DRIFT study of CO chemisorption on organometallics-derived Pd / MgO catalysts: the effect of chlorine

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Magnesia-supported palladium catalysts were prepared from chemical vapour deposition (CVD) of [Pd(C_3H_5)(C_5H_5)] and incipient wetness impregnation of [Pd(C_3H_5)Cl]$_2$ and [Pd(acac)$_2$]. DRIFT spectroscopy of adsorbed CO on prereduced catalysts indicates that the electronic state of metal particles depends on the preparation methodology and markedly on the organometallic precursor. In *n*-heptane reforming at 500°C, the highest activity and selectivity were shown by the CVD-based system. Chloride ions deriving from the impregnation solvent exchange with surface hydroxyls. Acidic Mg–Cl sites are thus formed, which induce a beneficial effect on the catalytic properties. The reforming activity collapsed when a chlorine-containing precursor was used, due to a partial coverage of the palladium surface with chemisorbed chlorine atoms.

Keywords: DRIFT spectroscopy; CO chemisorption; Pd/MgO catalysts; reforming; chlorine effect

1. Introduction

The use of basic support materials for noble metal catalysts has become the subject of increased attention [1–9]. Recently, aromatization yields in the *n*-hexane reforming reaction for platinum supported on aluminium-stabilized MgO were claimed to be comparable to that for a Pt/L zeolite catalyst [1,2], which is known to have an excellent performance for this reaction [10]. Palladium supported upon magnesia performs even better than its platinum counterpart [3,4]. This surprising result indicates that the presence of a zeolite or microporous support in general cannot explain completely the high aromatization selectivity of zeolite-supported Pt and Pd. Instead, Davis and Derouane [1,2] proposed the presence of a metal–support interaction between metal clusters and a high surface area basic support, although Derouane counterclaimed this quite recently [4]. Up to now, several research groups have explained the observed catalysis of magnesia-based catalysts with the occurrence of a metal–support interaction leading to an electron enrichment of the metal particles [5–7].

Very recently, the high aromatization selectivity of non-acidic Pd/MgO catalysts was also observed in our laboratory and it was reported that the catalyst prepared by chemical vapour deposition of an organometallic precursor (OM-CVD) proved to be very active [7]. The use of a chlorine-containing palladium precursor resulted in a dramatic loss of activity and selectivity to benzene from MCP, forming significant amounts of cracking products. This typical bifunctional reforming behavior was tentatively related to the formation of acidic MgCl sites.

In the present work, diffuse reflectance infrared (DRIFT) spectroscopy of adsorbed carbon monoxide and the catalytic conversion of *n*-heptane were employed to characterise the surface properties of the various Pd/MgO catalysts.

2. Experimental

2.1. Catalyst preparation

The MgO support material (Carlo Erba, reagent grade) was refluxed in doubly distilled water for 2 h; heated in air to 500°C and then evacuated ($p = 10^{-6}$ mbar) overnight at this temperature. This treatment results in magnesia with a surface area of ca. 200 m^2/g as measured with nitrogen adsorption.

[Pd(acac)$_2$] (acac = acetylacetonate) was purchased from Aldrich Chemicals Co. (batch 00816AY). [Pd(C_3H_5)Cl]$_2$ (C_3H_5 = allyl) was purchased from Strem Chemicals (batch 401-A). Both chemicals were used as received. [Pd(C_3H_5)(C_5H_5)] (C_3H_5 = allyl, C_5H_5 = cyclopentadienyl) was synthesised according to the literature method [11].

The metal content in all catalysts was 2 wt%, as determined by AAS upon dissolution of the catalysts in a HCl/HNO_3 mixture.

For organic solvent impregnation a weighed amount of the organometallic precursor ([Pd(acac)$_2$] or [Pd(C_3H_5)Cl]$_2$) was dissolved in anhydrous dichloromethane. The resulting slurry was dried in vacuo

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($p = 10^{-3}$ mbar) at room temperature, and stored under nitrogen.

