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Pt/CeO_2 catalysts in selective hydrogenation of crotonaldehyde: high performance of chlorine-free catalysts

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The hydrogenation of crotonaldehyde was conducted in gaseous phase, at atmospheric pressure, on Pt/CeO_2 catalysts prepared from metal precursors containing or not chlorine. The activities and selectivities were studied, at 253 K, as a function of the reduction temperature of the catalyst (473–993 K). The Pt/CeO_2 catalyst, prepared from tetraammineplatinum nitrate, led to 5–20% crotyl alcohol selectivity when the catalyst was reduced at low temperature (473–673 K), while increasing the reduction temperature up to 973 K, the crotyl alcohol selectivity reached more than 80%. Repeating a series of experiments after a re-calcination treatment at 673 K, the selectivity decreased to only 40% after 473 K reduction to reach again more than 80% after 673 K reduction temperature. A phase transformation of Pt to $CePt_5$ was observed by XRD analysis after 973 K reduction treatment. Differently on Pt/CeO_2 catalysts containing chlorine, prepared from either chloroplatinic acid or tetraammineplatinum chloride, the crotyl alcohol selectivity never exceeded 30% and did not form alloy up to 973 K reduction temperature. The main results are interpreted considering that the activity of $CePt_5$ for C=C hydrogenation is low compared to unmodified platinum catalyst and the activation of the carbonyl bond is induced by the presence of oxygen vacancies sites located at the interface between ceria and the metallic particles. The results are in good accordance with the information known at the present time on the metal–support interactions in Pt deposited on CeO_2.

Keywords: platinum, cerine, metal–support interactions, crotonaldehyde, selective hydrogenation

1. Introduction

The selective hydrogenation of α,β-unsaturated aldehydes is an important reaction in the production of many pharmaceutical, agrochemical, and fragrance compounds. One important step is the selective hydrogenation of the carbonyl bond, the olefinic bond remaining unaffected. This is generally achieved in a homogeneous phase using aluminium lithium hydride ($AlLiH_4$), aluminium alcoholates ($Al(OCH(CH_3)_2)_3$) or sodium borohydride ($NaBH_4$) as hydrogenating agent. The replacement of this process by a heterogeneous catalytic hydrogenation process is very attractive to facilitate the experiment and eliminate the waste production. Our approach to realize this objective is to optimize the catalyst for the selective hydrogenation of 2-butenal (crotonaldehyde) into 2-buten-1-ol (crotyl alcohol) in gaseous phase and to further extent the study in more industrial conditions, in liquid phase with more complicated molecules. In fact we could expect that the catalyst which is efficient for selective hydrogenation of a simple molecule as crotonaldehyde, will be still more efficient to hydrogenate selectively the carbonyl bond of larger molecules (3-methyl-2-butenal, 3-phenylpropenal, etc.) in which the hydrogenation of the C=C group is impeded by steric constraints.

Monometallic catalysts supported on Al_2O_3 or SiO_2 lead mostly to the formation of saturated aldehydes. To improve the selectivity towards unsaturated alcohols, the use of additives (promoters), bimetallic catalysts or easily reducible supports has been proposed [1]. A higher selectivity is commonly observed simultaneously to a lower activity. In fact the metallic sites, usually active for the hydrogenation of the olefinic bond, are transformed, by interaction with the promoter (or second metal or support), into polar sites to activate the carbonyl group. This is the typical catalytic behavior in crotonaldehyde hydrogenation of platinum deposited on TiO_2 in which an increase in selectivity was found simultaneously with an increase in the reduction temperature (until 773 K). This phenomenon was related with the so-called strong metal–support interaction (SMSI) effect in which the metal particle is thought to be covered by reducible oxide species when the reduction temperature reaches 773 K and new catalytic sites are created for the carbonyl adsorption. However, the selectivity of this system was found to reach a modest value [2–4] or, if it was initially high, it was decreasing rapidly with the time on stream [5]. More recently the Pt/ZnO catalysts [6] were found to be much more efficient. In this case it was clearly established that the unsaturated alcohol selectivity was increasing when Pt–Zn alloyed particles were formed and in addition a remarkable promoter effect of chlorine was observed.

