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Promoting Effect of Ceria on the Gas Phase Hydrogenation of Crotonaldehyde over Platinum Catalysts

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The platinum-ceria interaction, induced after high temperature reduction of platinum based catalysts, has been used to improve the selectivity towards crotyl alcohol in the gas phase hydrogenation of crotonaldehyde. Three catalysts have been used in this study, Pt/SiO_2, Pt/CeO_2, and Pt/CeO_2/SiO_2. They have been characterized by X-ray diffraction and temperature-programmed reduction, and their catalytic behavior in the gas phase benzene hydrogenation and crotonaldehyde hydrogenation reactions have been determined after reduction treatments in flowing hydrogen at 473 and 773 K. Results obtained in the gas phase hydrogenation of crotonaldehyde show that the presence of ceria clearly promotes the hydrogenation of the carbonyl bond when the sample is reduced at high temperature, this being attributed to the presence of oxygen vacancies or Ce^{3+} cations in the neighbourhood of platinum particles, induced by the thermal treatment under hydrogen. The promoting effect is more important for Pt/CeO_2; crotonaldehyde hydrogenation on this catalyst yields up to 80% crotyl alcohol after reduction at 773 K, whereas it produces 100% butanal after reduction at only 473 K. © 1998 Academic Press

1. INTRODUCTION

Unsaturated alcohols constitute a very important group of compounds for the chemical industry, as precursors to prepare fine chemicals. They can be obtained by hydrogenation of α,β-unsaturated aldehydes. This reaction can produce the saturated aldehyde (through the hydrogenation of the C=C bond), the unsaturated alcohol (through the hydrogenation of the carbonyl C=O bond), the saturated alcohol, and even the corresponding hydrocarbon. It is not easy to achieve a profitable selectivity towards the desired unsaturated alcohol with unpromoted metals, mainly due to the fact that the C=C bond is preferentially reduced by both thermodynamic and kinetic considerations. Thus, monometallic platinum catalysts usually hydrogenate the C=C bond with 100% selectivity, and it is necessary to promote the metal to obtain a certain selectivity towards the hydrogenation of the carbonyl bond. Support effects (1–5) and the addition of a second metal such as tin (5–10) or iron (5,10,11) have been commonly used to increase the catalytic selectivity towards the unsaturated alcohol.

It has been reported that the use of supports with SMSI (strong metal-support interaction) properties produces an important enhancement of the selectivity towards the unsaturated alcohols. Vannice *et al.* (2) compared the hydrogenation of crotonaldehyde (2-butenal) over platinum dispersed on silica, alumina, and titania, after either a high- or a low-temperature reduction. Whereas a 100% selectivity for butanal was obtained with the Pt/SiO_2 and Pt/Al_2O_3 catalysts, the high-temperature reduced Pt/TiO_2 yielded a 37% of crotyl alcohol (2-butenol). The authors attributed this effect to defect sites on titania created at the platinum–titania interface upon the reduction treatment at high temperature. Similar results were obtained by Yoshitake *et al.* in a study on the deuteration of acrolein on platinum supported on a series of partially reducible oxides: TiO_2, Y_2O_3, ZrO_2, and CeO_2 (12).

Cerium oxide has become one of the most studied and applied promoters in heterogeneous catalytic reactions during the last years, mainly due to its important role in the performance of three-way catalysts for the treatment of exhaust gas from automobiles (13). With regard to hydrogenation reactions, cerium oxide has been used both as support and additive in the hydrogenation of CO by metals such as Pd and Rh (14–16), where it favours the formation of oxygenates. Also, it has been reported that the addition of CeO_2 to Ru and Co (17) enhances the production of long chain hydrocarbons and alkenes. In all cases, the effects of ceria seem to be related to the activation of the C=O bond through the interaction of the oxygen atom with oxygen vacancies created at the ceria surface upon the reduction treatment.

The main objective of this study has been to analyse the promoting effect of ceria in the gas phase hydrogenation of crotonaldehyde on platinum based catalysts, both when it is used as support and when it is added as a promoter. To our knowledge, this is the first study in which ceria dispersed over an inert support has been used in the title or related reactions.

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2. EXPERIMENTAL

One of the support materials used in this study was SiO_2 (Silicagel 0.2–0.5 mm, pore diameter: ≈6 nm, from Acros), with a BET surface area (N_2 77 K) of 400 m^2g^{-1}. The Pt/SiO_2 catalyst was prepared by the incipient wetness method, impregnating the support with an ethanolic solution of H_2PtCl_6 of the appropriate concentration to load about 1 wt% Pt. Then, the sample was dried at 383 K and calcined in air at 673 K for 4 h. The CeO_2 support was prepared as follows: an aqueous solution of $(NH_4)_2CO_3$ was slowly added to a magnetically stirred boiling aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ (purity: 99.95%, from Ventron) at 423 K; the white precipitate of cerium carbonate formed was filtered, washed with deionized water, and dried overnight at 373 K in air; then, it was heated in air at 5 K min^{-1} up to 773 K and calcined at this temperature for 4 h. It had a BET surface area of 70 m^2g^{-1}. The Pt/CeO_2 catalyst was prepared as described above for Pt/SiO_2. Finally, a third support was prepared by impregnating the silica support with the minimum amount of aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ of the appropriate concentration to obtain a CeO_2 loading of 5 wt%. Then, the sample was dried overnight in air at 383 K and calcined at 673 K for 4 h. Platinum was introduced in the same way as the other catalysts to prepare catalyst Pt/CeO_2/SiO_2.

X-ray diffraction patterns of samples, both just calcined and reduced, were obtained with a JSO Debye-Flex 2002 system, from Seifert, fitted with a Cu cathode and a Ni filter, and using a 2° min^{-1} scanning rate.