For chemical vapour deposition (CVD), MgO was placed over a quartz frit in a U-tube reactor, and heated in flowing oxygen to 400°C for 1 h (10°C/min) [12]. After cooling to room temperature, a weighed amount of $[Pd(C_3H_5)(C_5H_5)]$ was placed at the bottom of the U-tube under argon. Sublimation was carried out overnight in flowing argon (5 ml/min) at 35°C resulting in a deep purple solid.

The impregnated catalysts were then pretreated in flowing hydrogen or oxygen from 25 to 500°C at a heating rate of 7°C/min, as reported in table 1.

2.2. *Chlorine measurements*

Determination of chlorine contents, as Cl^-, in Pd/MgO catalysts was carried out by potentiometric titration with 0.01 M $AgNO_3$ using a combined silver electrode connected to an Amel 338 mVmeter. The catalyst (200–400 mg) was dissolved in 1 M nitric acid, brought to a pH around 5 with concentrated KOH, and 5 ml of 3 M KNO_3 was added as ion-strength adjuster. Gran's methodology was employed for determining the endpoint of the titration [13].

2.3. *Catalytic measurements*

n-heptane conversion was performed at 500°C in a continuous-flow, fixed-bed microreactor, working at atmospheric pressure, with a H_2/MCP ratio of about 20. Product analysis was periodically carried out by an on-line gas-chromatograph (Carlo-Erba Instruments HRGC 5160) using a 50 m, 0.2 mm cross-linked methyl-silicone (Hewlett-Packard PONA) capillary column. Catalytic data were taken after 2 h on stream.

2.4. *DRIFT spectroscopy*

In situ diffuse reflectance infrared spectra were recorded on a Digilab FTS-40 fitted with a Harrick DRA-2CI diffuse reflectance accessory equipped with a Harrick HVC catalytic chamber, which allows spectra of the sample in granular form to be recorded under controlled temperature and pressure conditions.The DRIFT cell was connected to a flow-system suited to flow purified gases or to evacuate the cell at 10^{-3} mbar. In order to prevent volatile carbonyls to enter the flow-system, a trap containing activated alumina was installed between the CO cylinder and the flow-system. The Pd/MgO catalyst samples were transferred into the DRIFT cell and in situ reduced in a flow of H_2 at 350°C for 1 h, ramping at 3°C/min. An infrared spectrum was recorded at 350°C for analysis of the surface hydroxyl absorptions. After purging in argon at 350°C for 10 min, the reduced sample was cooled in flowing argon. Prior to CO adsorption, a spectrum of the reduced catalyst was taken at room temperature for background subtraction. Then the catalyst was saturated in 100% CO at atmospheric pressure for 10 min, after which the CO gas phase was removed by Ar purge and a spectrum measured. All spectra were recorded against a KBr standard at 4 cm^{-1} resolution with accumulation of 256 scans for each spectrum using a TGS detector. The spectra were converted into Kubelka–Munk units and plotted against wavenumber. The CO spectra presented in this paper were corrected for the catalyst background absorption using the spectrum accumulated before CO adsorption. Resolution enhancement was performed with standard Digilab software using a half bandwidth of 14 cm^{-1}, enhancement factor of 1.7 and Bessel apodization.

3. Results

3.1. *Catalyst preparation*

All the organopalladium precursors were strongly chemisorbed onto the MgO surface, as would be required for obtaining a good surface dispersion of the precursor itself on a non-porous oxide. Hydrogen reduction up to 500°C was thus required in order to remove the organic ligands and obtain a high-purity metal phase. The amount of residual chlorine in Imp2, as prepared from $[Pd(acac)_2]$ in CH_2Cl_2 (see table 1) is unexpected as the precursor was chlorine free and no chlorine was detected after pure MgO was treated with CH_2Cl_2. Equally surprising is that the Imp1 catalyst contains more chlorine (Cl/Pd = 1.3) than one would expect from the stoichiometry of its precursor. The additional level of chlorine in the impregnated catalysts is most probably formed after reaction of the palladium precursor with dichloromethane, in agreement with the known