At the present time a general description of the active sites involved in the carbonyl hydrogenation of α,β-unsaturated aldehyde on platinum deposited on reducible oxide cannot be formulated. For this purpose we have explored more numerous catalytic systems already known

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for their SMSI properties. In this sense we have studied the performances of Pt/CeO$_2$ catalysts in the title reaction knowing that SMSI effects in this system occur at higher reduction temperature compared to TiO$_2$. Moreover, Sepulveda et al. [7] have already noticed some beneficial effects of ceria at the first stages of the reaction in the gas phase hydrogenation of crotonaldehyde over platinum catalysts reduced at 773 K. In this paper, we present the results of the crotonaldehyde hydrogenation on Pt/CeO$_2$, prepared from different metallic salt precursors, containing or not chlorine, as a function of the catalyst pretreatments (reduction from 473 to 973 K, re-calcination at 673 K followed by re-reduction).

2. Experimental

2.1. Catalyst preparation

Three nominal 5% Pt/CeO$_2$ catalysts, A, B, and C, were prepared by wet impregnation of CeO$_2$ using an aqueous solution of, respectively, tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$), hexachloroplatinic acid (H_2PtCl_6) and tetraammineplatinum(II) chloride monohydrate ($Pt(NH_3)_4(Cl)_2 \cdot H_2O$). The water was slowly eliminated by evaporation on a hot plate. The samples were dried overnight at 383 K, calcined in air at 673 K for 4 h and stored until use. The contents of metal and chlorine were analyzed before and after use at CNRS, Vernaison, France (table 1).

The metallic salts were supplied by Strem Chemicals. CeO$_2$, Rhône-Poulenc, 240 m^2/g, was calcined in air at 1073 K for 8 h before impregnation. By this treatment the surface area decreased to 54 m^2/g. The surface area of the catalysts after different pretreatments was also measured (table 1) in a Coulter SA 3100 instrument, using BET calculation.

2.2. Catalytic test

Catalytic tests were carried out in a glass reactor, operating at atmospheric pressure. Changing the pumping rate at the end of the flow line varied the total gas flow, controlled by a flowmeter. The crotonaldehyde supplied by Fluka puriss and stored in argon was used as received. A known quantity of crotonaldehyde (30–280 μl) was drawn up from the bottle using a tight syringe and introduced through a vaccine cap into a reservoir, installed on-line and maintained at 273 K; therefore, crotonaldehyde at constant partial pressure (8 Torr) was carried over the catalyst by the hydrogen flow. The H$_2$ gas was first purified by passing through a trap, maintained at room temperature, containing the Pt/Al$_2$O$_3$ catalyst mixed with zeolite to remove oxygen and water. A further purification was made through

Table 1
Hydrogenation of crotonaldehyde on 5% Pt/CeO$_2$ at 353 K.[a]

	First pretreatment cycle calcination 673 K						Second pretreatment cycle recalcination 673 K			
	red.T (K): 473	573	673	773	873	973	red.T (K): 473	573	673	773
					A (precursor $Pt(NH_3)_4(NO_3)_2$)					
Surface area	54.6	56.3	52.5	64.9	52.3	36.9	37.9	43.8	46.4	36.6
Activity (μmol/s g-Pt)	24.8	48.07	55.9	48.7	14.4	2.1	13.2	15.1	13.7	10.4
Selectivity (%)										
Hydrocarbons	0.9	0.8	0.1	0.1	0.5	1	0.5	0.3	1.1	1.5
Butanal	85.6	73.6	66.9	35.8	16.9	9.5	43.1	30.0	13.6	6.5
Butanol	6.0	16.1	16.9	17.1	8.5	5.5	9.9	16.7	8.5	4.9
Crotyl alcohol	*7.5*	*9.5*	*16.1*	*47.0*	*76.1*	*83.0*	*46.5*	*53.0*	*76.8*	*87.1*
					B (precursor H_2PtCl_6)					
Chlorine (%)	2.29	1.51	–	1.5	–	1.03	1.24	–	–	1.21
Surface area	54.6	–	–	–	–	51.7	–	–	–	–
Activity (μmol/s g-Pt)	55.4	80.2	150.8	57	30	12	30	30	26	24
Selectivity (%)										
Hydrocarbons	3.8	2.2	1.9	1.7	2	1.7	4.5	2.84	2.1	1.5
Butanal	88.6	75.9	72.5	69.5	61.6	65.3	83.5	63.5	60.3	59.3
Butanol	3.9	10.3	12.1	10	8.9	8.7	6.0	12.7	15.1	16.4
Crotyl alcohol	*3.7*	*11.6*	*13.5*	*18.8*	*27.5*	*15.2*	*6.0*	*21.0*	*22.5*	*23.0*
					C (precursor $Pt(NH_3)_4Cl_2$)					
Chlorine (%)	2.1	–	–	–	–	0.98	–	–	–	–
Surface area	54.6	–	–	–	–	52.7	–	–	–	–
Activity (μmol/s g-Pt)	30.3	35.4	36.4	50.3	46.2	11.7	17.4	16.6	17.1	16.8
Selectivity (%)										
Hydrocarbons	6.4	4.8	3.9	1.2	1.6	1.6	2.8	3.6	2.7	2
Butanal	87.7	84.5	80.2	60.2	56	70.6	74.1	78.6	62.7	71.7
Butanol	2.8	5.1	6.6	18.9	20.7	8.2	8.7	7.2	11.8	11.0
Crotyl alcohol	*3.1*	*5.7*	*9.2*	*19.7*	*22.5*	*19.4*	*14.4*	*10.5*	*22.7*	*15.3*