Temperature-programmed reduction measurements on calcined catalysts were carried out in a U-shaped quartz cell, using a 5% H_2/He gas flow of 50 cm^3min^{-1} and about 0.15 g of sample. Hydrogen consumption was followed by on-line mass spectrometry and calibrated by carrying out the reduction of CuO and assuming that it is completely reduced to metallic copper.

Before the determination of their catalytic behaviour, the catalysts were reduced *in situ* in flowing hydrogen (50 cm^3min^{-1}) at 473 K or 773 K for 10 h, with a heating rate of 5 K min^{-1}. Benzene hydrogenation was studied in the temperature range from 323 to 398 K, with a reactant mixture containing purified hydrogen and benzene (Merck, reagent grade) in a H_2/C_6H_6 ratio of 11.0. Crotonaldehyde hydrogenation was performed at 313 K. The reduced catalysts were contacted with a reaction mixture (total flow: 50 cm^3min^{-1}; H_2/CROALD ratio of 26) formed by passing a hydrogen flow through a thermostabilized saturator (293 K) containing the unsaturated aldehyde. A Carbowax 20 *M* 58/90 25–30-m capillary column was used in both reactions to separate the reactants and the reaction products, which were analyzed by gas chromatography.

3. RESULTS AND DISCUSSION

3.1. *Characterization of the Fresh Catalysts*

X-ray diffraction has been used to elucidate the degree of platinum-support interaction in the catalysts after the calcination treatment, and its effect on the state of the catalysts after reduction in hydrogen. As indicated in the Experimental section, the fresh catalysts were stabilized by calcination at 673 K. It has been evidenced by Raman spectroscopy studies that calcination of Pt/CeO_2 catalysts results in the formation of Pt-O-CeO_2 species that further stabilizes the metal against sintering (18,19). These species are destroyed upon reduction, but their formation as a first step may influence the posterior behaviour of the reduced catalysts and, at least, may hinder the platinum sintering, yielding catalysts with better metal dispersion. Figure 1a shows the DRX pattern of the Pt/SiO_2 catalyst, in which the Pt(111) reflection at $2\theta = 39.65°$ and the Pt(200) reflection at $2\theta = 47.36°$ appear as two intense peaks, indicating a relatively large metal particle size. Figure 1b shows the XRD pattern of Pt/CeO_2/SiO_2. Now, the diffraction peaks corresponding to the ceria phase appear along with the peak for the Pt(111) reflection at 39.65°, which is broader and worse-defined than in Pt/SiO_2. Finally, Fig. 1c shows the DRX pattern of catalyst Pt/CeO_2; in this case, the peak of platinum at 39.65° is hardly discernible, indicating that, after calcination of Pt/CeO_2, platinum remains as a disperse phase. From the comparison of these figures it can be concluded that platinum is reduced to the metallic state in Pt/SiO_2 after the calcination treatment in air at 673 K, whereas it remains mainly in a disperse phase in the Pt/CeO_2 sample.

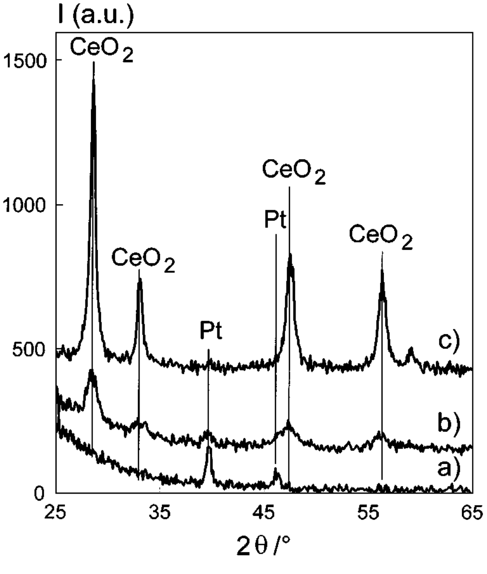

FIG. 1. X-ray diffraction patterns of calcined catalysts: (a) Pt/SiO_2; (b) Pt/CeO_2/SiO_2; (c) Pt/CeO_2.

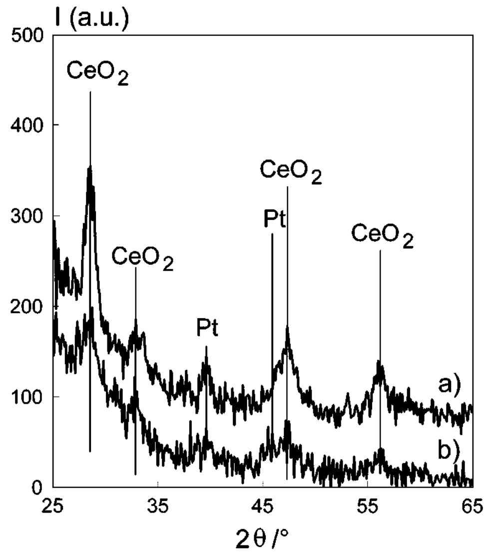

FIG. 2. X-ray diffraction patterns of catalyst $Pt/CeO_2/SiO_2$ reduced at 473 (a) and 773 K (b).

An intermediate situation is obtained in $Pt/CeO_2/SiO_2$, in which platinum placed close to the CeO_2 particles could be interacting with it and forming Pt-O-CeO_2 species, the remaining platinum being in the metallic state as in the unpromoted Pt/SiO_2 catalyst.

