Selective hydrogenation of phenol to cyclohexanone over supported Pd and Pd-Ca catalysts: an investigation on the influence of different supports and Pd precursors

Salvatore Scirè*, Simona Minicò, Carmelo Crisafulli
Dipartimento di Scienze Chimiche, Università di Catania, V.le A. Doria 6, I-95125 Catania, Italy

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Abstract

The gas-phase selective hydrogenation of phenol to cyclohexanone has been investigated over supported Pd catalysts in order to clarify the role of the support, the Pd precursor and the addition of Ca in controlling activity, selectivity and stability of the catalytic system. The catalytic results showed that over monometallic Pd catalysts prepared by PdCl2 as precursor the order of activity and selectivity to cyclohexanone was the following: Pd/La2O3 > Pd/CeO2 > Pd/Al2O3. The same order of activity was observed over ex-Pd(CH3COO)2 catalysts. However, over these latter samples the selectivity to cyclohexanone was very high regardless of the support used. Addition of calcium strongly improved the catalytic performance of both ex-chloride and ex-acetate Pd catalysts supported on alumina, whereas no significant improvement was observed on Pd catalysts supported on CeO2 and La2O3.

On the basis of characterization data (CO chemisorption, TPD and FT-IR) reported in this paper it has been suggested that the acid-base properties of supported Pd catalysts strongly influence the adsorption-desorption equilibrium of the reactant and products, being responsible for directing the selectivity to the reaction products. The catalytic activity of the system appears to be, instead, mainly controlled by the palladium sites on which hydrogen is activated.

Keywords: Phenol hydrogenation; Cyclohexanone; Palladium; Alumina; Ceria; Lanthana; Precursor; Acidity; FT-IR

1. Introduction

Cyclohexanone is the key intermediate in the manufacture of nylon 6 [1]. Nowadays the direct single-step selective hydrogenation of phenol is becoming the preferred industrial process for the production of cyclohexanone, being more advantageous in terms of capital costs and energy savings than the two-steps process via cyclohexanol [1,2]. The selective hydrogenation is industrially carried out in gas phase at 1–2 bar over Pd/Al2O3 catalysts promoted with alkali or alkaline earth metals, which improve activity, selectivity to cyclohexanone and stability of the Pd/Al2O3 system [1–4]. In spite of this reaction being studied over a range of Pd [5–21] and Pt [21–23] based catalysts, the results reported on the influence of the support and the Pd precursor are yet rather contradictory. Several reports indicate that a basic support favours cyclohexanone formation [6–10] whereas others indicate that an acid support is beneficial [11,12]. The effective role of promoters on the reaction mechanism is also debated [6,7,11,13–15]. In two previous works,
carried out on alumina supported catalysts [7,15], we have observed that promoters cause both a variation of the H-adsorption on palladium, probably caused by a modification of the electronic surroundings of Pd induced by the promoter [15], and a modification of the acid–base characteristics of the support [7], leading to a change in the adsorption-desorption equilibrium of the adsorbed species (phenol and cyclohexanone). Both these two effects could be involved in modifying the catalytic performance of the Pd/Al₂O₃ system. However, with the data available it was impossible to discriminate between the contributions of each single effect on the different features of the catalytic performance (activity, selectivity and stability).

In order to elucidate these aspects, in this paper we report a study on the influence of the use of supports with different acid–base properties (La₂O₃, CeO₂, Al₂O₃) on the catalytic performance of supported Pd and Pd-Ca catalysts. Moreover the effect of different palladium precursors has been also investigated.

2. Experimental

Supported Pd catalysts were prepared by impregnation of supports with acidified (with HCl, pH 3) aqueous solutions of PdCl₂ (Engelhard) or toluene solutions of Pd(CH₃COO)₂ (Fluka). γ-Al₂O₃ (Harshaw; BET surface area 95 m² g⁻¹), CeO₂ (Aldrich; BET surface area 28 m² g⁻¹) and La₂O₃ (Aldrich; BET surface area 11 m² g⁻¹) have been used as supports. Calcium was added to the supports after addition of palladium by using Ca(NO₃)₂ as precursor. Chemical analysis of palladium and calcium was performed by atomic absorption measurements. CO chemisorption was carried out at room temperature using a pulse technique. Code, support, chemical analysis and CO/Pd ratio are reported in Table 1.

