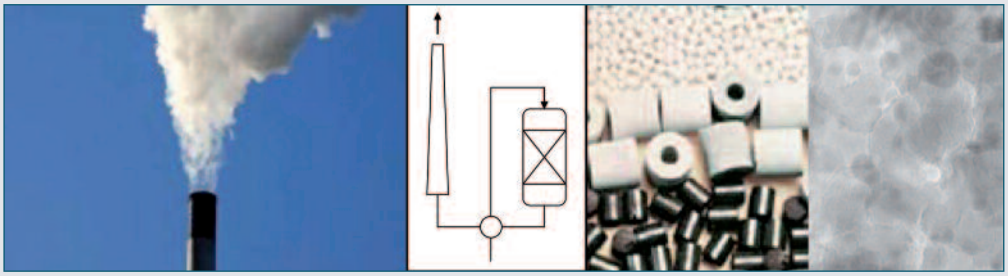

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# SURFACE SCIENCE AND INDUSTRIAL CATALYSIS: RED-OX STATES OF ALUMINA SUPPORTED Pd NANOPARTICLES

***Surface science and theoretical studies concerning aluminas, palladium, oxidized palladium surfaces, Pd/$Al_2O_3$ planar model surfaces are briefly reviewed and compared with experimental results on Pd/$Al_2O_3$ powder catalysts. The higher complexity of the picture arising from spectroscopic data on Pd/$Al_2O_3$ powder catalysts is evidenced, in particular in oxidizing conditions. The need of additional studies concerning the redox states of Pd/$Al_2O_3$ powder catalysts is emphasized.***

Most industrial chemical processes of large scale refinery and petrochemistry production are performed in heterogeneous catalytic conditions, i.e. with solid catalysts, reactant mixture being in the liquid, gaseous, or mixed liquid and gaseous phase.

Catalysis by solid metals, in particular noble metals, is very relevant in terms of both technology and business. Metal catalysts may be bulk or supported [1-3]. Enormous number of studies have been published concerning the effects of different catalyst characteristics (support type, dispersion of the metals, size and shape of metal particles, role of additives).

Surface science studies helped very much to the understanding of metal catalysis. Recognition of this work is represented by the Nobel Prize 2007 for Chemistry, awarded to Gerhard Ertl, the most eminent surface scientist. Experimental methods for metal-based materials characterization underwent further developments in recent years, with the development, among other techniques, of high resolution electron microscopies [4], monocrystal and surface layers spectroscopies [5], theoretical calculations [6]. These techniques allowed to propose refined models for active sites and reaction mechanisms of metal catalysis. Most of these studies, both experimental and theoretical, are performed on almost "perfect" extended faces of metal monocrystals, which can be quite easily performed. In fact both modelling and experiments concerning defects, edges, corners, as well as metal-to-support interfaces are by far more difficult to be performed. Thus, some of these techniques sometimes fail in elucidating the role of the supports in supported metal catalysis and in determining the existence and the possible role of metal species different from bulk crystals, including dispersed clusters and isolated atomic species which are detected by high resolution microscopy [7] and ionic species and support-metal interfaces, which can be observed by, e.g., infrared spectroscopy [8]. The knowledge on the chemistry of such "non bulk" species is indeed still very poor.

Additionally, even for some well established industrial processes authors still disagree on the real state of the working catalyst, the nature of the active sites and reaction mechanisms. Metal catalysts may indeed change significantly their surface and even bulk composition depending on the reactant environment: as for example, in the presence of oxidants such as oxygen and also water, they may be oxidized to some extent, in the presence of carbon oxides or hydrocarbons they may be carburized to some extent, in the presence of sulphur compounds they may be sulphided to some extent, etc.

On the frame of a systematic investigation on the surface chemistry of metal catalysts, aimed at checking the possible role of metal-support interfaces, we will review here some literature data on a very relevant system: $Pd/Al_2O_3$, and we will also present new experimental data on it.

## The aluminas surfaces as support for metal catalysts

As it is well-known, aluminum oxide is a polymorphic material [9, 10]. The thermodynamically stable phase is $\alpha$-$Al_2O_3$ (corundum) where all Al ions are equivalent in octahedral coordination in a hcp oxide array. All other alumina polymorphs are metastable, and most of them have structures which have been related to that of spinel, i.e. cubic $MgAl_2O_4$.

$\gamma$-$Al_2O_3$, which is the most used form of alumina, is mostly obtained by decomposition of the boehmite oxyhydroxide $\gamma$-AlOOH (giving medium surface area lamellar powders, ~100 $m^2/g$) or of a poorly crystallized hydrous oxyhydroxide called "pseudobohemite" at 600-800 K, giving highly microporous high surface area materials (~500 $m^2/g$). $\gamma$-$Al_2O_3$ is one of the most used materials in any field of technologies. However, the details of its structure are still matter of controversy. It has a cubic structure described by Lippens and de Boer [11] to be a defective non stoichiometric spinel. $^{27}$Al NMR spectra show that tetrahedral Al is near 25% of all Al ions but also show a small fraction of Al ions that is in coordination five [12], or highly distorted tetrahedral. XRD studies using the Rietveld method [13], suggested that $Al^{3+}$ cations can be in positions different from those of spinels, i.e. in trigonal coordination. Other possible structures such as that of a "hydrogen-spinel" [14] or of a stoichiometric spinel whose cation charge is balanced by hydroxyl-ions at the surface [15] have also been proposed. DFT calculations have been performed recently, but did not allow to completely solve the problem. The hydrogen spinel structure $HAl_5O_4$ was found very unstable [16] while the spinel structure with occupation of extra-spinel sites was considered possible [17, 18]. On the contrary, Digne *et al.* [19, 20] and Krokidis *et al.* [21] proposed a structure based on ccp oxide lattice but different from that of a spinel, with 25% of Al ions in tetrahedral interstices and no structural vacancies. According to these authors, this structure, although unstable with respect to corundum, is more stable than that the spinel based structures.

The calcination of $\gamma$-$Al_2O_3$ causes the formation of a slightly different structure denoted as $\delta$-$Al_2O_3$, assumed to be a tetragonal spinel superstructure [11, 22], which is formed continuously in the range 800-900 K. By decomposing Beyerite $Al(OH)_3$, $\eta$-$Al_2O_3$ is obtained, which is also considered to be a spinel-derived structure with more tetrahedrally coordinated (35%) and less octahedrally coordinated Al ions [23, 24] than $\gamma$-$Al_2O_3$.