Table 1
Thermal treatments and chlorine contents of different Pd/MgO catalysts

Catalyst	Precursor	Solvent	Pretreatment	Cl/Pd
Imp1	$[Pd(C_3H_5)Cl]_2$	CH_2Cl_2	H_2, 25–500°C	1.30
Imp1-ox	$[Pd(C_3H_5)Cl]_2$	CH_2Cl_2	O_2, 25–500°C	1.13
Imp1-red	$[Pd(C_3H_5)Cl]_2$	CH_2Cl_2	O_2, 25–500°C; H_2, 25–500°C	0.94
Imp2	$[Pd(acac)_2]$	CH_2Cl_2	H_2, 25–500°C	0.60
CVD	$[Pd(C_3H_5)(C_5H_5)]$	none	H_2, 25–500°C	0.0

activity of palladium for hydrogenolysis of carbon–chlorine bonds [14].

The potentiometric chlorine analysis shows that the chlorine content in the Impl catalyst gradually decreases with the severity of pretreatment in the order Impl > Impl-ox > Impl-red.

3.2. Catalytic measurements

Catalytic reforming of *n*-heptane was chosen as probe reaction for differentiating between monofunctional and bifunctional catalysts [15]; moreover, it can be regarded as a good model of commercial low-octane feed.

The activity and selectivity to aromatics of the Pd/MgO catalysts are reported in table 2.

The CVD-based catalyst is immediately shown to have the highest activity and selectivity to aromatics, with methane as the major byproduct. The use of a chlorine-containing precursor is instead detrimental; the catalyst prepared from $[Pd(C_3H_5)Cl]_2$ shows negligible activity and lower selectivity to aromatics. A conventional cycle of O_2 calcination and H_2 reduction at 500°C is then needed to partially restore the catalytic activity. The retention of chlorine from the impregnation solvent in the $[Pd(acac)_2]$-derived catalyst does not significantly modify the aromatic selectivity, but only a small decrease in activity is observed.

With respect to the chlorine-free CVD catalyst, methane formation is reduced, in favour of a number of by-reactions. These take place on acidic Mg–Cl sites of the support, leading to C_2–C_6 cracking products and polycyclic aromatic residues.

3.3. DRIFT spectroscopy

In the OH stretching frequency region of the chlorine-free catalysts, all spectra show a relatively sharp band in the region 3800–3700 cm^{-1} and a broad absorption between 3700 and 3200 cm^{-1}. A typical OH spectrum of the MgO support is shown in fig. 1a. In agreement with the literature on hydroxyls on MgO surfaces, the high frequency band is assigned to free OH groups formed on the edges and corners of the MgO microcrystals [16,17]. The broad low-frequency absorption is attributed to hydrogen-bonded OH groups formed on the extended faces of the support crystallites. The chlorine-containing catalysts (Imp2 and Impl) show a decrease in intensity of the OH bands (figs. 1b and 1c) that is probably due to the exchange of OH groups by chloride ions, forming surface MgCl species. The integrated OH band intensities after reduction at 350°C gradually decrease with increasing chlorine content.

Table 2
Activity and selectivity in *n*-heptane reforming of different Pd/MgO catalysts

Catalyst	Activity [a]	Selectivity to aromatics [b](%)
Impl	7.0	60
Impl-red	31.2	73
Imp2	51.0	80
CVD	57.8	83

[a] Expressed as mol%.
[b] As the sum of benzene + toluene.

The absorptions in the region between 1900 and 1100 cm^{-1} are typical for surface (bi)carbonate species formed after admission of CO. Fig. 2 shows a trend of decreasing carbonate formation with increasing chlorine content. The absorptions in the spectra of fig. 2 can be assigned to bidentate carbonate species (at 1672 and 1382 cm^{-1}), simple carbonate ions (at 1500 cm^{-1}) and bicarbonates (at 1646, 1425 and 1217 cm^{-1}) formed after reaction of CO with the MgO surface [18–21]. The weak band at 1600 cm^{-1} presents the formation of formates on the chlorine-free MgO surface of the CVD prepared sample (fig. 2a) [20]. Apparently, chloride ions originating from precursor and organic solvent cover the MgO surface after pretreatment and poison the formation of surface carbonate species in agreement with the literature [22,23].