X-ray diffraction patterns of samples reduced at 473 K under hydrogen are similar to those obtained for the calcined samples, indicating that the low temperature reduction treatment does not affect the phase composition of the catalysts, at least at a level discernible by this technique. However, when the catalysts are reduced at 773 K, the XRD pattern of sample $Pt/CeO_2/SiO_2$ does change appreciably, those of Pt/CeO_2 and Pt/SiO_2 remaining unmodified. Figure 2 compares the XRD patterns of catalyst $Pt/CeO_2/SiO_2$ after reduction at 473 (a) and 773 K (b). It can be seen how the diffraction peaks corresponding to the CeO_2 phase are worse-defined after the high temperature reduction treatment. These changes could be ascribed to the partial reduction of ceria taking place in the presence of hydrogen and the metal phase at this temperature, with the subsequent formation of oxygen vacancies. The relatively high ceria dispersion in this catalyst facilitates the observation of the changes by XRD. The same process is likely to occur in the Pt/CeO_2 catalysts but, in this case, the amount of ceria affected is small, compared to the bulk support, and the changes are not reflected in the XRD pattern.

3.2. Temperature-Programmed Reduction

The degree of reduction of ceria in the promoted catalysts after the different reduction treatments has been estimated by analyzing the TPR curves obtained with a 5% H_2/He flow. Figure 3 shows the temperature-programmed reduction profiles of CeO_2 (dashed line) and Pt/CeO_2 (full line). The TPR profile of CeO_2 shows two peaks, centered at 830 (0.44 mmol H_2 g^{-1}) and 1200 K (1.4 mmol H_2 g^{-1}), which are assigned to the reduction of CeO_2 to Ce_2O_3. The first peak, at a lower temperature, has been related to the reduction of the surface oxygen layer of CeO_2, whereas the peak at a higher temperature is assigned to the reduction of bulk oxygen (20). The total hydrogen consumption (1.9 mmol H_2 g^{-1}) is lower than that corresponding to the complete reduction of CeO_2 to Ce_2O_3 (2.9 mmol H_2 g^{-1}), indicating that the reduction is not complete in the temperature range used (up to 1300 K). The TPR profile obtained with Pt/CeO_2 is also similar to those found in the literature (21-22); The first intense peak centered at 570 K (0.65 mmol H_2 g^{-1}) is assigned to the surface reduction of ceria in close contact with the metal, as well as the platinum reduction (breakdown of Pt-O-CeO_2 species created upon calcination). The second peak, at about 665 K (0.14 mmol H_2 g^{-1}) is related to the surface reduction of CeO_2 not in close contact with platinum. It has to be noted that this peak appears at a lower temperature than for pure CeO_2, this being related to the easier hydrogen availability by spillover from the metal surface. Finally, the peak at 1170 K (1.84 mmol H_2 g^{-1}) corresponds to the bulk reduction of CeO_2. In this case, the total amount of hydrogen consummed (2.7 mmol g^{-1}) is closer to the one theoretically expected (2.9 mmol g^{-1}), this indicating the easier reduction of ceria in the presence of platinum.

Figure 4 shows the TPR profile of catalyst $Pt/CeO_2/SiO_2$. The same features as for Pt/CeO_2 can be observed, but with a downward temperature shift for peaks centered at lower (500 K) and higher temperatures, the later being split into

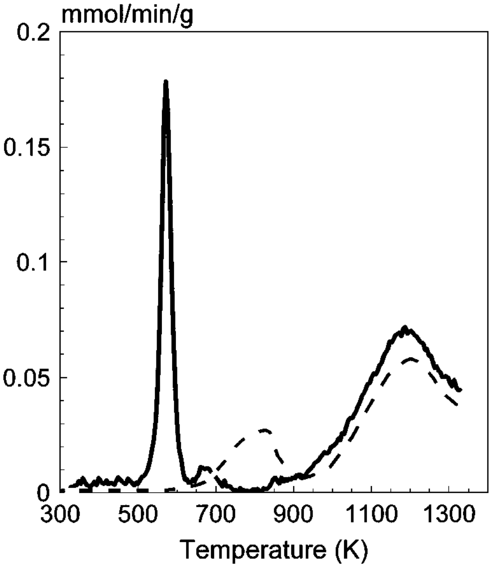

FIG. 3. TPR curves (H_2 consumption) for CeO_2 (dotted line) and Pt/CeO_2 (full line).

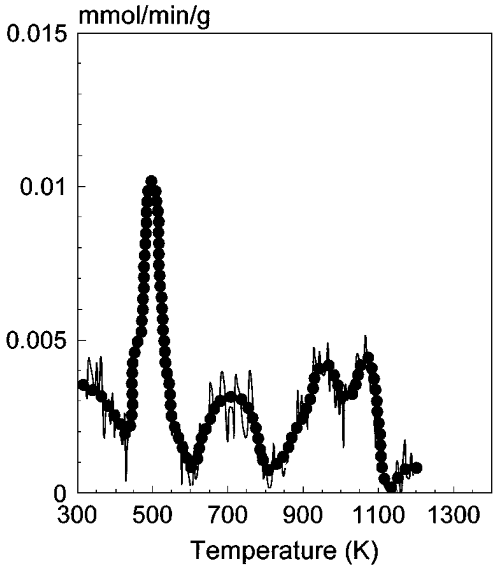

FIG. 4. TPR curve (H_2 consumption) for $Pt/CeO_2/SiO_2$.

two peaks at 950 and 1075 K). The peak centered at 700 K is again assigned to surface reduction of ceria not in close contact with platinum. The fact that this reduction takes place at a temperature somewhat higher than for Pt/CeO_2 could be due to the lack of continuity of the ceria surface (the system is composed of ceria particles deposited on the silica support), thus inhibiting the mobility of hydrogen spilt over from the metallic phase. In a similar way, the splitting of the high temperature peak would be due to the bulk reduction of ceria placed in the proximity of platinum (950 K) and at a larger distance (1075 K). In conclusion, it seems clear from these figures that the LTR treatment (473 K) of Pt/CeO_2 and $Pt/CeO_2/SiO_2$ does not produce ceria reduction; however, the HTR treatment (773 K) does produce the surface reduction of ceria, with the creation of oxygen vacancies and the presence of Ce^{3+} ions. Also, the surface reduction after the HTR treatment seems to be complete for Pt/CeO_2 but not for $Pt/CeO_2/SiO_2$, where the spillover of hydrogen from the metallic phase is hindered by the discontinuity of the ceria surface.