Calcination at increasing temperatures both of $\gamma$-$Al_2O_3$/$\delta$-$Al_2O_3$ and of $\eta$-$Al_2O_3$ gives rise first to $\theta$-$Al_2O_3$ and finally to $\alpha$-$Al_2O_3$ [22]. During the sequence $\gamma$-$Al_2O_3 \rightarrow \delta$-$Al_2O_3 \rightarrow \theta$-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ the lamellar morphology of bohemite is mostly retained but with progressive sintering of the lamellae and disappearance of the slit shaped pores. $\theta$-$Al_2O_3$ is formed above 900 K with simultaneous decrease of the surface area to near 100 $m^2/g$ or less. Its monoclinic structure, which is the same of $\beta$-gallia, can be derived from that of a spinel, with deformation and some ordering of the defects, with half tetrahedral and half octahedral Al ions [25].

The catalytic activity of "transitional" aluminas ($\gamma$-, $\eta$-, $\delta$-, $\theta$-$Al_2O_3$) are undoubtedly mostly related to the Lewis acidity [26] of a small number of low coordination surface aluminum ions, as well as to the high ionicity of the surface Al-O bond [27-29]. These sites are well characterized by adsorption of probe molecules followed by spectroscopies and calorimetry. The density of the strongest Lewis acid sites tends to decrease a little by increasing the historical calcination temperature of the alumina (i.e. upon the sequence $\gamma \rightarrow \delta \rightarrow \theta$, which is also a sequence of decreasing surface area). As a result of this the number of strongest acid sites per gram significantly decreases in this sequence, although catalyst stability increases. Surface spectroscopy provides also evidence of a complex pattern of surface hydroxyl groups with medium-high Brønsted acidity, and of its evolution by calcination.

Most authors agree that at least three different types of Lewis acid sites (weak, medium, strong) exist on transitional aluminas. Liu and Truitt [30] emphasized the close proximity of Lewis acid sites with surface OH's, while in their very recent study Lundie *et al.* [31] identified four different Lewis acid sites arising from coordinatively unsaturated octahedral (the weakest) and tetrahedral sites (the three strongest), three of which are considered to be associated to three different types of hydroxy groups.

Using the non-spinel-type structure they proposed, Digne *et al.* [20] justified the complexity of the OH stretching spectrum as well as the existence of different Lewis acid sites on $\gamma$-$Al_2O_3$ modeling CO and pyridine adsorption on tricoordinated $Al^{3+}$ on (110) face, tetracoordinated $Al^{3+}$ on (110) face, and pentacoordinated $Al^{3+}$ on (110) and (100) faces.

In recent years the group of Peden and coworkers emphasized the role of pentacoordinated Al ions, well detectable in the $^{27}$Al NMR spectra of $\gamma$-$Al_2O_3$ but also based on calculations considering flat $\gamma$-$Al_2O_3$ faces, as generating most of the surface and bulk chemistry of this material, i.e. as a structural promoter for phase transition [32], for anchoring of Pt oxide [33] as well as for the sintering of supported Pt metal particles [34]. Using the non-spinel structural model of Digne *et al.* [20] they modelled this adsorption site as located on the (100) face. The same group used the (100) and (110) faces of this non-spinel type structure to model the adsorption of $NO_x$ [35].

The existence on outgassed transitional alumina surfaces of Lewis sites less coordinated than fivefold is well substantiated by adsorption of probes but may depend on activation temperature and can be associated to a small number of defect sites on corners and edges of the crystal surface. On the other hand it seems very plausible that a bulk technique, such as $^{27}$Al NMR spectroscopy would only detect the most abundant species. Finally, the existence of more uncoordinated Al ions should be the fundamental reason of the much higher reactivity of transitional aluminas with respect to corundum $\alpha$-$Al_2O_3$, powders, where indeed weak Lewis acidity is found likely just due to pentacoordinated Al ions.

It must be taken into account that the surface activity of aluminas is also strictly dependent from its purity: in particular alkali metal impurities arising from the precipitating agent (mostly sodium ions) may decrease significantly surface reactivity [28]. Voluntary doping with alkali is largely used to reduce alumina activity in supported catalysts. It has also been shown that doping with alkali, alkali earth and rare earth cations increases stability of alumina against phase transition as well as loss of surface area. In practice to reduce surface activity and to increase stability of alumina when used as the support for metal catalysts, evoluted structures ($\theta$-$Al_2O_3$ or $\alpha$-$Al_2O_3$) with moderate to low surface area (100 to 5 $m^2/g$) are needed and doping with alkali, alkali earth or rare earth may also be useful.

Recently, few studies have addressed the problem of the location and the interaction of noble metal oxide species on gamma alumina surfaces. Such species should also be the precursors of supported metal particles. Sohlberg *et al.* [36] investigated the formation of rhodium oxide particles over gamma-alumina surfaces. They observed, by atomic-resolution Z-contrast STEM supported by first-principles density functional calculations, the formation of “rafts” of the $Rh_2O_3$-II phase on the (100) surface of spinel-type $\gamma$-alumina.

Ja Hun Kwak *et al.* proposed that bulk-like PtO layers form at the surface of $\gamma$-$Al_2O_3$ by interacting with pentacoordinated $Al^{3+}$ species modelled to occur over the (100) non-spinel type face [33]. Quite in contrast with this, for the same $Pt/Al_2O_3$ system, spectroscopic studies where interpreted as evidence of the “selective” location of Pt oxide species on the alumina surface, substituting or exchanging the OH sites located on tetrahedral Al species, giving rise to isolated oxidized Pt ions [37]. Data on $Pd/Al_2O_3$ system seem to be lacking from this respect.

## Industrial applications of $Pd/Al_2O_3$ based catalysts

Palladium based catalysts find a very relevant number of applications in different fields. Palladium is among the most active catalysts in the broad field of hydrogenation, both selective and unselective. A very relevant field of application of $Pd/Al_2O_3$ based catalysts is that of hydrogenation of acetylenics (acetylene, propine, vinylacetylene and ethylacetylene) as well as of dienes (propadiene and 1,2- and 1,3-butadienes) performed in order to limit the presence of such noxious compounds in C2, C3 and C4 cuts arising from steam reforming processes. Liquid-phase hydrogenation of these compounds can be performed over catalysts containing 0,03-0,5% Pd over low surface area $\alpha$-$Al_2O_3$ with surface area ranging from 5 to 25 $m^2/g$ [37, 38]. The Pd loading for gas-phase acetylene hydrogenation is far smaller than that of catalysts for liquid phase processes.