Phenol hydrogenation was carried out in a flow system using a tubular reactor at atmospheric pressure on powdered catalysts (80–140 mesh). Before catalytic activity measurements, catalysts were reduced in situ in flowing hydrogen at 400 °C for 1 h. The temperature of reaction was varied between 120 and 220 °C. Due to the difficulty of operating with pure phenol, an ethyl alcohol solution (ratio 1:1 by weight) was employed. Under the experimental conditions used, ethyl alcohol did not give hydrogenation and/or decomposition products, in accordance to literature data [6]. The reaction mixture was introduced by a syringe pump into a preheated zone maintained at 160 °C and vaporized into a N₂ stream. Then, before passing through the catalyst, the mixture was mixed with H₂ (H₂/phenol = 10). Analysis of the reaction mixture was carried out by gas chromatography (Hewlett Packard Model 5890 Series II with flame detector). The GC column employed was a 0.2% Carbowax 1500 on Carbopak C (60–80 mesh). Quantitative analysis was performed by a Hewlett Packard HP3394A electronic integrator. Preliminary runs carried out at different flow-rates showed the absence of external diffusional limitations. The absence of internal diffusion limitations was verified by running experiments with crushed pellets at different grain size.

<table>
<thead>
<tr>
<th>Code</th>
<th>Support</th>
<th>Chemical Composition</th>
<th>CO/Pd</th>
<th>CO/Pd ratio</th>
<th>CO/Pd ratio</th>
</tr>
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<tbody>
<tr>
<td>APd</td>
<td>γ-Al₂O₃</td>
<td>0.87</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APdCa</td>
<td>γ-Al₂O₃</td>
<td>0.89</td>
<td>0.93</td>
<td>0.20</td>
<td></td>
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<tr>
<td>APd(AC)</td>
<td>γ-Al₂O₃</td>
<td>0.94</td>
<td>0.20</td>
<td></td>
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</tr>
<tr>
<td>APdCa(AC)</td>
<td>γ-Al₂O₃</td>
<td>0.92</td>
<td>0.87</td>
<td>0.26</td>
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<tr>
<td>CPd</td>
<td>CeO₂</td>
<td>0.91</td>
<td>0.08</td>
<td></td>
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<tr>
<td>CPdCa</td>
<td>CeO₂</td>
<td>0.88</td>
<td>0.92</td>
<td>0.09</td>
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<tr>
<td>CPd(AC)</td>
<td>CeO₂</td>
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<tr>
<td>CPdCa(AC)</td>
<td>CeO₂</td>
<td>0.90</td>
<td>0.89</td>
<td>0.26</td>
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<tr>
<td>LPd</td>
<td>La₂O₃</td>
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<td>LPdCa</td>
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<td>0.16</td>
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<tr>
<td>LPdCa(AC)</td>
<td>La₂O₃</td>
<td>0.89</td>
<td>0.90</td>
<td>0.10</td>
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</table>
For IR studies the powdered samples were compressed (using a pressure of $15 \times 10^3$ bar) into thin self-supporting discs of about 25 mg cm$^{-2}$ and 0.1 mm thick. The disc was placed in an IR cell which allows thermal treatments in vacuum or in a controlled atmosphere. In the cell all samples were evacuated slowly increasing temperature up to 400°C and then reduced in pure H$_2$ at this temperature for 30 min. The sample was then evacuated at 400°C for 1 h and finally cooled at room temperature. CO or pyridine was then adsorbed on the samples at room temperature. In the case of CO the pressure was 2 mbar. In the case of pyridine, this substance, maintained at 5°C in a vessel, was adsorbed by opening the valve of the vessel for 15 s. Subsequent evacuations were then performed at room temperature or higher temperatures. Spectra were recorded with a Perkin-Elmer System 2000 FT-IR spectrophotometer with a resolution of 2 cm$^{-1}$.

Data are reported as difference spectra obtained by subtracting the spectrum of the sample before the admission of the adsorbate and are normalized to the same amount of catalysts per cm$^2$.