A DRIFT investigation of CO adsorption was carried out in the 2150–1750 cm^{-1} region for various reduced Pd/MgO catalysts (figs. 3 and 4). The strong variance in the spectra shown in fig. 3 illustrates the dependence of the surface characteristics on the preparation method and the nature of the organometallic precursor. The spectrum of CO adsorbed on the CVD sample exhibits relatively strong bands located at 2035, 1910 and 1870 cm^{-1} with weaker features at 2060 and 1950 cm^{-1} (fig. 3a). In fig. 3b, the spectrum of Imp2 shows a new band located at 1970 cm^{-1}, with a drastic change in the intensity ratio of bridging CO bands below 1900 cm^{-1}. Moreover, the two terminal CO absorptions shift to higher frequencies. This shift is even more dramatic for the Impl catalyst, being accompanied by a 60% reduction in the global absorption capacity of CO (fig. 3c). The 1970 cm^{-1} band is replaced by a new one at 1985 cm^{-1}, whereas all the bridging absorptions are retained.

The spectrum of fig. 3c was then subjected to a resolution enhancement treatment, and again shown in fig. 4a, in order to evidence the effects of high-temperature treatments. The absorption capacity of CO, as measured by the integrated peak area, is increased by about 30–50%, by sequential O_2/H_2 (fig. 4b) or $H_2/O_2/H_2$ (fig. 4c) treatments. Moreover, the 1985 cm^{-1} band, which dominates the original spectrum of fig. 4a, is gradually replaced by a new feature at 1975 cm^{-1}.

4. Discussion

Carbon monoxide is widely used as probe molecule

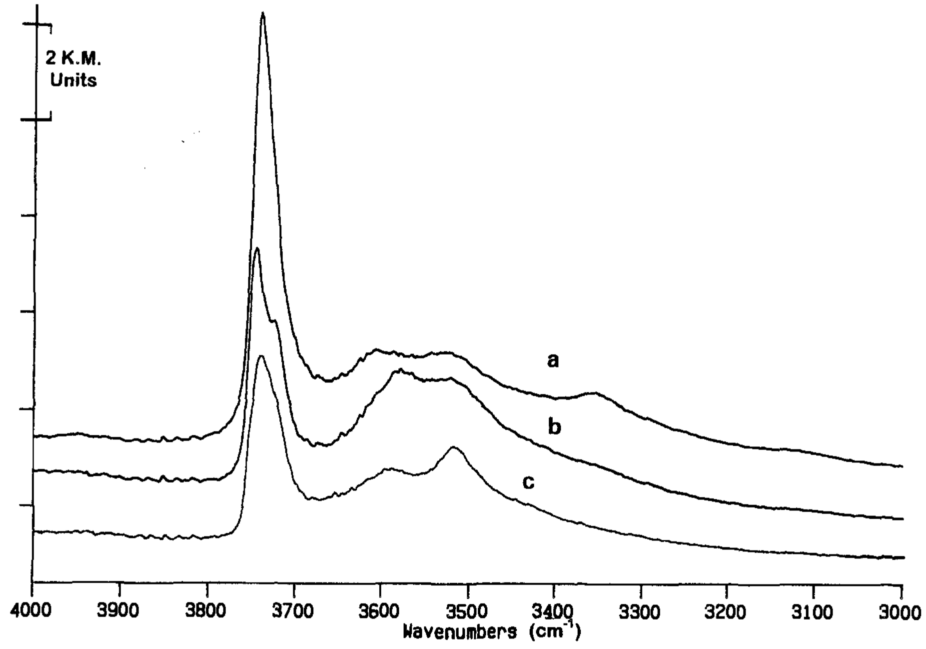

Fig. 1. DRIFT spectra in the OH stretching region of Pd/MgO measured at 350°C: (a) MgO, (b) Pd/MgO prepared from impregnation of $[Pd(acac)_2]$ in CH_2Cl_2 (Imp2), and (c) Pd/MgO prepared from impregnation of $[Pd(C_3H_5)Cl]_2$ in CH_2Cl_2 (Imp1).