3.3. *Benzene Hydrogenation*

It is not easy to assess the metallic dispersion in supported metal catalysts containing ceria (23). First, the poor contrast between cerium and metals such as platinum makes it difficult to detect highly dispersed metal particles in transmission electron microscopy images. On the other hand, hydrogen or carbon monoxide chemisorption cannot be used because these gases can also be adsorbed on the ceria phase, especially in the presence of metals, giving rise to partial reduction of ceria (24,25). The benzene hydrogenation reaction has been recently used as a tool for estimating the percentage of metal exposed on low loaded ceria supported rhodium catalysts (26), because of the structure insensitive character of this reaction (27). Thus, the catalytic activity in this reaction will only depend on the number of metal atoms available at the surface of the catalysts and would not be affected by the metal particle size or the crystallographic plane. Under this assumption, the turnover rate (number of benzene molecules transformed per second and per surface metallic atom) should be the same, at a given reaction temperature, for the different catalysts. The amount of surface metal atoms could be then estimated from the catalytic activity (reaction rate) in benzene hydrogenation at a given temperature if the turnover number at the mentioned temperature is known. With this approach, Fajardie *et al.* (26) have obtained a very good correlation between the amount of exposed metal atoms determined by benzene hydrogenation and that calculated from hydrogen chemisorption in chlorine containing samples, where hydrogen spillover from the metal atoms to the ceria support is inhibited (28). In chlorine-free samples, hydrogen chemisorption was affected by hydrogen spillover to the support and, thus, benzene hydrogenation gave more accurate percentages of metal exposed. Also cyclohexane dehydrogenation, another structure insensitive reaction over platinum, has recently been used to assess the accessible metallic area in model three-way catalysts (29), although in this case, the reduction treatment of the catalysts was carried out at just 573 K. This temperature may be too low as to produce the SMSI effect between ceria and the noble metals. Indeed, the determination of the exposed metal area by using these reactions could be affected by this metal–ceria interaction.

Despite a large number of investigations, there is not a complete agreement about the origin of the metal–ceria interaction produced after high temperature reduction. Decoration of metal particles by cerium suboxides patches (classic SMSI effect), formation of metal–cerium alloy and electronic transfer from the metallic phase to the reduced ceria have been invoked. The first two possibilities would not affect the structure insensitive character of benzene hydrogenation or cyclohexane dehydrogenation, but any electronic effect of reduced ceria on the metal atoms would modify their intrinsic activity; in this case, the use of the mentioned reactions to determine the amount of metal exposed would be questionable. To avoid this possibility, i.e., the existence of electronic effects as the origin of the SMSI effect, it has been preferred in this study to use the catalytic activity for benzene hydrogenation as a reference to analyze the effect of the reduction treatments on the catalytic behavior towards a very different reaction, crotonaldehyde hydrogenation.

Table 1 reports the catalytic activity for benzene hydrogenation (μmol s^{-1} gPt^{-1}) and the apparent activation energies obtained, for each catalyst, after reduction at 473 and 773 K. The increase in the reduction temperature for

TABLE 1

Benzene Hydrogenation at 373 K; Catalytic Activities and Apparent Activation Energies after Reduction at 473 and 773 K

Catalyst	Reduction temperature (K)	Activity (μmol s^{-1} gPt^{-1})	E_a (kJ mol^{-1})
Pt/SiO_2	473	159.3	50
	773	8.4	60
$Pt/CeO_2/SiO_2$	473	415.5	42
	773	54.7	52
Pt/CeO_2	473	203.3	37
	773	62.3	40

Pt/SiO_2 causes an important decrease in its catalytic activity; as no SMSI effect can be expected in this case, this effect can be assigned to a loss of accessible platinum atoms. However, as mentioned above, no differences could be appreciated in the XRD patterns of the catalysts after reduction at both temperatures; i.e., the decrease in the number of surface platinum atoms is not due the presence of larger platinum particles after reduction at 773 K. Then, these results can only be explained by some degree of encapsulation of the platinum particles by the silica support after the HTR treatment.

After the reduction treatment at 473 K, catalyst $Pt/CeO_2/SiO_2$ shows the highest catalytic activity, more than twice that of Pt/SiO_2. This result agrees, at least from a qualitative point of view, with data obtained from XRD measurements, and it is an evidence of the stabilizing effect of ceria against platinum sintering in an oxidizing environment (22). The catalytic activity is lower in Pt/CeO_2, probably because an important fraction of platinum is interacting with the support and it is not active for the benzene hydrogenation reaction.