TPD experiments were carried out in a quartz U-shape reactor in a flow of He with a constant heating rate of 10°C min$^{-1}$. The desorbed products were detected by a quadrupole mass spectrometer (Sensorlab VG Quadrupoles). Before TPD all samples were reduced in flowing H$_2$ for 1 h at 400°C, maintained at this temperature for 1 h in flowing He and then cooled to 30°C always in a flow of He.

3. Results

3.1. Catalytic activity

Fig. 1(a) shows the catalytic activity expressed in terms of turnover numbers ($N$) measured at $T = 160$°C ($W/F = 25.7 \mu$g catal/1 s$^{-1}$) as a function of time on stream over monometallic Pd catalysts. It must be noted that turnover numbers were calculated by assuming a chemisorption stoichiometry CO/Pd = 1 [12,17,24]. The reaction temperature of 160°C has been chosen for this comparison considering that on all samples tested in this work the conversion of phenol reaches a maximum in the 150–170°C range, as previously reported in the literature on Pd/Al$_2$O$_3$ [5,6,15] and Pd/MgO [13,17]. The results of Fig. 1(a) show that on both series of catalysts (ex-chloride and ex-acetate) the order of activity observed is: Pd/La$_2$O$_3$ > Pd/CeO$_2$ > Pd/Al$_2$O$_3$. It can be also seen that Pd/CeO$_2$ and Pd/La$_2$O$_3$ samples, regardless of the precursor used, are very stable, showing no significant deactivation during 8 h of operations. On the contrary on both Pd/Al$_2$O$_3$ samples (APd and APd(AC)) a decrease in the activity with time can be observed. The deactivation is more relevant on the
ex-chloride sample, on which in 8 h the activity drops to less than half.

CO chemisorption data, reported in Table 1, show that the precursor used affects the dispersion of palladium on the catalytic surface. In fact, Pd catalysts prepared starting from Pd(CH$_3$COO)$_2$ exhibit a higher CO/Pd ratio compared to the corresponding ex-PdCl$_2$ samples. This observation is in accordance to the results reported in the literature by several authors [12,13,17,25,26].

Under the experimental conditions used in the catalytic tests, cyclohexanone and cyclohexanol were the main products formed in the hydrogenation of phenol over supported Pd catalysts. Small amounts of other products (mainly benzene and cyclohexane) were also observed, with selectivities always lower than 1% at 160°C. The amount of these by-products was found to become relevant only at higher temperatures (>200°C) and chiefly on Al$_2$O$_3$ supported samples. Fig. 1(b) reports the selectivity to cyclohexanone as a function of conversion levels on ex-chloride and ex-acetate monometallic Pd catalysts. On all samples the selectivity decreases on increasing the conversion level, in agreement with the reaction mechanism reported in the literature [6,14,15,21], which considers that the hydrogenation of phenol follows a consecutive reaction pathway (phenol $\rightarrow$ cyclohexanone $\rightarrow$ cyclohexanol). In the case of ex-chloride samples the selectivity to cyclohexanone follows the same order previously observed for the catalytic activity, i.e. Pd/La$_2$O$_3$ $>$ Pd/CeO$_2$ $>$ Pd/Al$_2$O$_3$. Ex-acetate catalysts present a selectivity to cyclohexanone always higher than that of the corresponding ex-chloride samples, and practically independent from the support used.

Turnover numbers as a function of time on stream over calcium-doped Pd catalysts are reported in Fig. 2(a). It is possible to observe that Al$_2$O$_3$ supported Pd-Ca samples present a higher specific activity compared to those supported on CeO$_2$ and La$_2$O$_3$. From the comparison of Figs. 1(a) and 2(a) one can infer that addition of calcium strongly enhances the activity of Pd/Al$_2$O$_3$ samples whereas no improvement is observed on CeO$_2$ and La$_2$O$_3$ supported catalysts. It must be remarked that APdCa(AC) sample is more active than APdCa. It is also noticeable that alumina supported Pd-Ca samples present a moderate deactivation, which is in any case, lower than that observed on the corresponding undoped Pd samples. Fig. 2(a) also shows that Pd-Ca catalysts supported on CeO$_2$ and La$_2$O$_3$ are quite stable, analogously to that observed in the case of monometallic Pd samples on the same supports.

