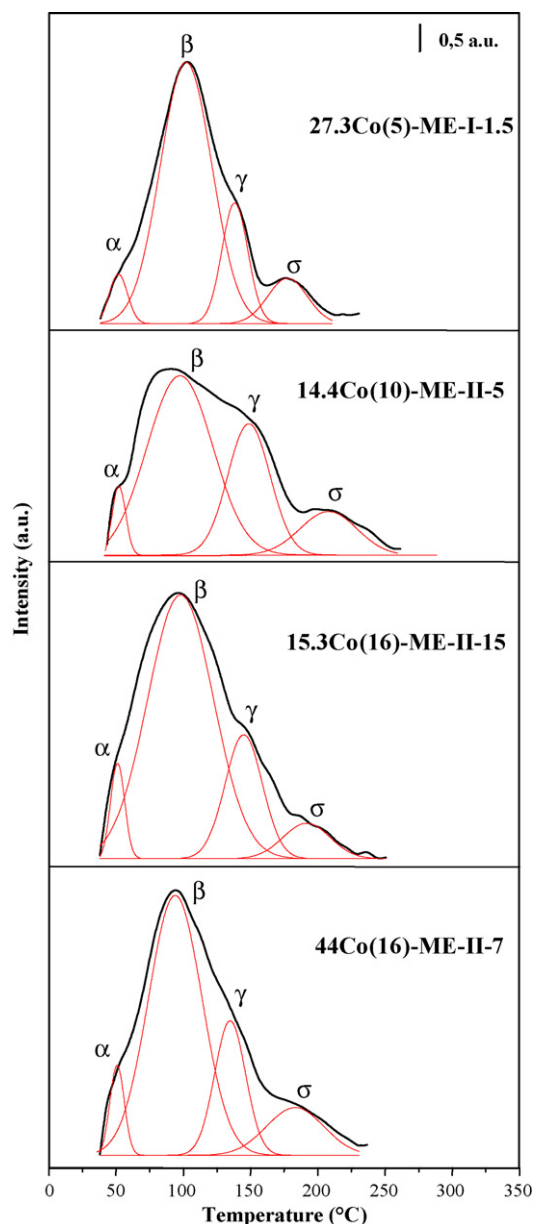


Fig. 5. H<sub>2</sub>-TPD profiles of various Co/SiO<sub>2</sub> catalysts prepared by w/o microemulsion.

### 3.3. Citral hydrogenation

The catalytic behaviour of the samples in the liquid-phase hydrogenation of citral was evaluated after reduction of the catalysts at 450 °C and transfer to the autoclave under inert atmosphere. The hydrogenation of citral occurs through the reaction

Table 2

Relative amounts of H–Co species on different microemulsion-prepared Co/SiO<sub>2</sub> catalysts determined by H<sub>2</sub>-TPD, and unsaturated alcohols (UA) selectivity at 30% citral conversion.

Catalyst	Hydrogen species (%)				UA selectivity (%)
	α	β	γ	σ	
27.3Co(5)-ME-I-1.5	4	71	16	9	87
9.4Co(10)-ME-II-14	9	36	29	26	72
14.4Co(10)-ME-II-5	7	56	25	12	85
15.3Co(16)-ME-II-15	6	69	19	6	90
44Co(16)-ME-II-7	3	71	15	11	89

pathway summarized in Fig. 6. Under our experimental conditions ( $T=90\text{ }^{\circ}\text{C}$ ,  $P_{\text{H}_2}=7\text{ MPa}$ ), the reaction products were geraniol and nerol (unsaturated alcohols, UA), citronellal and citronellol. The side reactions of acetalization and cyclisation were not observed, due to the absence of acid sites on the reduced catalysts [30].