When catalysts are reduced at high temperature, 773 K, a drastic decrease in the activity for benzene hydrogenation is observed for the two ceria-containing catalysts. This effect is related to the strong metal–support interaction induced upon the thermal treatment. As commented above, several explanations have been invoked to explain these results. For example, it has been argued that the decrease in both hydrogen chemisorption and benzene hydrogenation activity observed in Pt/CeO_2 catalysts after high temperature reduction can be due to the formation of an intermetallic compound such as Pt_5Ce. This would cause the dilution of platinum and the consequent decrease of the amount of accessible platinum atoms (30). The coverage of platinum crystallites by ceria patches, after reduction, has also been invoked as the origin of the SMSI in the Pt-CeO_2 system (31), and it could also explain the above-mentioned results. Also an electronic transfer from the platinum particles to the partially reduced ceria, which would stabilize the anionic vacancies created after the reduction treatment, could account for these results; thus, the electron deficiency in platinum would strength the platinum-benzene bond, hindering the benzene hydrogenation. In conclusion, the presence of ceria hinders the platinum sintering upon the calcination treatment of the catalysts in such a way that after the LRT treatment (no SMSI effect) the ceria-containing catalysts are more active for benzene hydrogenation than the unpromoted Pt/SiO_2 catalyst. After reduction at 773 K, the SMSI effect induced in the ceria-containing catalysts causes an important decrease in activity. This decrease is even higher for Pt/SiO_2 but, in this case, it has been attributed to platinum encapsulation by the silica support. This different deactivation mechanism will be better appreciated after the analysis of the catalytic behavior in the gas phase hydrogenation of crotonaldehyde, where, in addition to the catalytic activity, the product selectivity will also be affected by the presence of ceria.

3.4. *Crotonaldehyde Hydrogenation*

Figure 5 shows the evolution of the overall activity (μmoles of crotonaldehyde transformed per gram of platinum and second) of catalysts Pt/SiO_2, $Pt/CeO_2/SiO_2$, and Pt/SiO_2 in the gas phase hydrogenation of crotonaldehyde, as a function of time on stream at 313 K, after being reduced at 473 K (LRT). Two different processes take place simultaneously during the first stages of the reaction: the reaction itself and the adsorption of the reactant (and, likely, also the products) on the support. The adsorption equilibrium is reached after about 5 min on stream, depending on the porous texture of the support and, consequently, initial reaction rates cannot be measured. During this stage, a

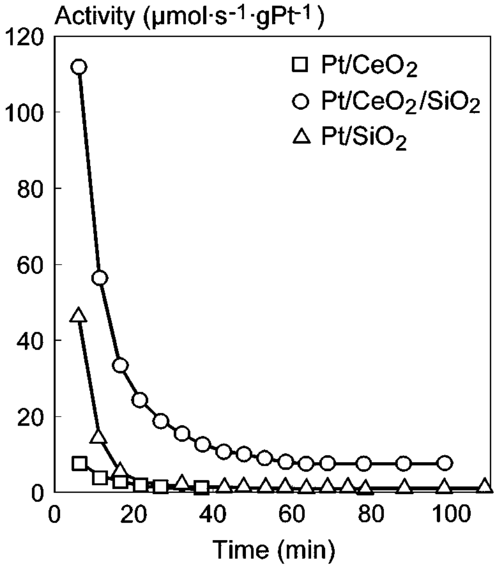

FIG. 5. Evolution of catalytic activity for crotonaldehyde hydrogenation for samples Pt/SiO_2, $Pt/CeO_2/SiO_2$, and Pt/CeO_2 as a function of time on stream at 313 K, after reduction at 473 K.

very high crotonaldehyde consumption is observed, which is not matched by the evolution of products. Once the carbon balance is obtained, i.e., once the amount of crotonaldehyde leaving the reactor is equal to that fed minus that transformed into the products, reaction rates deeply decrease during, at least, 20 min on stream. This deactivation of the catalysts has been related to the decarbonylation of the reactant molecule yielding carbon monoxide, which is irreversibly adsorbed on platinum at the reaction conditions (32). Unfortunately, limitations in the column used for the GC analysis made it impossible to determine the presence of C_3 hydrocarbons in our system, given that they cannot be separated from butane. It can be seen in Fig. 5 that catalytic activities after 6 min on stream follow the order $Pt/CeO_2/SiO_2 > Pt/SiO_2 > Pt/CeO_2$. Catalyst $Pt/CeO_2/SiO_2$ was also the most active for benzene hydrogenation, and this can be ascribed to its higher platinum dispersion, assuming the absence of SMSI effect after reduction at 473 K. However, Pt/SiO_2 and Pt/CeO_2 showed a similar activity for benzene hydrogenation after reduction at 473 K (somewhat higher for Pt/CeO2), but the ceria-supported catalyst is much less active for crotonaldehyde hydrogenation. This can be seen better in Fig. 6, where the ratios between the corresponding activities (after 6 min on stream) for crotonaldehyde hydrogenation and for benzene hydrogenation are plotted. After reduction at 473 K catalysts Pt/SiO_2 and $Pt/CeO_2/SiO_2$ present a very similar ratio, but that of Pt/CeO_2 is much lower. Vannice and Sen found similar results when comparing silica- and titania-supported platinum catalysts, the latter being reduced at low temperature (473 K) (2). After 90 min on stream, when a nearly steady-state activity has been achieved, catalysts Pt/SiO_2 and Pt/CeO_2 show a very close activity (1.0 and 0.8 $\mu mol\, s^{-1}\, gPt^{-1}$, respectively), whereas $Pt/CeO_2/SiO_2$ remains more active (7.5 $\mu mol\, s^{-1}\, gPt^{-1}$), despite the stronger deactivation.

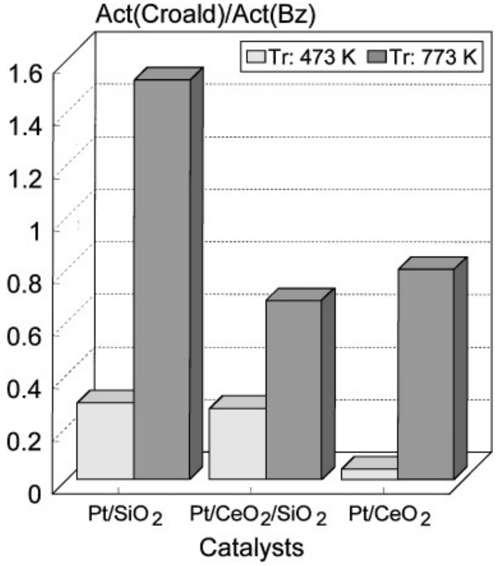

FIG. 6. Activity ratios for crotonaldehyde hydrogenation and benzene hydrogenation for catalysts reduced at 473 and 773 K.