for the study of the surface of palladium particles [24–31]. The different types of adsorbed species on the metal surface absorb in the infrared spectrum in distinct regions. It is well established that linearly bound CO gives rise to bands in the region 2100–2000 cm^{-1}, two-fold bridging (B1 and B2) in the region 2000–1900 cm^{-1}, and three-fold bridging (B3) in the lower range from 1900 to 1700 cm^{-1}. Within these boundaries the stretching frequency of adsorbed CO and its preferred surface coordination are affected by a range of experimental conditions as well as catalyst properties, e.g. CO coverage, coadsorbates, surface distribution of CO, promoters, metal particle size and catalyst support [24–31]. In view of the standardised CO adsorption procedure, the metal particle size, the presence of chlorine and metal–support interactions are considered the cardinal contri-

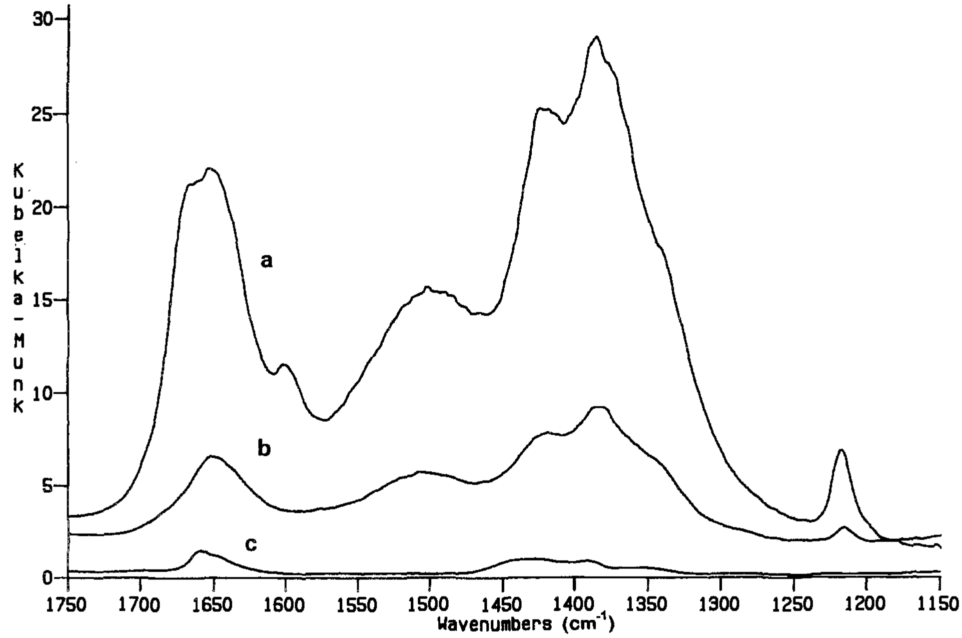

Fig. 2. DRIFT spectra in the 1750–1150 cm^{-1} region of Pd/MgO after reduction at 350°C and admission of CO at RT: (a) Pd/MgO prepared via CVD of $[Pd(C_3H_5)(C_5H_5)]$, (b) Pd/MgO prepared from impregnation of $[Pd(acac)_2]$ in CH_2Cl_2 (Imp2), and (c) Pd/MgO prepared from impregnation of $[Pd(C_3H_5)Cl]_2$ in CH_2Cl_2 (Imp1).

