

Preparation and characterization of alumina supported Pd-W and Pd-Mo catalysts photogenerated from group VI metal carbonyls

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Abstract

Tungsten and molybdenum were introduced in γ -Al₂O₃ and Pd/ γ -Al₂O₃ using metalcarbonyls [W(CO)₆ and Mo(CO)₆] photoactivation. DRIFTS FT-IR spectra of the surfaces prior to thermal decomposition reveal the presence of unstable metalsubcarbonyl species, in contrast with the ones found previously, when the photoactivation was performed in the presence of triphenylphosphine. The ν (CO) band intensities did not reflect the tungsten and molybdenum uptakes determined by AAS, the loadings being higher in the presence of palladium. After thermal treatment, the catalysts were further characterized by hydrogen chemisorption and FT-IR spectra of adsorbed CO and NO. The results showed that a reaction between the hexacarbonyls and the supported palladium particles takes place leading to bimetallic catalysts, with clear palladium–tungsten and palladium–molybdenum interactions. Pd + Mo(CO)₆ ⇒ ^{uv}Pd + Mo(CO)_{6-x} ⇒ Pd-Mo(CO)_{6-x} ⇒ ^{uv}Pd-Mo. Both group VI metals strongly modify the chemisorption properties of palladium, while molybdenum seems to be present in a reduced state in close association with palladium.

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1. Introduction

In order to improve the catalytic activity of palladium catalysts for hydrocarbons and NO_x removal from exhaust gases, they have been modified by the addition of different promoters such as MoO₃ [1], Co₃O₄ [2], La₂O₃ [3] and WO₃ [4]. The close proximity between metals is an essential requirement to change the activity and selectivity of palladium. It has been demonstrated that the incorporation of metal oxides by using inorganic precursors leads to preparations with metal–metal contact, but it requires the

use of high loadings. Consequently, a large fraction of the added promoter becomes isolated on the support material. As an alternative, organometallic precursors could be used to obtain preparations with low loadings and to control the interaction between the metals. It is well known that the interaction of transition metal carbonyls with Lewis acid sites on alumina allows the preparation of Mo/Al₂O₃ and W/Al₂O₃ catalysts [5,6]. However, it is difficult to obtain the cations in a low oxidation state by this procedure, due to metals oxidation by surface hydroxyl groups. In addition, the loadings have been rather low. Recently, a Pt-W/MgO catalyst where the metal–metal interaction was maintained even in the presence of oxygen, has been prepared from a bimetallic precursor [7]. It is of interest to obtain similar results using a more typical support

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material such as alumina. The deposition of chromium [8] and tungsten [9] hexacarbonyls on alumina has been performed in a fluidized bed reactor by vapor phase adsorption. The loading was controlled by the number of depositions realized. Metal agglomerates were obtained with this method. On the contrary, it was shown by Nagy et al. [10] that photochemical activation of ironcarbonyl led to smaller metal particles that interact with the support more strongly than those derived from thermal decomposition. This was explained by a charge transfer from the excited ironcarbonyl fragment to the support. An improved procedure to deposit tungsten, molybdenum and chromium species on alumina is based on the photochemical reaction of $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) with triphenylphosphine (PPh_3) [11]. The substitution of CO for PPh_3 ligands enhances the interaction of metal carbonyls with the alumina support. In addition, the irradiation time could be adjusted to control the metal loading.

This method was recently applied to the preparation of $\text{Pd-W}/\gamma\text{-Al}_2\text{O}_3$, where the photochemical reaction was carried out in the presence of a reduced $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst [12]. As a result, tungsten was found to be present in a partially reduced state in close association with palladium. Moreover, we found evidence of a specific interaction between hexacarbonyl species and the metal surface. Although this method of preparation provides a new route to obtain bimetallic catalysts with metal–metal interaction, the use of PPh_3 leads to phosphorus and carbon residuals that might affect their catalytic activity.