Quite similar liquid phase processes are the hydrogenation of the byproduct $\alpha$-methyl-styrene (AMS) in the cumene synthesis processes and the hydrogenation of vinylacetylene in the styrene synthesis process, both performed too on $Pd/Al_2O_3$ based catalysts.

Palladium based catalysts are also applied for catalytic oxidation. Pd appears to be the most active catalyst for methane combustion [39-41]. Alumina is the most largely used support, although addition of ceria is reported to be beneficial [42]. Zirconia [43] and zirconia-ceria [44] have also been proposed for this reaction.

The aftertreatment of Otto-cycle gasoline engines is satisfactorily achieved by the so called Three Way Catalysts (TWC), a technology developed after the Seventies allowing the efficient abatement of unburnt hydrocarbons (HC), CO, and NOx. The original TWC composition was Pt-Rh on alumina, deposed on ceramic monolyths. In recent years [45], typical TWC formulations have included Pd as the active metal, ceria-zirconia as promoters according to the Oxygen Storage Capacity (OSC) of ceria and the thermal stability of zirconia, and alumina as support as well as other minor components mainly present in order to enhance thermal stability. Perovskite materials can also be present to help limiting of noble metal sintering. The use of the different noble metal formulation (Pt-Rh, Pd-Rh, Pd only) is due in part to purely economic reasons, resulting from the high cost and scarcity of Rh and from the variable relative prices of Pd and Pt.

Most of commercial combustion catalysts are based on supported noble metals, which are needed to burn refractory compounds such as hydrocarbons. Alumina is the most frequent support, due to its stability at the required temperature. A typical composition of industrial VOC combustion catalysts is 0.5% Pd on alumina, with 109 $m^2/g$ [46].

## CO adsorption on palladium monocrystal surfaces

CO adsorption followed by vibrational spectroscopies (like Infrared Reflection Absorption Spectroscopy, IRAS, and High Resolution Electron Energy Loss Spectroscopy, HREELS) represents a largely used technique in metals surface science studies. CO adsorption followed by Transmission/Absorption or Diffuse Reflectance IR spectroscopies is also largely used in the field of powder catalysts characterization. These techniques allow good comparison among the respective results.

Early low temperature and pressure studies [47, 48] provided evidence of a coverage-dependent surface structure of CO overlayers on the basal fcc Pd(111) face. According to these studies, at very low coverages up to a 0.33 monolayers (ML), the structure of the CO adsorbate layer on Pd(111) is (√3x√3)R30°-1 CO, where the only adsorption sites occupied are the 3-fold hollow sites. By increasing coverage a new adsorbate structure forms, the c(4x2)-2 CO structure, at 0.50 ML coverage. During this process a progressive shift of a CO stretching band is observed from 1823 $cm^{-1}$ to 1936 $cm^{-1}$. In early vibrational studies is was suggested that only bridging (twofold) sites were populated at this coverage, but more recent photoelectron diffraction studies suggest population of the 3-fold sites too. At even higher CO coverage (0.75 ML), the adsorbate structure transforms from c(4x2)-2 CO to a (2x2)-3 CO structure, where both 3-fold hollow sites and the atop sites are populated. Accordingly, two sharp bands are evident at 1895 $cm^{-1}$ and 2110 $cm^{-1}$, typical of triply bridging and terminal carbonyl species.

More recent PM-IRAS studies [49] allowed to at least partially the overcome the “temperature and pressure gap” previously existing between surface science monocrystal studies and studies on real catalytic powder, although the ”material gap” is retained. PM-IRAS studies performed at higher pressure (600 mbar) as a function of temperature allowed to revealed the presence of the (2x2)-3 CO structure (bands at 2109 and 1895 $cm^{-1}$, due to terminal and triply bridging species) at the highest coverage observed at 210 K. At higher temperatures 650 K, a broad feature appearing at about 1933 $cm^{-1}$ was observed which can be associated with the CO molecules located on either the bridging or 3-fold sites on the Pd(111) surface. As the CO coverage is increased by decreasing the temperature, this broad feature sharpens and shifts to a higher frequency at 1957 $cm^{-1}$, consistent with a more-ordered adsorbate superstructure in which only the bridging sites are occupied.

On the (100) face the IR frequency was 1895 $cm^{-1}$ at low coverage, and this shifted continuously to 1950 $cm^{-1}$ at 0.5 ML, where it displays a c(2p2 xp2)R45 low-energy electron diffraction (LEED) pattern [48, 50]. A further increase in coverage causes additional shifts in the vibrational frequency to 1995 $cm^{-1}$. Only sites of 2-fold coordination were assumed to exist on this face.

On Pd (110) studies performed at low temperature (i.e. below 100 K) one only band is observed by HREELS shifting from 1895 to 1976 $cm^{-1}$ by increasing coverage [51]. IRAS studies at 180 K show this band at 1882 $cm^{-1}$ at the lowest coverages. At the highest coverages at both low and room temperature this band is observed at 2003 $cm^{-1}$ [52]. HREELS spectra allow complete spectroscopic characterization of this species, showing six types of normal vibrations [53]. At room temperature and intermediate coverages very complicated spectra have been found by IRAS interpreted as being due to a missing row surface reconstruction.

On the open (210) surface a single band was found to shift from 1880 to 1996 $cm^{-1}$ [48].

CO adsorption on oxidized Pd monocrystal surfaces, such as Pd(110)-c(2x4)-O show invariably a typical band near 2140 $cm^{-1}$. This band, that does not shift with coverage, has been assigned by Fukui *et al.* to CO interacting with Pd centers directly coordinated by oxygen atoms, where CO-O interactions predominate over CO-CO interactions [54]. A similiar band observed over the (√5x√5)R27° surface oxide on Pd(100) has been attributed to “multilayer” CO species [54]. According to this research group a similar band is also observed over other Pd monocrystal faces, when oxidized.