The selectivity to cyclohexanone as a function of conversion levels over Pd-Ca catalysts is reported in Fig. 2(b). It appears clearly that the selectivity is quite similar on all Pd-Ca samples. From the comparison between this figure and Fig. 1(b) it appears that, on the
ex-chloride series, calcium addition increases remarkably the selectivity to cyclohexanone, which becomes comparable to that observed on the ex-acetate series. It is noteworthy that on this latter series the selectivity to cyclohexanone is practically independent on the presence of calcium and/or the support used.

3.2. Characterization measurements

Fig. 3 shows the FT-IR spectra after admission of pyridine and subsequent evacuation at 150 °C over ex-chloride Pd and Pd-Ca samples. All samples show a spectrum which is characteristic of the adsorption of pyridine on Lewis acid sites. The main features of the spectra are, in fact, the \( \nu_{19b} \) band (1450–1440 cm\(^{-1}\) region) and the \( \nu_{8a} \) band (1625–1596 cm\(^{-1}\) region) involving ring stretching vibrations of coordinatively adsorbed pyridine[27]. The absence of bands at around 1540 and 1640 cm\(^{-1}\) indicates that no Bronsted acid sites are present on the catalytic surface of all investigated samples[27].

From Fig. 3(a) it is possible to observe that on APd \( \nu_{8a} \) and \( \nu_{19b} \) bands are, respectively centred at 1615 and 1450 cm\(^{-1}\). Similar values of frequency have been reported in the literature on various alumina [27,28–30]. On CPd (Fig. 3(b)) the frequencies of both \( \nu_{8a} \) and \( \nu_{19b} \) bands are sensibly lower (respectively, 1603 and 1445 cm\(^{-1}\)) compared to those observed on APd. On LPd (Fig. 3(c)) the above bands are further shifted down to 1598 and 1443 cm\(^{-1}\) and exhibit an intensity much lower compared to APd and CPd samples. These results indicate that the order of acidity of ex-chloride undoped Pd samples, both in terms of acid strength and number of acid sites, is APd > CPd > LPd. The same trend of acidity has been reported in the literature in the case of the oxides alone [31,32].

From Fig. 3 it can be also noted that on Ca-doped samples the intensity of all bands (in particular the \( \nu_{19b} \) band) is strongly reduced compared to the corresponding undoped sample, whereas no change can be observed in the frequency. This indicates that calcium causes a decrease in the number of acid sites of the ex-chloride samples without affecting significantly their strength.

The FT-IR spectra after admission of pyridine and subsequent evacuation at 150 °C over ex-acetate Pd and Pd-Ca samples are reported in Fig. 4. Analogously to that observed on ex-chloride samples, bands related exclusively to Lewis acid sites were revealed. In particular on monometallic Pd samples the frequency of \( \nu_{8a} \) and \( \nu_{19b} \) bands is respectively, 1614 and 1448 cm\(^{-1}\) on APd(AC), 1598 and 1441 cm\(^{-1}\) on CPd(AC), 1596 and 1439 cm\(^{-1}\) on LPd(AC). It must be noted that the intensity of the bands is lower than that measured on the corresponding monometallic ex-chloride samples. Fig. 4 shows also that addition
of calcium leads to a small decrease in the intensity of all bands.

The FT-IR spectra of CO adsorbed at room temperature on Pd and Pd-Ca samples at the same CO pressure (2 mbar) are reported in Fig. 5. On all samples two main bands were observed, respectively in the 2060–2090 cm\(^{-1}\) (HF band) and 2000–1700 cm\(^{-1}\) (LF band) ranges. In accordance to the literature [33,34] the HF band can be assigned to CO linearly adsorbed on Pd\(^{0}\), whereas the broad LF band can be ascribed to different bridged CO species on Pd\(^{0}\).