The hydrogenation of a molecule such as crotonaldehyde, containing two conjugated double bonds (C=C and C=O) can yield a series of products, mainly depending on the preferential hydrogenation of one of them. Hence, the hydrogenation of the olefinic carbon-carbon double bond yields butanal, whereas the hydrogenation of the carbonyl C=O bond yields crotyl alcohol:

$$CH_3\text{-}CH{=}CH\text{-}CHO + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO$$

$$CH_3\text{-}CH{=}CH\text{-}CHO + H_2 \rightarrow CH_3\text{-}CH{=}CH\text{-}CH_2OH.$$

However, these compounds can be further hydrogenated to produce butanol and butane:

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$$

$$CH_3\text{-}CH{=}CH\text{-}CH_2OH + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2O.$$

And crotyl alcohol may also isomerize to yield butanal:

$$CH_3\text{-}CH{=}CH\text{-}CH_2OH \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO.$$

The extent of these secondary reactions is determined by the overall conversion, in such a way that selectivity towards crotyl alcohol decreases as the conversion degree increases (2,4,7,8).

The hydrogenation of crotonaldehyde over the three catalysts under study after reduction at 473 K, in the experimental conditions used, yields only butanal; i.e., only the olefinic C=C bond is hydrogenated. This is the expected behaviour for monometallic platinum catalysts in the absence of any support effect (2,4), although some authors have reported that an important selectivity to crotyl alcohol can be obtained with Pt/SiO_2 catalysts if platinum particles are large enough (32). This latter behaviour is not observed here even although the platinum dispersion is very low, especially for Pt/SiO_2. Thus, it can be concluded that the presence of ceria does not affect the selectivity of platinum after low temperature reduction (473 K).

The catalytic behaviour of ceria containing catalysts drastically changes after high temperature reduction (773 K). Figure 7 shows the evolution of the overall activity with time on stream at 313 K after reduction at 773 K. Now, the activities after 6 min on stream follow the order $Pt/CeO_2 > Pt/CeO_2/SiO_2 > Pt/SiO_2$. That is, after reduction at high temperature, the presence of ceria promotes the catalytic activity in a very important way. The activity ratios between crotonaldehyde hydrogenation and benzene hydrogenation after this reduction treatment are plotted in

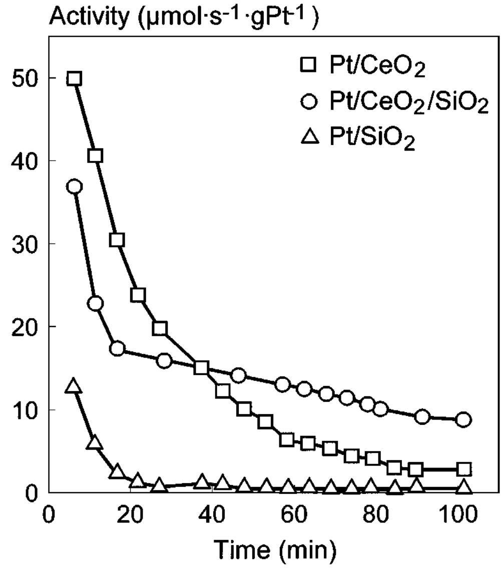

FIG. 7. Evolution of catalytic activity for crotonaldehyde hydrogenation for samples Pt/SiO$_2$, Pt/CeO$_2$/SiO$_2$, and Pt/CeO$_2$ as a function of time on stream at 313 K and after reduction at 773 K.

Fig. 6; all of them are enhanced with regard to those obtained after reduction at 473 K, but the increase is higher for Pt/SiO$_2$. This could be due to a particle size or morphology effect by which larger particles would be more active (32). Deactivation with time on stream strongly affects all the catalysts, but it is faster for Pt/SiO$_2$, in such a way that it loses 95% of its initial activity within the first 20 min on stream. After 90–100 min, when a nearly constant activity has been achieved, Pt/CeO$_2$/PtSiO$_2$ remains as the most active catalyst due to its slower deactivation as compared to Pt/CeO$_2$.

From these results, no relevant effect of ceria on the catalytic behaviour of platinum for the title reaction seems to be easily envisaged. After reduction at low temperature, catalytic activities at 313 K obtained with Pt/SiO$_2$ and Pt/CeO$_2$/SiO$_2$ are consistent with results found in the literature for similar Pt/SiO$_2$ catalysts (2) but the Pt/CeO$_2$ catalyst is much less active than expected. On the other hand, reduction at 773 K increases the catalytic activity for crotonaldehyde hydrogenation as compared to benzene hydrogenation, with Pt/CeO$_2$ and Pt/CeO$_2$/SiO$_2$ reaching nearly the same values. However, ceria does play its role in modifying the intrinsic selectivity of platinum in the title reaction. It has been mentioned above that the three catalysts produced only butanal after reduction at 473 K. When the reduction treatment is carried out at 773 K, Pt/SiO$_2$ also yields only butanal, but the ceria-containing catalysts produce both butanal and crotyl alcohol; i.e., these catalysts are able to hydrogenate the carbonyl C=O bond. No more hydrogenated products (neither butanol nor butane) are obtained, and thus, a higher selectivity to crotyl alcohol means a lower yielding of butanal.