## Surface science studies on planar model catalysts

As already said, a “materials gap” exists between surface science studies performed on monocrystal surfaces and those performed on real catalyst powders. In fact, complete understanding of catalytic reactivity cannot be achieved by utilizing metal single crystals alone, because the interaction between a metal and its support and particle size effects can alter the activity and selectivity of supported catalysts in a remarkable way. This can be due to changes in the average metal atom coordination number, in the morphology, and in the different nature of metal-support interaction as the fraction of metal atoms in direct contact with the substrate varies. As for example, recent studies provided evidence of non-bulk properties (such as negative thermal expansion) of small supported Pt particles [55, 56] as well as of the possible existence of very small clusters (such as $Pt_3$), and even of monoatomic species [7, 57] in the cases of $Pt/Al_2O_3$ systems. In fact IR spectroscopic studies appear to give a more complex picture of real supported metal catalysts.

The preparation of model oxide supported metal catalysts in UHV represents an approach to partially overcome this gap. This approach, developed by Freund and coworkers [5], allowed the preparation and the characterization of Pt particles deposed from vapour phase over an alumina layer formed by oxidation and annealing of a NiAl(110) single crystal surface. These solids allow IR reflection/absorption spectroscopy studies as well as IR-VIS sum frequency generation SFG vibrational spectroscopy [58]. Scanning tunneling microscopy (STM) images indicate that well-shaped Pd crystallites form with an average size of approximately 6 nm. They grow in the (111) orientation and predominantly expose (111) facets as well as a small fraction of (100) facets [59]. Adsorption of CO was studied in detail and showed main features ascribable to CO/Pd(111) interactions. However, the presence of bridging carbonyls absorbing between 2000 and 1950 $cm^{-1}$ over the full temperature range (100-300 K) was attributed to CO adsorbed on edges and corners or other defects [60].

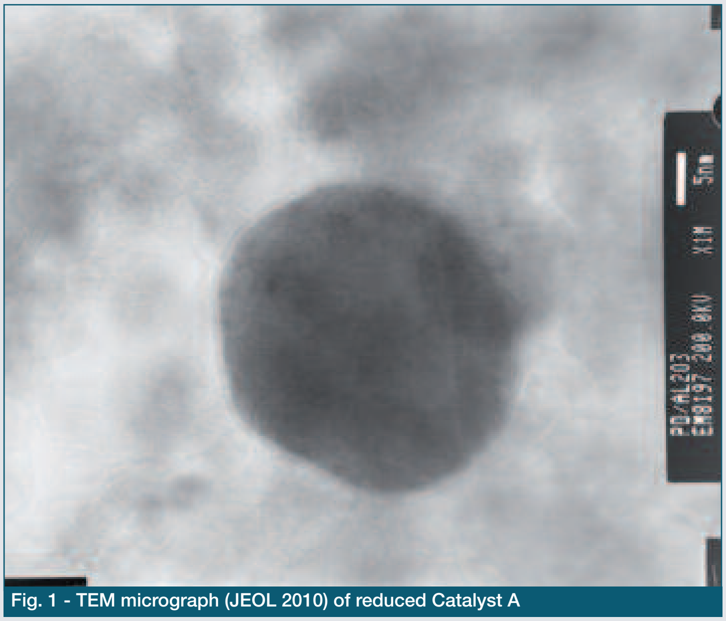

Fig. 1 - TEM micrograph (JEOL 2010) of reduced Catalyst A

## Experimental studies over $Pd/Al_2O_3$ catalyst powders

In Fig. 1 the TEM micrograph of a typical Pd particle found in a reduced 10% $Pd/\gamma\text{-}Al_2O_3$ catalyst (Degussa alumina support, Catalyst A) is shown. The amount of noble metal loaded over this catalyst is far excessive with respect to those of industrial catalysts but the amount related to the support surface area (90 $m^2/g$) is comparable to that of typical $Pd/\alpha\text{-}Al_2O_3$ hydrogenation catalysts. Both shape and dimension of such a particle is comparable to those of nanopolyhedra called multiply twinned particles (MTP) frequently observed for supported Pd [39, 61] and Au catalysts [62]. These nanopolyhedra appear to be hexagonal at TEM analysis. According to Xiong *et al.* [63] and Berhault *et al.* [39] they are formed by six icosahedra subunits, covered only by (111) planes.

For IR adsorption studies, pressed disks of the pure catalysts powders were activated "in situ" in the infrared cell connected to a conventional gas manipulation/outgassing ramp. All catalysts were submitted to different treatments in dynamic vacuum, in oxygen and or in hydrogen at temperatures of 350-500 °C, followed by evacuation before the adsorption experiments. CO adsorption was performed either at r.t. or at -140 °C by the introduction of a known dose of the gas (10 torr) inside the infrared cell (which can be cooled by liquid nitrogen) containing the previously activated wafers. IR spectra were collected in the presence of the gas or under evacuation at increasing temperatures between -140 and 500 °C by a Nicolet Nexus FT instrument.

On Fig. 2 the IR spectra of adsorbed CO on the above 10% $Pd/\gamma\text{-}Al_2O_3$ catalyst (Catalyst A), after reduction in hydrogen at 400 °C, are reported. At full CO coverage the spectrum shows the band of CO stretching of terminal carbonyls on Pd at 2100 $cm^{-1}$, as well as the peak of bridging species at 1981 $cm^{-1}$. A shoulder is also evident at ca 1925 $cm^{-1}$. By outgassing (thus decreasing CO coverage) the band of terminal carbonyls decreases faster in intensity while its maximum shifts down to 2086 $cm^{-1}$. Additionally, a shoulder becomes evident near 2070 $cm^{-1}$, shifting also down to 2057 $cm^{-1}$ at the lowest coverage. Upon outgassing we can observe also the slightly slower decrease of the intensity of the band of bridging carbonyls corresponding to a shift down to ca. 1945 $cm^{-1}$, while the further lowest frequency component seems to even increase a little bit in intensity shifting also down to near 1900 $cm^{-1}$.

The spectra we observe do not seem to reflect only the presence of (111) exposed faces which, as discussed above, does not show bridging species at full coverage. The presence of the strong band of bridging carbonyls at 1995 $cm^{-1}$ strongly suggests that part of the surface is composed by (100), (110) and/or (210) faces where a band in this range is predominant at high coverages.