On APd and APd(AC) (Fig. 5(a)) the HF and LF bands are, respectively centred at about 2080 and
In the case of APdCa and APdCa(AC) (Ca-doped samples) the frequency of the HF band (about 2060 cm\(^{-1}\)) is 20 cm\(^{-1}\) lower than on undoped samples, whereas the LF band is practically at the same frequency (maximum at about 1950 cm\(^{-1}\)). It must be also pointed out that the HF to LF intensity ratio appears to be moderately lower in the presence of calcium. This behaviour suggests that electronic palladium surroundings are somehow modified in the presence of calcium \cite{15,35}. No significant change in the dispersion of palladium has been in fact observed for addition of calcium that could explain the downshift of the HF band. The occurrence of a strong electronic effect induced by alkali over Pd particles have been also reported in the literature \cite{36–38}. On CPd (Fig. 5(b)) the HF band is detected at 2090 cm\(^{-1}\) whereas the LF band has a maximum at 1966 cm\(^{-1}\). The linearly Pd–CO band has been reported at the same frequency value by Badri et al. on a Pd/CeO\(_2\) sample of similar Pd dispersion \cite{39}. The presence of calcium does not modify the position of both HF and LF bands, but causes a decrease in the intensity of the LF band. This indicates that on ceria the presence of calcium probably results in a dilution effect of Pd sites. A similar trend is observed also on ex-acetate CeO\(_2\) supported samples. However, it is noteworthy that on CPd(AC) and CPdCa (AC) the HF band is at 2067 cm\(^{-1}\), frequency much lower than in the case of CPd and CPdCa samples. This can be justified considering that ex-acetate samples exhibit (Table 1) Pd particle sizes considerably lower than ex-chloride samples \cite{39}. On LaO\(_2\) supported monometallic Pd samples (Fig. 5(c)) the HF and LF bands are respectively, at about 2070 and 1920 cm\(^{-1}\). Analogously to that above reported for CeO\(_2\) supported samples also in this case calcium does not seems to affect the position of both bands, but causes a relevant increase in the HF/LF intensity ratio, thus suggesting the occurrence of a strong dilution effect of Pd sites.

Fig. 6 reports the TPD profiles after adsorption of cyclohexanone at room temperature on ex-chloride supported Pd and Pd–Ca catalysts. On APd sample (Fig. 6(a)) it is possible to observe an intense desorption peak of cyclohexanone with a maximum at ca. 160 °C. A small peak at 300 °C is also present. On CPd catalyst (Fig. 6(b)) the amount of cyclohexanone adsorbed appears to be quite lower compared to the APd sample as indicated by the ca. five times lower desorption peak intensity. It is noteworthy that the maximum of the peak was observed at ca. 110 °C. On CPdCa sample (Fig. 6(c)) TPD profile shows two desorption peaks of very small intensity with maxima at 90 and 250 °C. Addition of calcium leads, in all cases, to an evident decrease in the intensity of desorption peaks, clearly indicating that the amount of cyclohexanone adsorbed is negatively affected by the presence of calcium. It must be underlined that on all ex-acetate samples, independently from the support.
used, the TPD profiles are completely flat until 700 °C (data not shown), indicating that no cyclohexanone was adsorbed on these samples.

4. Discussion

It has been reported that the hydrogenation of phenol on supported palladium catalysts occurs between hydrogen activated on palladium and phenol adsorbed on the support, as a phenolate species, nearby the metal particles [6,7,11,15–17]. The cyclohexanone formed can desorb from the catalytic surface or be further hydrogenated to cyclohexanol [6,7,14,15,21]. Following these considerations it seems reasonable that both the support and the surface metal atoms may be involved in determining the performance of catalysts. The support should influence the adsorption strength of phenol and cyclohexanone whereas the nature of the surface palladium atoms should control the activation of hydrogen.

The catalytic activity data reported in this paper showed that over supported Pd catalysts prepared by PdCl₂ as precursor the order of activity and selectivity to cyclohexanone was Pd/La₂O₃ > Pd/CeO₂ > Pd/Al₂O₃. The same order of activity was also observed over ex-acetate monometallic Pd catalysts. Over these latter samples, however, the selectivity to cyclohexanone was higher than that of the corresponding ex-chloride samples and rather independent from the support used. It must be noted that Pd/CeO₂ and Pd/La₂O₃ samples appear to be quite stable whereas Pd/Al₂O₃ catalysts show a relevant deactivation which is higher on the ex-chloride samples.