#### 3.3.1. Catalysts prepared from ME-I protocol ( $x\text{Co}(x_0)\text{-ME-I-1.5}$ samples)

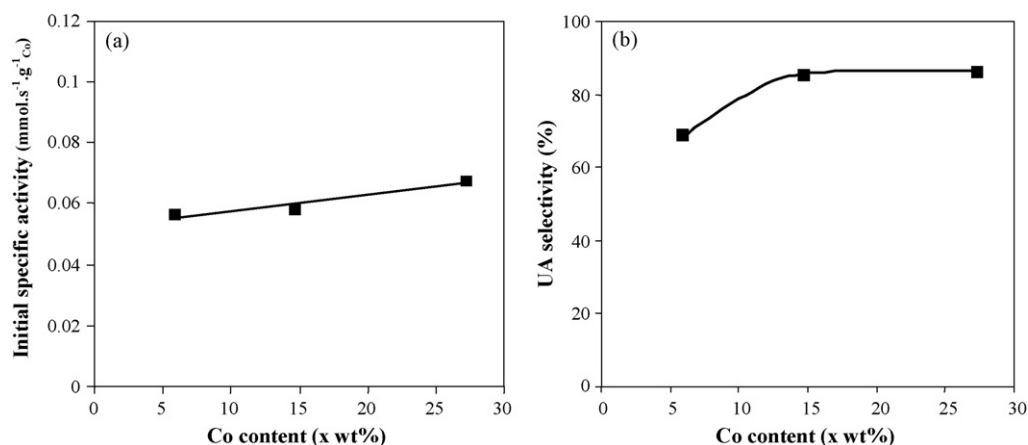
Fig. 7 presents typical temporal concentration profiles of the reactant and the main products during citral hydrogenation obtained in the case of the 27.3Co(5)-ME-I-1.5 sample. Citral disappears as a function of time to form mainly unsaturated alcohols, while the formation of citronellal is rather low. When citral is totally converted, unsaturated alcohols are further transformed into citronellol. These observations suggest that in the course of the C=C/C=O adsorption competition, Co/SiO<sub>2</sub> catalysts prepared by the ME-I protocol favour the C=O adsorption and consequently the formation of unsaturated alcohols.

Fig. 8a and b shows the initial specific activity and the UA selectivity, respectively, as a function of the cobalt content of the different Co-ME-I catalysts. All the selectivities are given at 30% citral conversion. It must be noticed that the UA selectivity remains constant in the 10–90% citral conversion range. The activity of the catalysts slightly increases with the metallic content (Fig. 8a). Since the particle size increases with the Co content, as shown by TEM, this means that the large particles possess the most active sites for citral hydrogenation. In addition, Fig. 8b shows that the UA selectivity increases with the cobalt content. Nevertheless, the two highest contents (14.7 and 27.3 wt%) give nearly the same selectivity (around 86%) at citral isoconversion.

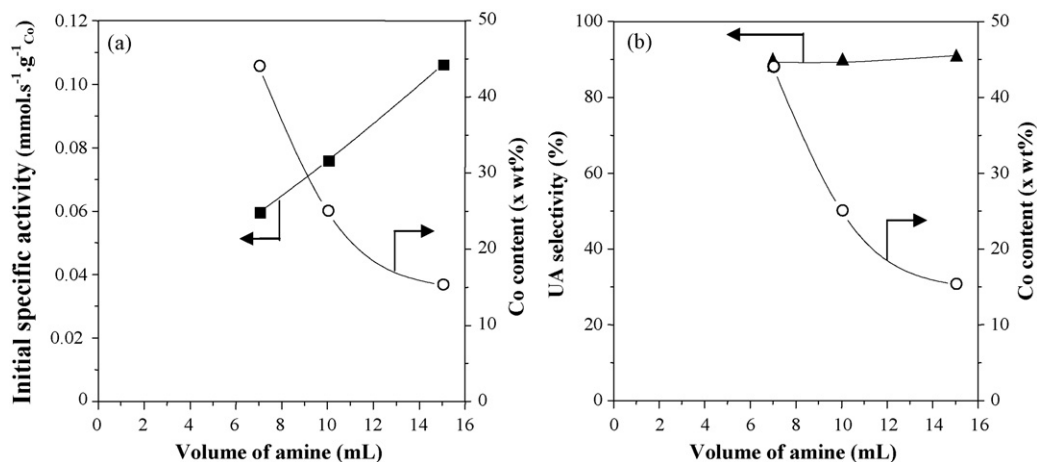
#### 3.3.2. Influence of the amine volume introduced during the ME-II catalysts preparation