[a] $P_{\text{crotonaldehyde}} = 8$ Torr, $P_{H_2} = 752$ Torr.

a MnO trap at 293 K, installed just before the crotonaldehyde reservoir. Beyond the crotonaldehyde reservoir, the gas line was thermostated at about 333 K to avoid any condensation. The stability of the crotonaldehyde pressure and the duration of the experiment were controlled by two catharometers inserted upstream and downstream with respect to the reactor, enabling the crotonaldehyde flow rate (mol/s) to be measured. The reaction products were drawn off the flow line at different times during the catalytic run and analyzed by gas–liquid chromatography (GLC, with a 30 m long, 0.546×10^{-3} diameter DB-Wax column (J&W Scientific), at 358 K and using a flame ionization detector).

Before each catalytic experiment, the catalyst (between 20 and 200 mg) was reduced at the desired temperature for 1 h and cooled down to the reaction temperature (353 K) under H_2 flow. The reaction activities were calculated as equal to $\alpha F/\omega$, where α is the crotonaldehyde conversion, F the crotonaldehyde flow in mol/s, and ω the weight of platinum in g. The selectivity to the different products was calculated as the molar ratio of the selected product to the total formed products. The sensitivity factors are taken as 1 for crotonaldehyde, crotyl alcohol, butanal, butanol, and 1.4 for hydrocarbons.

2.3. X-ray diffraction analysis (XRD)

XRD analyses were carried out in a Siemens D5000 polycrystalline diffractometer using Cu K_α radiation. Some spectra were recorded in a rapid scanning mode, 2.0 s per step, step size 0.05° in 2θ range (5°–90°). Such spectra showed all the lines of the cerianite structure of CeO_2 (JCPDS, 34-0394) and in some cases, other lines characteristic of Pt (JCPDS, 4-0802) or $CePt_5$ (JCPDS, 17-0071). The spectra were recorded in 38.5°–42.5° 2θ range for better accuracy, with 0.01° in step size and 5.0 s per step. This corresponds to the region of the Pt and $CePt_5$(111) lines.

3. Results

When performing the catalytic test under crotonaldehyde and H_2 constant flow, at constant temperature (353 K), the overall activity was found to decrease during the time on stream to reach a quasi steady state after about 20 min. The selectivities reached constant values in a shorter time. The values of activity and crotyl alcohol selectivity obtained in the steady-state regime are reported in table 1 as a function of the reduction temperature.

For catalyst A, the activity rises to a maximum after 673 K reduction temperature (673 K red.T) and strongly decreases after 873 and 973 K red.T. After a second pretreatment cycle (re-oxidation at 673 K and re-reduction at 473 K), the catalyst does not recover totally its initial activity. However, the activity after 473 K red.T is higher than the one reached at the end of the first pre-treatment cycle and it remains nearly constant when increasing the reduction temperature. The crotyl alcohol selectivity increases steeply when the activity decreases to reach 76 and 83% after, respectively, 873 and 973 K red.T in the first pretreatment cycle. The re-oxidation followed by 473 K red.T treatment leads to a decrease in crotyl alcohol selectivity (46%) which re-increases up to 77–87% after 673–773 K red.T, respectively. The high selectivities (more than 80%) in the second pre-treatment cycle are obtained at a reduction temperature 200 K lower than in the first pre-treatment cycle. It is worthwhile to emphasize that these high crotyl alcohol selectivity values, obtained in the 5–50% conversion range, on the catalysts reduced at 973 K or after recalcination and rereduction at 773 and 873 K, are stable with the time on stream (figure 1); only the points in the