In Fig. 3 the IR spectra of a different 2.7% $Pd/\gamma\text{-}Al_2O_3$ catalyst (support surface area 193 $m^2/g$, Condea, catalyst B) are reported. This catalyst after reduction in hydrogen at 400 °C (Fig. 3, dashed line) shows the formation of a very dominant band at 1985 $cm^{-1}$, certainly associated to bridging species, together with a weak band at 2075 $cm^{-1}$, certainly associated to terminal species, and a second likely bridging species too absorbing at 1945 $cm^{-1}$. This spectrum suggests that at least part of Pd species here do not show well structured faces similar to those of Pd monocrystals. In particular, the CO stretching at so low frequencies at full coverage as 2075 $cm^{-1}$ for terminal carbonyls and 1945 $cm^{-1}$. for bridging carbonyls at full coverage are quite anomalous, suggesting the presence, together

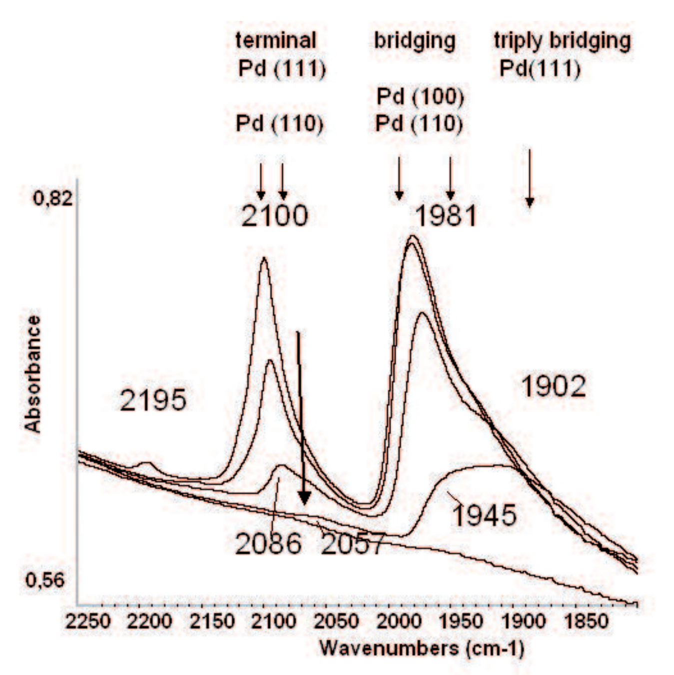

Fig. 2 - FT-IR spectra of carbon monoxide adsorbed on 10% $Pd/\gamma\text{-}Al_2O_3$ catalyst A, after reduction in hydrogen 1 atm at 400 °C. The first spectrum has been recorded in contact with CO 10 torr at 130 K for 5 min. The other spectra (following the arrow) were recorded upon outgassing ($10^{-3}$ torr) on progressive warming to 270 K

with larger particles, of very highly dispersed Pd species possibly of the monoatomic type. Isolated Pd atoms should adsorb CO only in a terminal state and should be more electron rich (due to the basicity of the oxide ions acting as ligands) than "normal" metallic platinum atoms. This could justify a very low CO stretching frequency for such species.

The spectra of catalysts A and B after calcining at 400 °C in oxygen followed by outgassing at the same temperature are reported in Fig. 4 and in Fig. 3, full line, respectively. In both cases a strong absorption is evident at ca. 2150 cm$^{-1}$, that disappears totally after reduction in hydrogen. In both cases XRD patterns of the fresh catalysts show the peaks of PdO. In the case of catalyst A an additional component can be found at 2160 cm$^{-1}$. These bands are certainly associated to CO interacting with cationic sites identified as $Pd^{2+}$ [8]. In both cases a second band is present in the region 2110-2100 cm$^{-1}$, i.e. in the region typical for on-top carbonyls over zerovalent Pd, or a little above, with a broad tail to lower frequencies. The band of bridging CO is observed, very weak and broad, centered at 1930 cm$^{-1}$ over unreduced catalyst A (Fig. 4) where the bands of multiply bridging species are totally absent. On unreduced catalyst B (Fig. 3, full line) also the band of bridging species is absent. These data indicate that either nearly isolated Pd metal species exist where only on-top adsorption is possible, or partially oxidized Pt metal particles are formed, where the sites for bridging and multiply bridging adsorption are "poisoned" by oxygen. This, however, contrasts what happens on Pd single crystal surfaces where oxygen poisons also sites for on-top CO adsorption [56]. The slightly higher than usual CO stretching of atop CO (2110 cm$^{-1}$ on catalyst A) may also be due to a partial oxidation of the metal particle.

In Fig. 5, heavy lines, the spectra of CO adsorbed at low temperature on a 2% Pd/$\theta$-$Al_2O_3$ (calcined Puralox, 109 m$^2$/g, catalyst C) treated only by outgassing at 350 °C are reported. No bands at $\nu$<2130 cm$^{-1}$, assignable to Pd metal centers, can be detected. A strong band is observed at 2151 cm$^{-1}$, not shifting significantly by outgassing. Low temperature CO adsorption over the pure support gives rise a strong band at 2187 cm$^{-1}$, whose maximum shifts up to 2208 cm$^{-1}$ at very low coverage. The expansion of the spectra obtained by outgassing at -40 and -10 °C show the presence of additional components near 2215 and 2235 cm$^{-1}$, showing how complex is the surface of alumina. The bands at 2235, 2215 and 2208-2187 cm$^{-1}$ are assigned to at least three different $Al^{3+}$ Lewis acid sites on the "transitional" alumina surfaces. The shift up of the CO stretching frequency shows how strong are the very low coordination sites present, although in small amounts. The overall coordination of these sites before CO adsorption is certainly lower than 5, likely 3. In any case, the strong Lewis acid sites of alumina have disappeared in the case of 2% Pd/$\theta$-$Al_2O_3$ sample. These results suggest that Pd ionic species are present, which interact with CO giving rise to the band at 2151 cm$^{-1}$. Such species are likely located just on the part of the alumina surface where the most reactive sites