The specific activity of monometallic Pd catalysts does not seem to be greatly affected by the precursor used. In fact on each support the difference of turnover numbers between ex-chloride and ex-acetate samples is not significant. Nevertheless chemisorption data (Table 1) showed that the precursors used affect substantially the CO uptake, with ex-acetate samples which have a higher CO/Pd ratio than the corresponding ex-chlorides. This suggests that hydrogenation of phenol on supported Pd catalysts is not substantially influenced by the metal particles size and then it can be regarded, at least in the Pd particle size range (5–15 nm) of the investigated samples, as a structure insensitive reaction. This is in accordance to the results reported in the literature on Pd/Al₂O₃ [15] and Pd/MgO [13,17].

Catalytic results showed that the precursor used affects considerably the selectivity towards the products of phenol hydrogenation. It is known that metal particles size can have influence on the products distribution of a reaction and therefore it could be responsible of the different selectivity to cyclohexanone observed by us on the two series of catalysts (ex-chloride and ex-acetate). However, it must be considered that the difference in the dispersion is not so relevant in the case of alumina supported catalysts where, on the contrary, the highest variation in the selectivity was observed. Therefore, other effects must be claimed in order to explain the different selectivity shown.

FT-IR spectra of pyridine adsorbed showed that the order of acidity, in terms of strength and number of acid sites, is Pd/La₂O₃ > Pd/CeO₂ > Pd/Al₂O₃ for both series of catalysts. Moreover ex-acetate samples present a lower number of acid sites than that of corresponding ex-chlorides. This difference is more evident on Al₂O₃ supported samples. The above trend of acidity suggests the existence of a correlation between acidity and the catalytic behaviour of supported monometallic Pd samples: the lower the acidity of the catalyst, the higher the activity and the selectivity to cyclohexanone. This is in agreement to the results of Neri et al. which reported a higher selectivity to cyclohexanone on Pd/MgO compared to Pd/Al₂O₃ [6]. Chen et al. [8] and Narayanan et al. [9] have also reported that Pd supported on calcined Mg/Al hydroxides exhibit high reactivity and selectivity to cyclohexanone and attributed these performance to the presence of strong basic sites. In order to explain the higher selectivity to cyclohexanone observed on basic supports, a different orientation of phenol adsorbed on the surface has been proposed by some researchers [6,10,40]. They have suggested that on silica–alumina (acidic supports) phenol is adsorbed with the aromatic ring coplanar with the surface, whereas on MgO (basic support) a non-planar form is preferred. This should control the selectivity to the reaction products, with the non-planar form favouring the formation of cyclohexanone. It must be underlined, however, that until now there does not exist any experimental evidence which confirms this hypothesis. On the basis of TPD experiments reported in this paper we suggest
that the trend of selectivity observed (the lower the acidity of the support, the higher the selectivity to cyclohexanone) can be related to the degree of interaction between cyclohexanone and the catalytic surface. This interaction appeared, in fact, to be strongly reduced by a decrease in the catalyst acidity (Fig. 6). A lower interaction, should favour cyclohexanone desorption so hindering its further transformation to cyclohexanol.

The comparison between catalytic activity of Pd and Pd-Ca samples (both ex-chloride and ex-acetate), reported in Fig. 7, shows that addition of calcium strongly enhances the activity of Pd/Al₂O₃ samples whereas no improvement is observed on Pd/CeO₂ and Pd/La₂O₃ catalysts. As regards of the influence of calcium on the products distribution, it has been seen (Figs. 1(b) and 2(b)) that, on the ex-chloride series, calcium addition increases remarkably the selectivity to cyclohexanone, rising to that observed on the ex-acetate series. It is noteworthy that on this latter series the selectivity to cyclohexanone is practically independent on the presence of calcium and/or the support used. In order to clarify in which way the presence of calcium affects the catalytic properties of supported Pd samples and the reason for the influence of calcium is support dependent, we have investigated the changes induced by the promoter both on Pd metal sites and on support acidity.