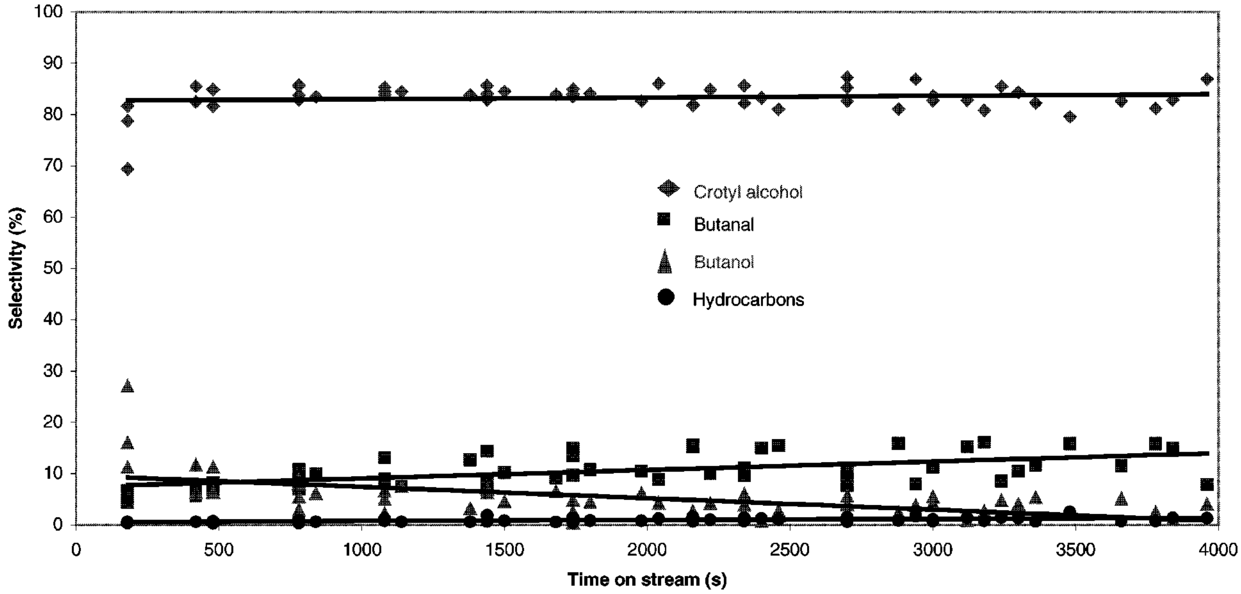

Figure 1. Hydrogenation of crotonaldehyde on 5% Pt/CeO$_2$ after reduction at 973 K (two experiments) and recalcination at 673 K + re-reduction at 773 and 873 K (three experiments); precursor Pt(NH$_3$)$_4$(NO$_3$)$_2$. Crotyl alcohol selectivity as a function of time on stream.