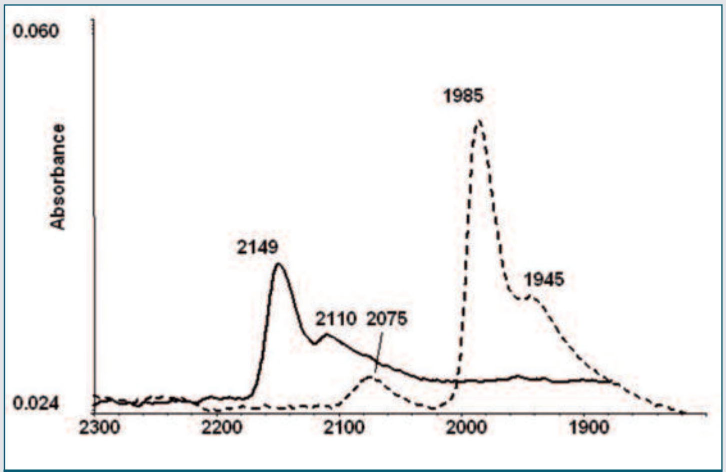

Fig. 3 - FT-IR spectra of carbon monoxide adsorbed on 2,7% Pd/$\gamma$-$Al_2O_3$ catalyst B after previous calcination in air at 400 °C and outgassing at 400 °C (full line) and after reduction in $H_2$ 1 atm at 400 °C and outgassing at 400 °C (broken line), in contact with CO 10 torr at -140 ◦C for 5 min. The corresponding activated surfaces spectra were subtracted

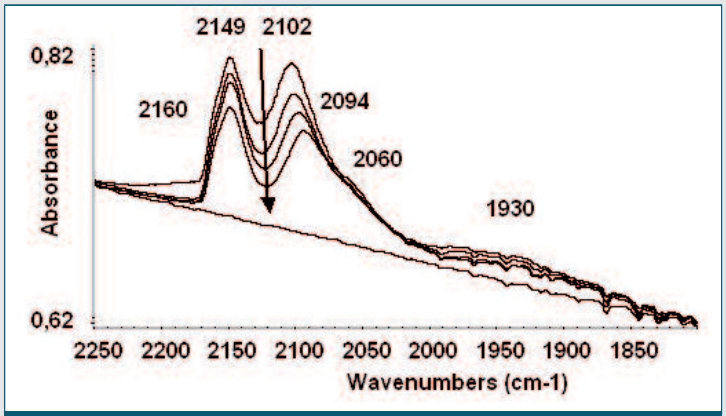

Fig. 4 - FT-IR spectra of carbon monoxide adsorbed on 10% Pd/$\gamma$-$Al_2O_3$ catalyst A, after calcination and outgassing at 400 °C. The first spectrum has been recorded in contact with CO 10 torr at 130 K for 5 min. The other spectra (following the arrow) were recorded upon outgassing (10$^{-3}$ torr) on progressive warming to 270 K

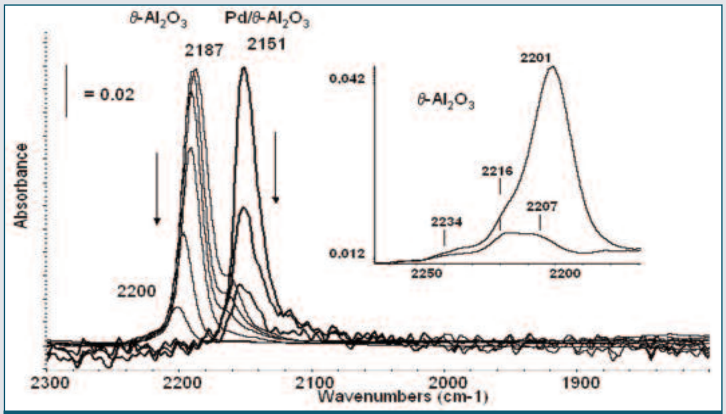

Fig. 5 - Heavy lines: FT-IR spectra of carbon monoxide adsorbed on 2% Pd/$\theta$-$Al_2O_3$ catalyst C, after outgassing at 350 °C, contact with CO at -130 °C and outgassing upon warming from -130 to -80 °C. Light lines: FT-IR spectra of carbon monoxide adsorbed on $\theta$-$Al_2O_3$ catalyst support, after outgassing at 500 °C, contact with CO at -130 °C and outgassing upon warming from -130 to -80 °C. In the insert: expanded spectra of CO adsorbed on $\theta$-$Al_2O_3$ after outgassing at -80 and -60 °C. The activated surface spectra have been subtracted

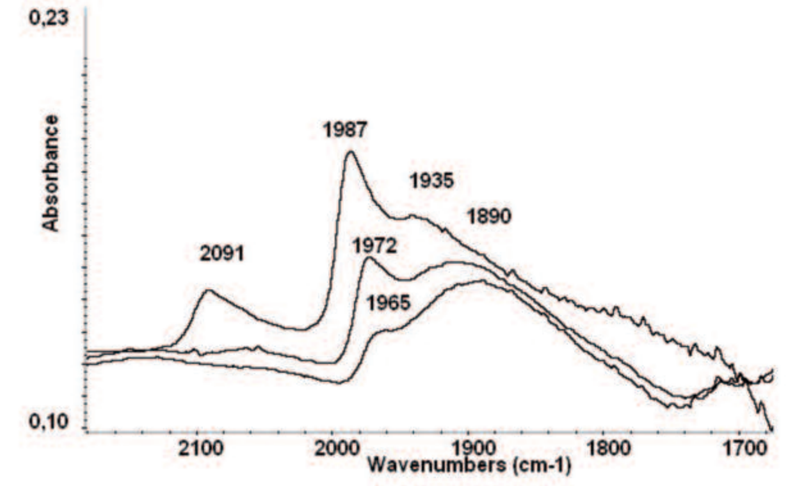

**Fig. 6 - FT-IR spectra of carbon monoxide adsorbed on 2% Pd/θ-$Al_2O_3$ catalyst C, after reduction in $H_2$ at 500 °C, contact with CO at r.t and outgassing upon heating up to 100 °C**

are present, which are very likely those located on edges and corners of the crystals, giving rise to very low coordination sites. In these positions the most acidic as well as the most basic sites are likely located. Pd ions and oxide ions should adsorb there and cover the alumina Lewis sites.