Fig. 3. DRIFT spectra of CO adsorbed on Pd/MgO reduced at 350°C: (a) Pd/MgO prepared via CVD of [Pd(C_3H_5)(C_5H_5)], (b) Pd/MgO prepared from impregnation of [Pd(acac)$_2$] in CH_2Cl_2 (Imp2), and (c) Pd/MgO prepared from impregnation of [Pd(C_3H_5)Cl]$_2$ in CH_2Cl_2 (Imp1).

butions for changes in the DRIFT spectra from CO on Pd/MgO. On palladium, unlike for example on platinum [32], considerably stronger absorption bands are commonly observed from bridging CO species than from linear CO species (only onto very small palladium colloidal particles CO binds in an exclusively linear mode [33]). CO adsorbed on the CVD sample is preferentially coordinated in the bridging B1, B2 and B3 positions with bands located at 1950, 1910 and 1870 cm^{-1}, respectively. Several authors have proposed that the B1 and B2 bridging bands can be associated with Pd (100) and (111) surfaces, based on the similarity of the band positions with those reported by Bradshaw and Hoffmann [28–30] for CO adsorption on Pd single crystals. The correspondence between adsorption on small Pd particles and single-crystal surface was recently confirmed by Szanyi et

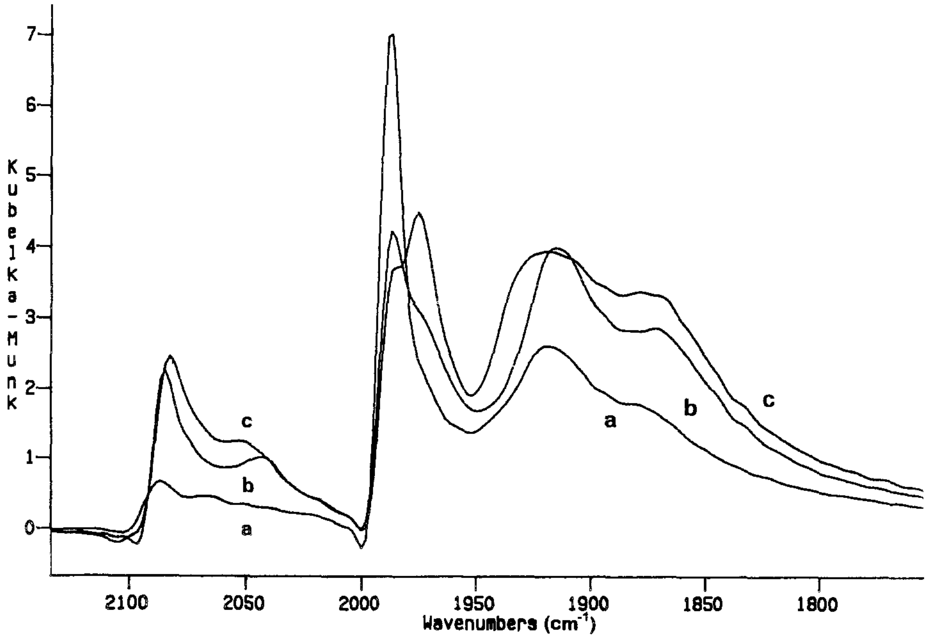

Fig. 4. Resolution enhanced DRIFT spectra of CO adsorbed on Pd/MgO prepared from impregnation of [Pd(C_3H_5)Cl]$_2$ in CH_2Cl_2 following (a) in situ reduction at 350°C (Impl), (b) calcination at 500°C and in situ reduction at 350°C (Impl-ox), and (c) ex situ reduction at 500°C, calcination at 500°C and in situ reduction at 350°C (Impl-red).