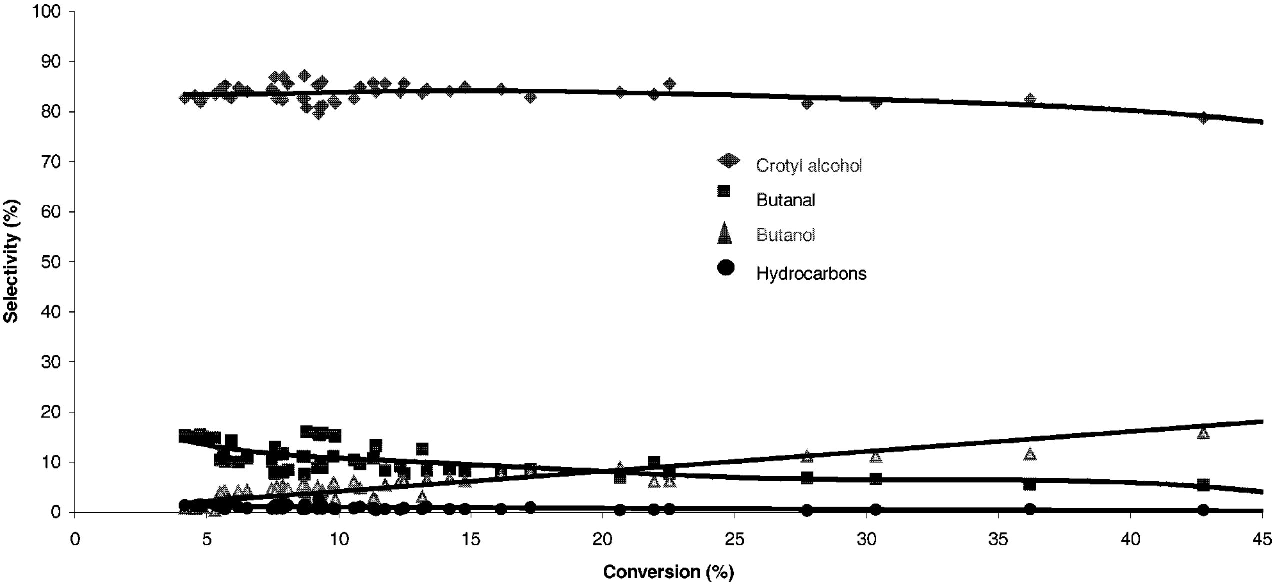

Figure 2. Hydrogenation of crotonaldehyde on 5% Pt/CeO$_2$ after reduction at 973 K (two experiments) and recalcination at 673 K + re-reduction at 773 and 873 K (three experiments); precursor Pt(NH$_3$)$_4$(NO$_3$)$_2$. Crotyl alcohol selectivity as a function of conversion.

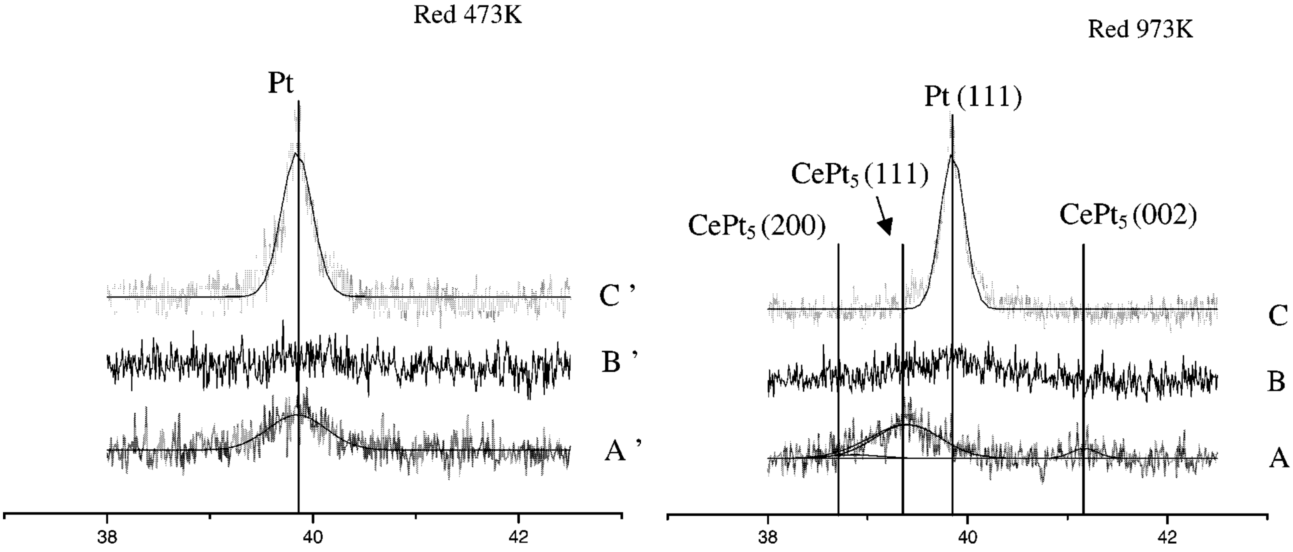

Figure 3. XRD analysis of 10% Pt/CeO$_2$ prepared from three different metal precursors (A′: Pt(NH$_3$)$_4$(NO$_3$)$_2$, B′: H$_2$PtCl$_6$, C′: Pt(NH$_3$)$_4$Cl$_2$) reduced at 473 and 973 K.

first minutes of the time of stream show higher quantities of butanol and then a decrease in butanal and crotyl alcohol selectivities. In fact, after elimination of these first points and using all the other points obtained during the time on stream for these five experiments we can draw the curves representing the product selectivities as a function of the conversion (figure 2). It can be noticed that the high crotyl alcohol selectivity is stable until 40% conversion.