The catalytic properties of the Co(16)-ME-II samples prepared with different amounts of amine (7–15 mL) were evaluated in citral hydrogenation (Fig. 9). The initial specific activity increases with the volume of amine, therefore decreases when the cobalt content increases (Fig. 9a). On the other hand, the UA selectivity remains similar and closed to 90% for the three catalysts whatever the volume of amine, i.e. whatever the cobalt content (Fig. 9b). This last result can be related to the fact that these samples present the same proportion of β H–Co species ( $\approx 70\%$ ) as detected by H<sub>2</sub>-TPD (Table 2). According to Table 2, the UA selectivity of the various ME catalysts seems in relation with the proportion of β H–Co species, the more the UA selectivity is high, the more the proportion of β H–Co species is important. In Ref. [10] concerning impregnated Co catalysts, we already observed that the samples with the highest UA selectivities present these particular H–Co species labelled β. Therefore, this work confirms that the metallic sites which desorb the β H–Co species are the key factor for C=O hydrogenation during citral hydrogenation on Co-supported catalysts. Rodriguez et al. [27–29] studied Co/SiO<sub>2</sub> catalysts prepared by impregnation for selective hydrogenation of crotonaldehyde. These authors largely characterized the catalysts structure by various techniques, including H<sub>2</sub>-TPD and diffuse reflectance FTIR spectroscopy (DRIFTS) of adsorbed CO. They concluded that the sites adsorbing β hydrogen species dominate in relation to those adsorbing γ and σ hydrogen species when an intermediate or strong interaction between the cobalt and the silica support exists. They also identified by DRIFTS of CO adsorption four different metallic superficial structures at 2050, 2030, 2005 and 1985–1930 cm<sup>-1</sup>, respectively. As they obtained a good correlation between the ratio of the hydrogen species  $\beta/(\gamma + \sigma)$  and the ratio of intensity of the three bands  $I_{2030}/I_{(2005+1950)}$  (when  $I_{2030}$ ,  $I_{2005}$  and  $I_{1950}$  correspond to the intensity of bands at 2030, 2005 and 1985–1930 cm<sup>-1</sup>, respectively),