al. [34]. However, the relative band intensities in the spectrum of the CVD sample are different from those reported in the literature for silica or alumina supported palladium catalysts at high CO coverage, but similar to those recorded at low coverage [24–26]. Generally at high coverage, CO chemisorbed on Pd/SiO_2 shows linear-CO bands between 2090 and 2050 cm^{-1} of medium intensity and strong B1 bridged CO bands between 1990 and 1910 cm^{-1}; B3 absorption bands centred below 1900 cm^{-1} are only observed at low CO coverage. The dominance of the B2 and B3 species in the Pd/MgO spectrum cannot be the result of low CO coverage, it must be caused by a chemical effect. Comparison of the spectrum in fig. 3a with that reported recently by Mojet et al. [35] for an alkaline Pd/L zeolite catalyst shows that both spectra are quite similar. It was shown in the latter paper that with decreasing support acidity the infrared absorption bands shift to lower frequency while the band intensity ratio changes in favour of the bridging CO species. A higher electron density on the metal particles results in more back-donation into the $2\pi^*$ orbitals of adsorbed CO, leading to a shift to lower absorption frequencies. The electron-rich character of Pd in alkaline L zeolites was also evidenced by data from XPS, EXAFS and catalysis [35]. Based on the similarity of CO spectrum from alkaline Pd/L catalysts, it is concluded that the palladium particles in the CVD sample are electronically modified by the basic MgO support through the presence of a metal–support interaction. In the Imp2 and Imp1 catalysts the CO absorption bands are shifted to higher absorption frequencies and the adsorption geometry shifts towards linear and B1 coordination. The change in CO coordination and the band shift to higher frequencies in the impregnated catalysts indicates that palladium is less electron enriched than in the CVD catalyst. This change in metal–support interactions could be attributed to a modification of the MgO support by the partial formation of high Lewis acidity Mg–Cl sites [22,23]. Moreover, the presence of such sites has the additional effect of blocking the surface sites for carbonate (or bicarbonate) formation (fig. 2).

Finally, chlorine may also interact with the metal surface directly, as was observed for SiO_2-supported Rh, Ru [36,37] and MgO-supported Ru [38]. This seems to be case for the Imp1 catalyst because of the presence of Pd–Cl bonds on the original precursor. Chlorine chemisorbed on metal particles withdraws electron density from the metal surface and leads to partial poisoning of the active metal sites, which may be evidenced by the marked decrease in CO adsorption and the appearance of the high frequency B1 band at 1985 cm^{-1} (fig. 3c). Ex situ reduction and calcination at 500°C markedly decreases the amount of chlorine in the Imp1-red and Imp1-ox samples, but the OH absorption intensities do not change proportionally.

In agreement with such a hypothesis, the Imp1 sample showed low activity and selectivity in *n*-heptane aromatization to toluene and benzene due to the presence of chlorine atoms onto palladium particles, blocking the sites for hydrocarbon reactivity. The increase in catalytic activity upon calcination and reduction of the Imp1 catalyst may thus be explained as the result of a selective dehalogenation of the palladium particles, restoring a partially clean metal surface. In fact, CO surface coverage increases steadily in the sequence Imp1, Imp1-ox and Imp1-red indicating that chlorine is released from the Pd particles in accordance with the fall of the absorption at 1985 cm^{-1} and the growth of the band at 1975 cm^{-1}.

In contrast, the high activity of the Imp2 sample indicates that chlorine derived from the impregnation solvent is primarily located onto the support. The presence of chloride residues on the MgO surface may even be beneficial for the catalytic properties, since it may (i) promote acid–base reactions, like cracking to C_1–C_6 alkanes and to provide alternative routes for 1–6 dehydrocyclization to aromatics as in bifunctional Pd/NaY catalysts [15], and/or (ii) prevent, or minimize, sintering of metal phase under catalytic conditions, following the mechanism originally called by Sachtler "hydrocarbon induced agglomeration" [39].

It must be evidenced, however, that the highest catalytic performance is shown by the CVD-based catalyst. The absence of any impregnation solvent is a decisive advantage for this technique since metal–support interactions are enhanced, resulting in an electron-rich metal surface of high stability toward sintering under reaction conditions [10].

5. Conclusions

DRIFT data of CO adsorption on Pd/MgO indicate that the surface properties of the palladium phase strongly depend on the organometallic precursor and the preparation method. When prepared by CVD, metal particles are shown to be electron-rich as a result of metal–support interaction. Moreover, due to the absence of alkali promoter cations in Pd/MgO, electron-enrichment of the metal particles must be solely the result of an interaction between palladium atoms and oxygen atoms of the support. The presence of chlorine deriving from the impregnation solvent is demonstrated to modify the magnesia surface only. The use of a chlorine-containing palladium precursor leads, instead, to chemisorption of chlorine on the metal surface. Both forms of chlorine doping strongly affect the catalytic performance of Pd/MgO catalysts.

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