Consequently, in the present study we have examined the photochemical reaction of $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ with $\gamma\text{-Al}_2\text{O}_3$ and $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ in the absence of PPh_3 . After reaction, DRIFTS FT-IR spectra were taken. Following a thermal treatment to fully decompose the adsorbed carbonyls, the catalysts were further characterized by atomic absorption spectroscopy (AAS), hydrogen chemisorption and FT-IR spectra of adsorbed CO and NO to observe changes on the palladium surface arising from the deposition of tungsten and molybdenum.

2. Experimental

The palladium catalysts were prepared by impregnation of the support ($\gamma\text{-Al}_2\text{O}_3$, Rhone-Poulanc,

$96\text{ m}^2\text{ g}^{-1}$) with a benzene solution of palladium acetylacetonate (Aldrich; $2.2 \times 10^{-3}\text{ g Pd ml}^{-1}$). Two support sizes with different pretreatment were used; in one preparation, the original alumina particle size (spheres with an average diameter of 3 mm) was retained and activated at 773 K in air. The derived samples are identified as $\gamma\text{-Al}_2\text{O}_3(\text{I})$. Another was obtained by grinding the solid to a grain size of about $840\ \mu\text{m}$, followed by activation in air at 973 K. This is $\gamma\text{-Al}_2\text{O}_3(\text{II})$. The solid (10 g) and the benzene solution (50 ml) were left in contact for 24 h at room temperature. The liquid was then removed, the solid dried under nitrogen flow, followed by calcination in air at 573 K for 2 h and finally reduced in hydrogen under the same conditions.

Using the pure alumina support and the palladium catalysts, $\text{W}/\gamma\text{-Al}_2\text{O}_3(\text{I})$, $\text{Mo}/\gamma\text{-Al}_2\text{O}_3(\text{II})$, $\text{Pd-W}/\gamma\text{-Al}_2\text{O}_3(\text{I})$ and $\text{Pd-Mo}/\gamma\text{-Al}_2\text{O}_3(\text{II})$ catalysts were prepared. In order to ensure the absence of oxygen and water, the photochemical reaction was carried out in an inert atmosphere (Schlenk technique). The $\gamma\text{-Al}_2\text{O}_3$ and the $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ samples were first treated in H_2 at 573 K. Approximately 1 g of solid was added to 40 cm^3 of hexane containing 0.038 g of $\text{W}(\text{CO})_6$ (Aldrich; $1.08 \times 10^{-4}\text{ mol}$) or 0.055 g of $\text{Mo}(\text{CO})_6$ (Aldrich; $2.08 \times 10^{-4}\text{ mol}$).

The photochemical reaction was performed at room temperature in an Ar atmosphere using a Philips HPL-N (125 W) UV lamp fitted into a Pyrex cold finger. In order to observe the reaction progress, small liquid samples were withdrawn to be analyzed by FT-IR. After an irradiation time of 6 h, the solid was filtered and washed with hexane. A small amount of solid was removed for DRIFTS analysis, while the remaining material was treated in vacuo at 723 K for 2 h, in order to decompose the adsorbed carbonyl species. The samples were then stored under Ar. Metal contents were determined by AAS.

Diffuse reflectance (DRIFTS) spectra were recorded at ca. 293 K on a Bomem MB-102 spectrometer, coadding 32 scans at a resolution of 4 cm^{-1} . The study was restricted to the mid-IR region ($4000\text{--}1100\text{ cm}^{-1}$), due to strong bulk absorption of alumina in the low wavenumber region. The solid phases were analyzed as powder in a DRIFT accessory, equipped with sampling cups. These cups were filled with the alumina or palladium–alumina powder and transferred to the equipment as fast as possible, to prevent

decomposition. These spectra were collected as reflectance units and transformed to Kubelka–Munk (KM) units. The solutions were analyzed with a pair of matched NaCl solution cells (0.10 nm pathlengths).