Over the same powder after reduction in hydrogen at 500 °C (Fig. 6) the spectrum of adsorbed CO recorded at r.t. is similar to those previously discussed. At the highest coverages the band of terminal species is observed at 2091 $cm^{-1}$ but a broad lower frequency tail is evident. In fact, at very low coverages a broad feature seems to be still present, weak, centred near 2020 $cm^{-1}$. The quite sharp band due to bridging CO is also evident at 1987 $cm^{-1}$ shifting to lower frequencies by outgassing. However, the most stable species is a broad but intense and resistant band centered near 1895 $cm^{-1}$, very likely associated to triply bridging species.

On the sample after the same reduction treatment (Fig. 7), the spectra of CO adsorbed at -140 °C are even more complex. In the region of terminal CO stretching modes (2250-2000 $cm^{-1}$) we can distinguish 5 different modes. The highest frequency band, shifting from ca 2190 to above 2200 $cm^{-1}$, is certainly that corresponding to CO adsorbed on the support, reappearing after reduction and evident at low temperature. The lowest frequency one in this region is found in the region 2110-2100 $cm^{-1}$ and is confidently assigned to terminal CO on Pd metal faces, possibly partially oxidized. However, additional bands are observed at 2160-70, 2150-40 and near 2130 $cm^{-1}$. These species are due to CO interacting with partially oxidized Pd centers. Interestingly, by warming under outgassing, when these bands decrease in intensity with a rate which roughly inversely depends from the CO stretching wavenumber, a strong band at 2345 $cm^{-1}$, due to adsorbed $CO_2$, first increases in intensity, than decreases when another new band at 1645 $cm^{-1}$ starts to grow (Fig. 8). This behaviour suggests that strongly oxidizing Pd species exist and convert (at so low a temperature) CO into $CO_2$, which further converts into carbonate species possibly by spill over to he support. In fact the band at 1645 $cm^{-1}$ is associated to weaker ones at 1445 and 1230 $cm^{-1}$, being all due to bicarbonate species.

The species responsible for the band in the region 2140-2150 $cm^{-1}$ is observed also on the unreduced sample and does not seem to be strongly oxidizing, being not associated to the formation of $CO_2$. It is present always on unreduced $Pd/Al_2O_3$ and can be due to CO adsorbed on nearly stoichiometric PdO. The band at 2160-2170 $cm^{-1}$ could be associated to CO adsorbed on highly dispersed and highly ionic $Pd^{n+}$ species, while that near 2130 $cm^{-1}$ should be associated to CO adsorbed on substoichiometric $PdO_x$ species, similar to those formed at the surface of Pd monocristals by oxygen adsorption. It seems likely that this species is the most active in CO oxidation in these low temperature conditions.

Another interesting datum obtained from Fig. 7 and 8 is that during adsorption and partial reduction by CO, the metal particles tend to restructurate. In fact it is evident that the band at 1982 $cm^{-1}$, certainly due to CO bridging over metallic Pd, grows while the features at 1823 and 1778 $cm^{-1}$, associated to multiply bridged CO in hollow sites, which are usually not detected on $Pd/Al_2O_3$, decrease in intensity down to disappear. The possibility of high mobility of Pd carbonyl-like species causing sintering of Pd particles supported on silica was already mentioned [65].

In Fig. 9 the spectra of the θ-$Al_2O_3$ support and of catalyst C (2% Pd/θ-$Al_2O_3$) after outgassing at 500 °C and after reduction at 500 °C

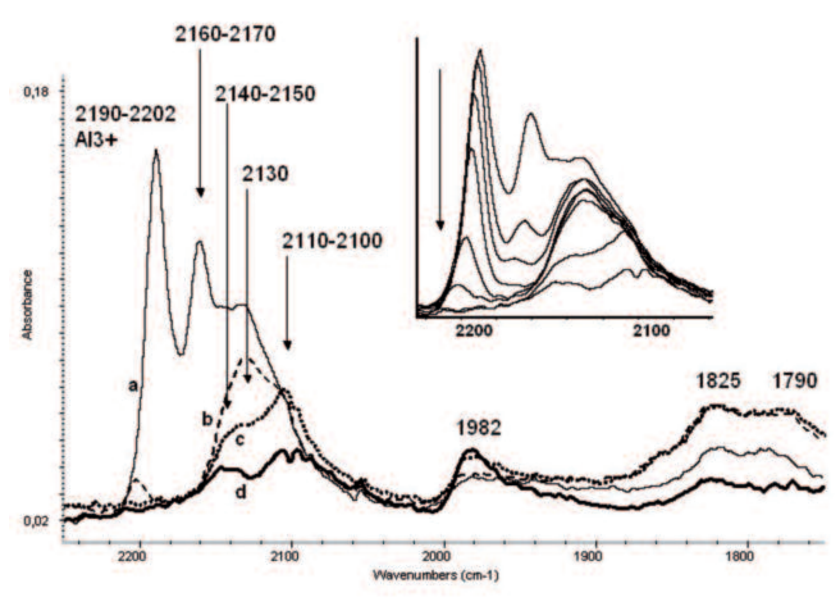

**Fig. 7 - FT-IR spectra of carbon monoxide adsorbed on 2% Pd/θ-$Al_2O_3$ catalyst C, after reduction in $H_2$ at 500 °C and contact with CO at -130 °C. Outgassing upon warming at (a) -130 °C; (b) -80 °C; (c) - 40 °C; (d) 0 °C. The reduced surface spectrum has been subtracted. In the insert, continuously recorded spectra under outgassing**