FT-IR spectra of CO adsorbed on Al₂O₃ supported samples showed that on calcium-doped samples the electronic surroundings of palladium are somehow modified. Considering that on our samples Ca should be present as calcium oxide, formed by thermal decomposition of the nitrate precursor, it seems reasonable to suggest that an electronic interaction between Pd and CaO occurs on the catalytic surface of Pd-Ca/Al₂O₃ samples, leading to an electronic enrichment of the Pd metallic phase [15,35]. This should cause a better activation of the hydrogen on the palladium sites, so explaining the improvement of the catalytic activity observed in the case of Pd-Ca/Al₂O₃ samples. On the other hand, over CeO₂ and La₂O₃ supported catalysts, FT-IR spectra of CO adsorbed pointed out just
to a dilution effect of Pd sites by calcium. Therefore, it appears clearly that the support used plays a key role in directing the interaction between Pd and the promoter on the catalytic surface. A strong influence of the support in controlling the nature and the degree of surface metal-metal interactions has been reported in the literature on bimetallic systems [41,42]. FT-IR of pyridine adsorbed showed that addition of calcium also has a strong negative influence on the number of Lewis acid sites of the ex-chloride samples. The effect of Ca addition on the acidity of the ex-acetate samples is much less evident. This is quite reasonable if one considers that the acidity of the ex-acetate monometallic Pd samples is indeed very low.

On the basis of the results here reported, it can be deduced that the changes in the activity observed on Ca-doped Pd catalysts are substantially related to modifications of electronic surroundings of active metal Pd sites caused by the presence of the promoter. In fact an evident enhancement of the turnover number was obtained only in the case of alumina supported samples (ex-chloride and ex-acetate) where calcium is responsible for a strong electronic effect on palladium. On the contrary on supports CeO2 and La2O3 where calcium is not able to modify the electronic properties of Pd atoms, the activity is not altered by the promoter. Considering that, on these two latter systems, the acidity is decreased by calcium addition, this is more evident on CeO2 it appears clearly that, on each support, the acid–base properties of the system have an effect on the catalytic activity which is much lower than that induced by the Pd sites features. Taking into account that the hydrogenation of phenol has been reported to proceed through a surface reaction between phenol strongly bounded on the support and hydrogen activated on palladium [6,7,11,13,15–17], the results reported in this paper indicates that the activation of hydrogen is crucial in controlling the total reaction rate [7,15]. The acidity is instead determinant in affecting the distribution of reaction products. Effectively a strong correlation between extent of increase in cyclohexanone selectivity and decrease in the number of acid sites by calcium addition was observed. Therefore calcium affects positively the selectivity to cyclohexanone essentially by reducing the surface acidity of the support [6,7]. As discussed before, this modifies the adsorption–desorption equilibrium of cyclohexanone, favouring its desorption from the support and thus, increasing the selectivity to this product.

A lower acidity appears also to inhibit the deactivation rate of the catalyst. It is well known that catalyst deactivation occurs by carbon deposition catalyzed by acid sites on the surface [6,12,13]. On the basis of the results reported in this paper it is highly probable that strong acid sites are mainly responsible for the deactivation of the Pd catalysts. This explains the high deactivation rate observed on alumina supported samples, on which strong Lewis acid sites were detected, and the high resistance to deactivation of ceria and lanthanum supported samples, on which just very weak Lewis acid sites are present.

5. Conclusions

On the basis of the results reported in this paper, it can be concluded that the catalytic behaviour of supported Pd catalysts towards the selective hydrogenation of phenol to cyclohexanone is strongly affected both by the acidity of samples and by the electronic surroundings of metal active sites (Pd). In particular it can be reasonably suggested that the acid-base properties of the catalysts have a strong influence on the adsorption–desorption equilibrium of reactants and products, being responsible to direct the selectivity towards the reaction products. The catalytic activity of the system appears to be, instead, controlled mainly by the state of the palladium sites on which H2 is activated. Finally the deactivation rate of the catalyst is strongly dependent on the presence of strong acid sites.

References