Figure 8 plots the evolution of the selectivity towards crotyl alcohol with time on stream, at 313 K, after reduction at 773 K; in all cases, the overall conversion degree is below 8% (some values are indicated in the figure). The different behaviour of each catalyst is clearly evidenced. As mentioned above, unlike Pt/SiO$_2$ both Pt/CeO$_2$/SiO$_2$ and Pt/CeO$_2$ yield crotyl alcohol, the latter to a greater extent. Production of crotyl alcohol with Pt/CeO$_2$/SiO$_2$ is initially very low, but it increases with time on stream to yield around 10% after 20 min. On the other hand, the carbonyl bond is nearly selectively hydrogenated on Pt/CeO$_2$ in the first stages of the reaction, yielding around 80% crotyl alcohol and, then, selectivity decreases. This loss of selectivity, slow during the first 50 min and then faster, may be due to a different deactivation mechanism. It has to be noted that the selectivity values presented are not affected by the conversion degree at which they have been obtained, given that the expected effect is a decrease of the selectivity towards crotyl alcohol as the conversion degree increases, due to the occurrence of secondary reactions.

Some recent papers have dealt with the beneficial effect of using titania as support for platinum to prepare catalysts which are very selective towards the formation of crotyl alcohol from crotonaldehyde (2, 32). This effect, which is attained mainly after reduction at high temperature (773 K), is attributed to the removing of oxygen atoms from TiO$_2$ to form titania suboxides, TiO$_x$, which can decorate the platinum particles. Thus, crotonaldehyde would adsorb onto platinum through the C=C double bond, but the presence of coordinatively unsaturated Ti cations at the platinum–titania interface would activate the C=O bond through the interaction with the electron pair donor of the oxygen atom

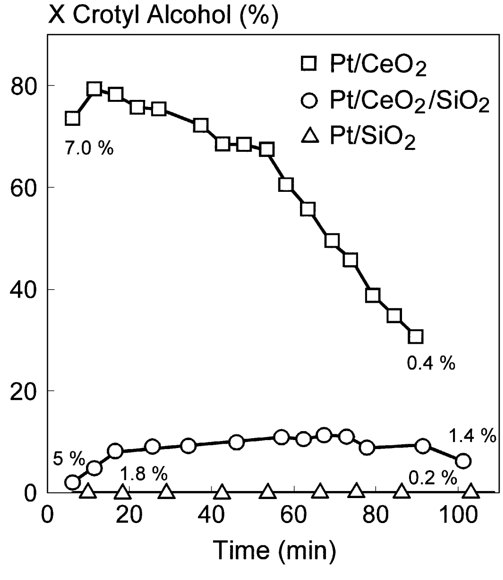

FIG. 8. Evolution of selectivity towards crotyl alcohol for catalysts Pt/SiO$_2$, Pt/CeO$_2$/SiO$_2$, and Pt/CeO$_2$ at 313 K and after reduction at 773 K.

in the carbonyl group. In this way, the carbonyl group is hydrogenated, by hydrogen adsorbed on platinum or spilt over from it to the Pt-TiO_x interface, at a higher rate than if low reduction temperatures are used, and enhanced selectivities towards crotyl alcohol are obtained.

This model can also be used to explain the observed behaviour of the ceria-containing catalysts in this study: creation of oxygen vacancies on ceria upon the high temperature reduction treatment, which are able to activate the carbonyl bond. Poisoning of these sites by strong adsorption of reactant and/or products would account for the loss of selectivity with time on stream, which is also accompanied by the decrease in the overall activity. This classical strong metal–support interaction (SMSI) effect, which is well established for titania supported catalysts, is not as straightforward in the Pt/CeO_2 system and, as mentioned above, the formation of a Pt-Ce alloy has also been invoked to explain the different behaviour of high temperature reduced Pt/CeO_2 catalysts (30). Results presented in this paper can add some light to this controversy.

Thus, the decrease in catalytic activity for benzene hydrogenation can be explained by: (i) the formation of Pt-Ce alloy, with the dilution of the active metal (Pt) by an inactive one (Ce); (ii) the decoration of platinum particles by patches of ceria suboxides; and (iii) electronic effects on platinum due to the partial reduction of ceria. The dilution of platinum with cerium (alloy formation) would affect the catalytic activity for crotonaldehyde hydrogenation as well. But it is difficult to understand how it can influence so strongly the selectivity towards the hydrogenation of the carbonyl bond, unless the preferred adsorption mode of crotonaldehyde onto the alloy surface is completely different from that on platinum. On the other hand, no evidences of platinum decoration by ceria have been obtained by HRTEM in the Pt/CeO_2 system (33), but the platinum particles are indeed surrounded by ceria (mostly in the Pt/CeO_2 catalyst), whose surface is partially reduced. In any case, it seems clear that the existence of oxygen vacancies or Ce^{3+} cations in the neighbourhood of platinum particles can explain the results obtained for the selectivity towards crotyl alcohol. The formation of Pt-Ce alloys and/or electronic effects may help to decrease the activity for the hydrogenation of the C=C bond, as has been shown in the platinum–tin system (7,8), which in turn favours the production of crotyl alcohol. The small induction period observed in catalyst Pt/CeO_2/SiO_2, during which the selectivity to crotyl alcohol increases from nearly 0 to about 10% (Fig. 8), could be explained by the partial oxidation of cerium atoms in the alloy under reaction conditions to yield active sites for activation of the carbonyl bond. This effect is not observed in the Pt/CeO_2 catalysts, because the amount of such sites after reduction at high temperature is high enough as to yield a very important selectivity to crotyl alcohol. Anyway, this is just a tentative explanation, given that the presence of such an alloy is not proved at this stage.