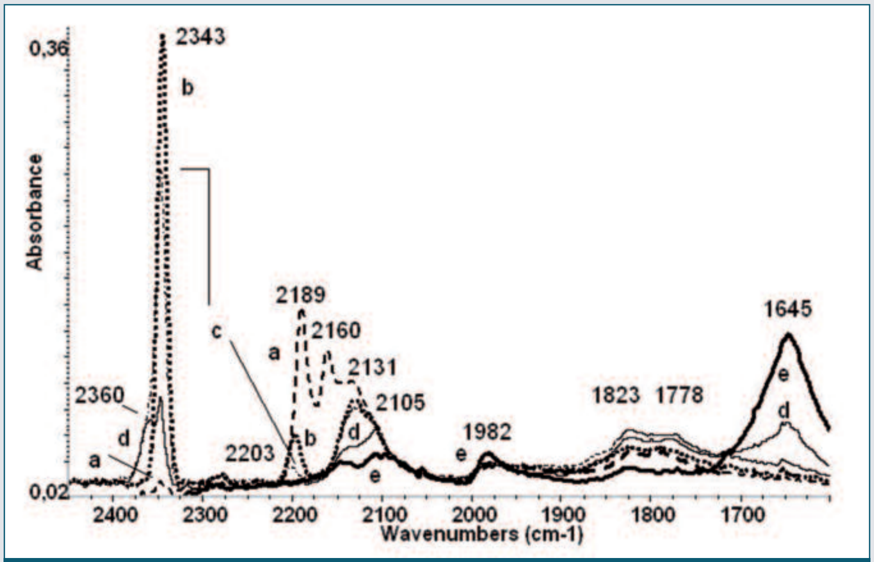

Fig. 8 - As Fig. 7: Outgassing upon warming at (a) -130 °C; (b) -100 °C; (c) - 80 °C; (d) - 40 °C; (e) 0 °C

are reported. As expected, all samples show bands in the region 3800-3400 cm$^{-1}$, due to OH stretchings of surface hydroxy groups. In the case of $\theta$-alumina support we find maxima at 3790, 3770, 3724 and 3675 cm$^{-1}$. This spectrum is quite typical for transitional $Al_2O_3$ samples outgassed at medium temperature. Our previous studies [66] suggested that the higher frequency components at 3790 and 3770 cm$^{-1}$ are due to terminal hydroxy-groups bonded to Al ions in a tetrahedral-like environment, the splitting being associated to vacancies with respect to the spinel-type composition. The band at 3724 cm$^{-1}$, instead, is present also at the surface of $\alpha$-$Al_2O_3$ and of stoichiometric spinels, and is consequently likely due to terminal OH's on Al ions in octahedral-like environment. The additional component at 3675 and 3575 cm$^{-1}$ have been assigned to bridging and triply bridging OH's, respectively.

The Pd/$\theta$-$Al_2O_3$ sample shows, in these conditions, a quite similar spectrum with respect to the support, but the intense band at 3790 cm$^{-1}$ is almost disappeared. The unreduced catalyst seem to show additional low frequency absorption in the region 3700-3500 cm$^{-1}$, all higher frequency components are definitely decreased in intensity. After reduction, instead, the spectrum of alumina is restored with the exception of the component at 3790 cm$^{-1}$. This suggests that $Pd^{n+}OH$ species may exist on the surface on the unreduced catalyst, and that the location of Pd species is somehow selective, mostly being associated to tetrahedral-like Al species on the surface.

## Conclusions

Although very important improvements have been made on the synthesis, characterization and mechanistic studies concerning metal catalysts, actually many points still reserve further investigation. One of the main points concerns the real state of the catalytic surface upon reaction as well as the nature of the active sites, in particular for metals working in oxidizing conditions. The experimental data reported here show how complex may be the situation of a real noble metal supported catalyst, with the presence of several different redox states: oxide particles, dispersed ions, partially oxidized metal particles, highly dispersed (monoatomic or clustered) reduced metal centres, bulk metal nanoparticles exposing different surfaces and with different sizes.

Our data also suggests that the interaction of the oxide and the metal with the surface are different and "selective". In fact, the catalyst in the oxidized state no more shows the typical features of the alumina support, likely due to the dispersion of the cations and oxide anions just over the more reactive sites of the support surface which are likely at the corners and edges of the support crystals. Reduction of the "oxide" to the metal regenerates only part of the support surface, likely due to the partial coalescence of the metal atoms. It is evident that this picture is far more complex than that arises from several theoretical studies, which usually look at the simplest situations (almost always flat single crystal faces for the metal [67] or "canonical" bulk structures for the metal oxide particles on flat single crystal faces of the support [33, 36]). Also experimental studies on single crystal metal surfaces obviously give only a partial information on the real catalytic phenomena occurring over supported metal catalysts.

It is evident that the knowledge of the redox behaviour of supported metal catalysts needs to be further improved.

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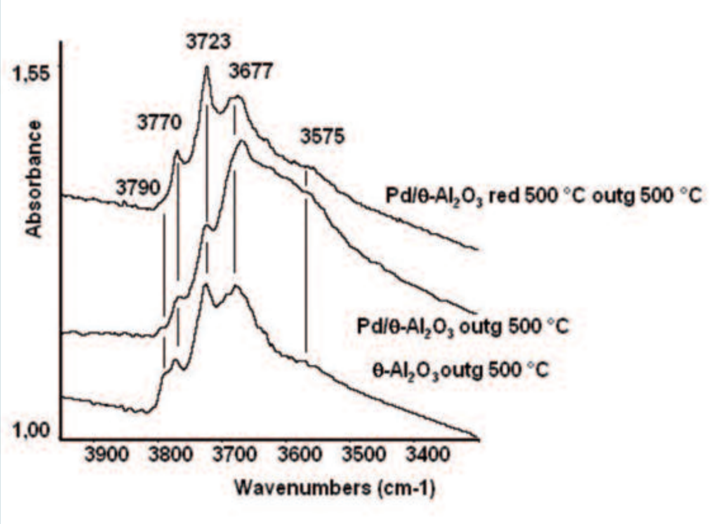

Fig. 9 - FT IR spectra of pure powder samples of 2% Pd/$\theta$-$Al_2O_3$ catalyst C, after outgassing at 500 °C and after reduction in hydrogen at 500 °C and of the support $\theta$-$Al_2O_3$ after outgassing at 500 °C

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## RIASSUNTO

### *Scienza delle superfici e catalisi industriale: stati ossido-riduttivi di nanoparticelle di palladio supportate su allumina*

*I risultati degli studi teorici e di scienza delle superfici riguardanti le allumine, il palladio, le superfici ossidate di palladio, e le superfici dei modelli planari di palladio su allumina sono brevemente riassunti e confrontati con i risultati sperimentali sui catalizzatori* $Pd/Al_2O_3$ *in polvere. Si dà evidenza della maggior complessità del quadro che deriva dagli studi spettroscopici sui catalizzatori* $Pd/Al_2O_3$ *in polvere in particolare in condizioni ossidanti. Si enfatizza anche la necessità di studi addizionali riguardanti gli stati ossido-riduttivi dei catalizzatori* $Pd/\ Al_2O_3$ *in polvere.*