For catalysts B and C the evolution of the activity as a function of the catalytic pre-treatments is qualitatively similar to catalyst A. The maxima in activity are obtained after 673 and 773 K red.T on, respectively, catalysts B and C. After the re-oxidation treatment, the activities are independent of the reduction temperature. Catalyst B is twice more active than catalysts A and C. Regarding the crotyl alcohol selectivity, for catalysts B and C, it does not exceed 30%, whatever the reduction temperature in the first or second pre-treatment cycle. These selectivities are obtained in the same range of conversion as on catalyst A.

X-ray diffraction has been used to elucidate the degree of platinum support interactions in the catalysts after various pre-treatments. However, analyzing the 5% Pt/CeO$_2$ catalysts A and B no lines were visible in the 38.5°–42.5° 2θ range whatever the reduction pre-treatment, suggesting that the metal particles are too small to give a diffraction pattern. We have performed XRD analyses on more loaded catalysts, 10% Pt/CeO$_2$ samples, A′, B′, and C′, prepared similarly to A, B, and C. The results are reported in figure 3. For C′ the Pt(111) line is well defined evidencing the presence of large particles at even 473 K red.T. In contrast, on catalyst B′ the particles are too small to give an XRD pattern, just a slight hump could be distinguished revealing the Pt(111) line after 973 K red.T. For catalyst A′, the Pt(111) line is visible at 473 K red.T, while after 973 K red.T the preceding line disappears to give a definite line at 39.45° and two small humps at 38.83° and 41.24° which correspond nicely to, respectively, (111), (200), and (002) reflections of the CePt$_5$ compound. Therefore, it is reasonable to conclude that the same phase transformation of Pt into CePt$_5$ would occur on the 5% Pt/CeO$_2$ catalysts after reduction at 973 K. On the other hand, it was checked that both 5 and 10% Pt/CeO$_2$ catalysts present a similar catalytic behaviour concerning the evolution of the crotyl alcohol selectivity as a function of the precursor salt and the catalytic pre-treatment. Therefore, we will take the liberty to analyse the catalytic results presented in this paper for the 5% Pt/CeO$_2$ catalyst using in parallel the characterization study performed on the 10% Pt/CeO$_2$ catalyst.

4. Discussion

It is worth recalling the most striking results emerging from this study and further discussed. An exceptional high crotyl alcohol selectivity, 83–87%, was obtained on the 5% Pt/CeO$_2$ catalyst prepared from nitrate precursor after reduction at high temperature while on the catalysts prepared from chloroplatinic acid or from tetraammineplatinum chloride the selectivity never exceeds 30%. We shall discuss these results taking into account the wealth of information available at present time concerning the particle size effects in the title reaction and the strong metal–support interactions (SMSI) in the M/CeO$_2$ (M = Pd, Pt, Rh) catalysts.