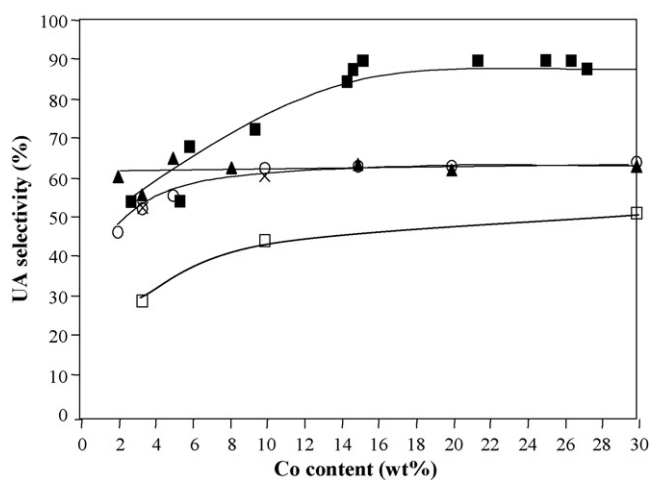




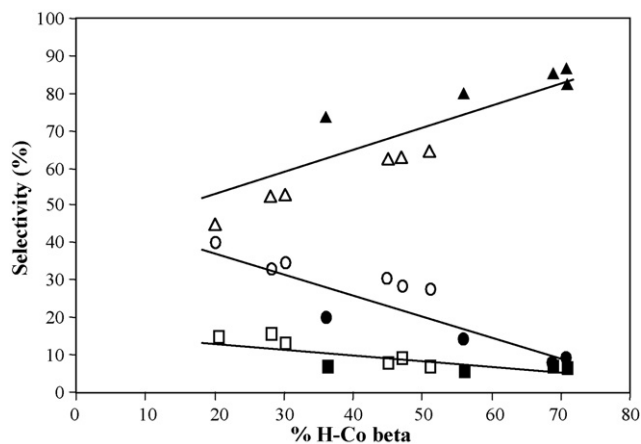
**Fig. 8.** Citral hydrogenation on Co/SiO<sub>2</sub> catalysts prepared by ME-I protocol: (a) initial specific activity as a function of Co content and (b) unsaturated alcohols selectivity as a function of Co content (at 30% citral conversion).



**Fig. 9.** Citral hydrogenation on the xCo(16)-ME-II catalysts prepared with various amounts of amine: (a) initial specific activity and Co content as a function of the volume of amine; (b) unsaturated alcohols selectivity (at 30% citral conversion) and Co content as a function of the volume of amine.



**Fig. 10.** Unsaturated alcohols selectivity as a function of Co content (at 30% citral conversion) on Co-supported catalysts prepared by w/o microemulsion (ME) or impregnation (IMP) method: (■) Co-ME/SiO<sub>2</sub>; (▲) Co-IMP/SiO<sub>2</sub>-HS; (○) Co-IMP/SiO<sub>2</sub>-LS; (□) Co-IMP/Al<sub>2</sub>O<sub>3</sub>; (×) Co-IMP/TiO<sub>2</sub> (HS = high surface area; LS = low surface area).



**Fig. 11.** Correlation between the selectivities (at 30% citral conversion) and the percentage of the  $\beta$  H-Co species for Co-supported catalysts prepared by w/o microemulsion (ME, full caption) or impregnation (IMP, empty caption) method: (▲, △) unsaturated alcohols; (●, ○) citronellal; (■, □) citronellol.

#### 4. Conclusion

Co/SiO<sub>2</sub> catalysts with different metal loadings were prepared by w/o microemulsion using a nitrate-based precursor salt, TEOS as silica source, CTAB as surfactant, trimethylamine as precipitating agent, water and hexanol as solvents. After preparation, the systems were reduced at 450 °C and tested for the selective hydrogenation of citral. The performances of these Co/SiO<sub>2</sub> samples were compared to those of previously studied Co-impregnated catalysts [10].

The main conclusions of the present paper are the followings:

- (i) Many parameters must be controlled during the preparation of supported catalysts by microemulsion method. This work put in evidence the determining role of the hexanol/water ratio and of the precipitating agent quantity to obtain Co/SiO<sub>2</sub> systems with expected metallic content and with a good synthesis yield.
- (ii) In contrast with Co impregnated catalysts, TEM revealed that ME-derived samples present well homogeneously dispersed Co particles on the silica support. Moreover, these particles present two shapes: spherical and cylindrical.
- (iii) Beyond a 15 wt% Co content, the selectivity to unsaturated alcohols is markedly higher on the microemulsion catalysts compared to the impregnated ones (90% versus 45–65% depending on the nature of the support). This result can be directly related to the higher proportion of β H–Co species detected by H<sub>2</sub>-TPD on these microemulsion samples.

In our previous study [10], we suggested a relationship between the structure of the Co-impregnated catalysts and their selectivity for citral hydrogenation. The present work confirms that the selectivity to UA increases with the proportion of metallic sites able to desorb β H–Co species. Finally, the present study highlights the interest to use the w/o microemulsion to improve the selectivity to unsaturated alcohols of Co-supported catalysts.

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