4. CONCLUSIONS

Cerium dioxide is able to promote the synthesis of crotyl alcohol from crotonaldehyde over platinum catalysts, by favouring the hydrogenation of the carbonyl bond. This effect, which is obtained only after high temperature reduction (773 K) of the catalysts, can be explained by the existence of oxygen vacancies, or coordinatively unsaturated Ce^{3+} cations, near the platinum particles after the reduction treatment. The interaction of the oxygen atom of the carbonyl group in crotonaldehyde with these vacancies can activate it, thus favouring its hydrogenation by hydrogen atoms adsorbed on the platinum particles or spilt over from them to the Pt-CeO_x interface. The main result is an enhanced selectivity towards crotyl alcohol, which is as high as 80% for Pt/CeO_2 during the first stages of the reaction. The selectivity is lower for the ceria-promoted platinum catalyst, Pt/CeO_2/SiO_2, probably due to the lower amount of ceria interacting with the platinum particles, compared with the ceria-supported platinum catalyst.

REFERENCES

1. Richard, D., Gallezot, P., Neibecker, D., and Tkatchenko, *Catal. Today* **6**, 171 (1989).
2. Vannice, M. A., and Sen, B., *J. Catal.* **115**, 65 (1989).
3. Blackmond, D. G., Oukaci, R., Blanc, B., and Gallezot, P., *J. Catal.* **131**, 401 (1991).
4. Coloma, F., Sepúlveda-Escribano, A., Fierro, J. L. G., and Rodríguez-Reinoso, F., *Appl. Catal. A: Gen.* **150**, 165 (1997).
5. Da Silva, A. B., Jordao, E., Mendes, M. J., and Fouilloux, P., *Appl. Catal. A: Gen.* **148**, 253 (1997).
6. Poltarzewski, Z., Galvagno, S., Pietropaolo, R., and Staiti, P., *J. Catal.* **102**, 190 (1986).
7. Coloma, F., Sepúlveda-Escribano, A., Fierro, J. L. G., and Rodríguez-Reinoso, F., *Appl. Catal. A: Gen.* **136**, 231 (1996).
8. Coloma, F., Sepúlveda-Escribano, A., Fierro, J. L. G., and Rodríguez-Reinoso, F., *Appl. Catal. A: Gen.* **148**, 63 (1996).
9. Marinelli, T. B. L. W., and Ponec, V., *J. Catal.* **156**, 511 (1995).
10. Marinelli, T. B. L. W., Nabuurs, S., and Ponec, V., *J. Catal.* **151**, 431 (1995).
11. Beccat, P., Bertolini, J. C., Gauthier, Y., Massardier, J., and Ruiz, P., *J. Catal.* **126**, 451 (1990).
12. Yoshitake, H., and Iwasawa, Y., *J. Chem. Soc. Faraday Trans.* **88**, 503 (1992).
13. Trovarelli, A., *Catal. Rev.-Sci. Eng.* **38**, 439 (1996).
14. Diagne, Idriss, H., Hindermann, J. P., and Kiennemman, A., *Appl. Catal.* **51**, 165 (1989).
15. Lavalley, J. C., Saussey, J., Lamotte, J., Breault, R., Hindermann, J. P., and Kiennemann, A., *J. Phys. Chem.* **94**, 5941 (1990).
16. Turner, M. L., Byers, P. K., and Maitlis, P. M., *Catal. Lett.* **26**, 55 (1994).
17. Guerrero-Ruiz, A., Sepúlveda-Escribano, A., and Rodríguez-Ramos, I., *Appl. Catal. A: General* **120**, 71 (1994).
18. Brogan, M. S., Dines, T. J., and Cairns, J. A., *J. Chem. Soc., Faraday Trans.* **90**, 1461 (1994).
19. Murrel, L. L., Tauster, S. J., and Anderson, D. R., *Stud. Surf. Sci. Catal.* **71**, 275 (1991).
20. Yao, H. C., and Yao, Y. F. Y., *J. Catal.* **86**, 254 (1984).
21. Trovarelli, A., Dolcetti, G., De Leitenburg, C., and Kaspar, J., *Stud. Surf. Sci. Catal.* **75**, 2781 (1993).

22. Diwell, A. F., Rajaram, R. R., Shaw, H. A., and Truex, T. J., *Stud. on Surf. Sci. Catal.* **71**, 139 (1991).
23. Duplan, J. L., and Praliaud, H., *Appl. Catal.* **67**, 325 (1991).
24. Jim, T., Zhou, Y., Mains, G. J., and White, J. M., *J. Phys. Chem.* **91**, 5931 (1987).
25. Le Normand, F., Hilaire, L., Kili, K., Krill, G., and Maire, G., *J. Phys. Chem.* **92**, 2561 (1988).
26. Fajardie, F., Tempére, J-F., Djèga-Mariadassou, G., and Blanchard, G., *J. Catal.* **163**, 77 (1996).
27. Bond, G. C., Garin, F., and Maire, G., *Appl. Catal.* **41**, 313 (1988).
28. Bernal, S., Calvino, J. J., Cifredo, G. A., Gatica, J. M., Perez Omil, J. A., Laachir, A., and Perrichon, V., *in* "Third International Congress on Catalysis Automotive Pollution Control, Capoc3, Brussels, April, 1994," p. 275.
29. Rogemond, E., Essayem, N., Frety, R., Perrichon, V., Primet, M., and Mathis, F., *J. Catal.* **166**, 229 (1997).
30. Meriaudeau, P., Dutel, J. F., Dufaux, M., and Naccache, C., *Stud. Surf. Sci. Catal.* **11**, 95 (1982).
31. Golunski, S. E., Hatcher, H. A., Rajaram, R. R., and Truex, T. J., *Appl. Catal. B: Env.* **5**, 367 (1995).
32. Englisch, M., Jentys, A., and Lercher, J. A., *J. Catal.* **166**, 25 (1997).
33. Datye, A. K., Kalakkad, D. S., Yao, M. H., and Smith, D. J., *J. Catal.* **155**, 148 (1995).