Englisch et al. [4] considered the crotonaldehyde hydrogenation as a structure sensitive reaction since they found an increase in the crotyl alcohol selectivity when studying a series of Pt/SiO$_2$ catalysts in which the Pt particle sizes were increased by rising the reduction temperature from 473 to 1073 K. The high fraction of Pt(111) on large particles was assumed to favor the adsorption of the C=O group of the α,β-unsaturated aldehyde in accordance with theoretical [8] and other experimental [9,10] works. If these conclusions are retained and applied to our work, catalyst C which contains the largest metal particles compared to catalysts A and B, as deduced from the XRD pattern, would be expected to lead to the highest crotyl alcohol selectivity. As this is not the case, it is concluded that the particle size is not the key factor which governs the selectivity in our studied catalysts. In contrast, the presence of chlorine found in catalysts B and C after calcination and reduction treatments (table 1) rather seems to be the driving force of the observed catalytic behaviour. The effect of residual chlorine atoms in M/CeO$_2$ catalysts originating from the catalyst preparation method was already mentioned to affect different processes as hydrogen and CO chemisorption [11–13], benzene hydrogenation [14], oxido-reduction reactions of CO–CO$_2$ in gas exhaust treatment [15–17]. In fact the Cl$^-$ anions, released from the metallic salt, move on the ceria support and, during the reduction treatment, replace the O^{2-} to form CeOCl species in which cerium ions have been reduced from Ce^{4+} to Ce^{3+} [18]. These CeOCl species are proposed to block the oxygen vacancies created at the catalyst surface during the high-temperature reduction step and then to block the operations of both direct and back spillover process of hydrogen or oxygen [19]. Now let us assume that the same processes occur in our catalysts during the reduction treatment. It means that oxygen vacancies are present in the interface domain between metal and ceria when catalyst A is reduced at high temperature while on catalysts B and C they are filled by Cl$^-$. Therefore, catalysts B and C would react as Pt particles unmodified by the support since the interactions between Pt and ceria would be prevented by the presence of CeOCl species; therefore they give rise to the C=C hydrogenation reaction. Differently, crotyl alcohol is formed on catalyst A by a mechanism which would take place at the interface between metal and support where the carbonyl group of crotonaldehyde is activated due to the presence of O^{2-} vacancies. Moreover, the large decrease of the C=C bond hydrogenation observed on this A catalyst reduced at 973 K could be in addition attributed to the phase transformation of Pt into CePt$_5$. However, although platinum alloys are generally considered as poor catalysts compared to platinum more investigations are required to understand the catalytic behavior of CePt$_5$. Bernal et al. [20] had observed a similar phase change when the Pt/CeO$_2$ catalyst was reduced at 1173 K. In our case a lower temperature of the phase transformation is found which could be due to the higher surface area of our support (38 m^2 after 973 K red.T) compared to the sample used in [20] (5 m^2/g).

The formation of CePt$_5$ alloy is clearly shown in our experiment when the A type catalyst is reduced at 973 K while no alloy was formed on B and C type catalysts for similar pre-treatments. That could be once more explained by the blocking effect of chlorine atoms at the interface of the metal particle and the support. The CeOCl species would be more stable than the CeO$_x$ species and then a deeper reduction of cerium and interactions with platinum to form alloy would not occur.

It is important noting that the SMSI process as it is revealed in our reaction (increase of crotyl alcohol selectivity) is only partly reversible. When, after a reduction treatment at high temperature, the A catalyst is re-calcined and re-reduced at low temperature, it does not recover the initial state. It suggests that the oxygen vacancies which are created after high-temperature reduction and certainly re-filled during the re-calcination treatment re-form at low reduction temperature.

5. Conclusion

On chlorine-free Pt/CeO$_2$ catalyst the crotyl alcohol selectivity in crotonaldehyde hydrogenation increased up to more than 80% when the reduction temperature of the catalyst reached 973 K. That ranks this catalyst among the best catalysts for this reaction. Moreover, this high selectivity was found stable during the time on stream and was observed up to 40% conversion. Afterwards a re-calcination treatment at 673 K followed by mild re-reduction temperature gave rise to only a slight decrease of this selectivity and 673 K reduction temperature was then sufficient to induce the recovery of the high selectivity. As long as crotyl alcohol selectivity is taken into account the performances of Pt/CeO_2 are comparable to the ones of Pt/ZnO [6] and superior to Pt/TiO_2 [4]. Continuing the comparison between these three catalytic systems it is worthwhile noticing the different reduction temperatures necessary to obtain high selectivity, 473, 773, and 973 K, respectively, on ZnO, TiO_2, and CeO_2. These values progress in line with that observed for the SMSI formation [19,21]. The dramatic role of chlorine has also to be underlined since it affects negatively Pt/CeO_2 and it is a promoter in Pt/ZnO. In addition, when Pt/CeO_2 as well as Pt/ZnO formed very selective catalysts, the platinum phase was found transformed into alloy, $CePt_5$ and PtZn, respectively.

A large part of these features are interpreted as originating from strong metal–support interactions (SMSI) and then provide additional information to characterize the so-called SMSI effects reported elsewhere [19]. However, an investigation on the intrinsic properties of $CePt_5$ alloy in this reaction is necessary to complete the information and then to define confidently the selective hydrogenation mechanism of crotonaldehyde on these catalytic systems.

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