The fraction of exposed palladium atoms was derived from sorption and back sorption hydrogen isotherms measured on a volumetric glass apparatus. Prior to these measurements, the samples were treated in H₂ at 573 K for 1 h and evacuated overnight at the same temperature. The first isotherm, measured at room temperature, gave the amount of adsorbed and absorbed gas. After evacuation for 0.5 h a second isotherm was measured to determine the amount of absorbed hydrogen. The extent of irreversible adsorbed gas (H/Pd)_{irr}, was obtained by subtracting the second isotherm from the first. Assuming that the surface stoichiometry is unity, the fraction of exposed palladium atoms is given by (H/Pd)_{irr}. For those samples not available in enough quantity to perform the chemisorption measurements, the exposed Pd surface area was estimated from the FT-IR spectra of adsorbed CO and reported as CO/Pd.

FT-IR spectra of CO and NO adsorption were obtained in a NICOLET 20 DXB instrument at 4 cm⁻¹ resolution. Catalyst samples of approximately 20 mg were pressed to form transparent disks of 10 mm in diameter, that were mounted in a metal holder. The holder was placed in the beam path of a stainless steel cell, sealed with CaF₂ windows, and coupled to a vacuum system for evacuation to 10⁻⁶ Torr. It was possible to perform heat treatments up to 673 K, to dose small amounts of CO and NO through a leak valve and to maintain a steady flow of H₂ or He. A MKS Baratron (310-BH) pressure transducer allows pressure control in the 0.1–10 Torr range. In typical experiments, samples were reduced at 573 K in

flowing hydrogen, purged with helium and cooled to room temperature. Following evacuation of the cell, an FT-IR spectra was obtained and used as a background. Adsorbates were dosed at a pressure of 1 Torr and the sample was exposed to the gas phase for 2–5 min prior to spectra measurement. Scanning time was about 1 min. Gas pressures, contact time and temperature were well-controlled in order to facilitate the comparison of results for different samples.

3. Results and discussion

3.1. DRIFTS studies

Our previous results [11–13] showed that, in the presence of PPh₃, well-defined and stable IR bands were seen in the $\nu(\text{CO})$ region on alumina and palladium–alumina surfaces. Fig. 1a shows the DRIFTS spectra of Pd/Al₂O₃(I) after W(CO)₆+PPh₃ addition. The observed bands are due mainly to mono and disubstituted metacarbonyl species adsorbed on the alumina support, that were stable in air. It is well known that hexacarbonyl and subcarbonyl species adsorbed on dehydroxylated alumina, by interaction of a carbonyl ligand with Al³⁺ sites, can be detected and identified by IR or DRIFTS, if the measurements are carried out in an inert atmosphere. A detailed IR study of the adsorption of Cr(CO)₆, Mo(CO)₆ and W(CO)₆ on γ -Al₂O₃, under this condition, was carried out by Zecchina et al. [14], while Suvanto and Pakkanen [9] characterized the interaction of tungsten hexacarbonyl on alumina by DRIFTS observing mainly pentacarbonyl species in a nitrogen atmosphere. In general, the location and intensity of the IR bands depends mainly on the degree of dehydroxylation of the support.

Table 1
Main catalyst properties

Catalysts	BET (m ² g ⁻¹)	Pd (wt.%)	W (wt.%)	Mo (wt.%)	(H/Pd) _{irr}	CO/Pd ^a
Pd/ γ -Al ₂ O ₃ (I)	85	0.73	–	–	0.50	0.47
W/ γ -Al ₂ O ₃ (I)	–	–	0.70	–	–	–
Pd-W/ γ -Al ₂ O ₃ (I)	–	0.73	0.95	–	–	0.31
Pd/ γ -Al ₂ O ₃ (II)	90	0.85	–	–	0.47	–
Mo/ γ -Al ₂ O ₃ (II)	–	–	–	0.16	–	–
Pd-Mo/ γ -Al ₂ O ₃ (II)	–	0.85	–	0.55	0.20	–

^a From FT-IR spectra of adsorbed CO assuming an extinction coefficient of 7×10^{-17} cm⁻¹ per molecule.

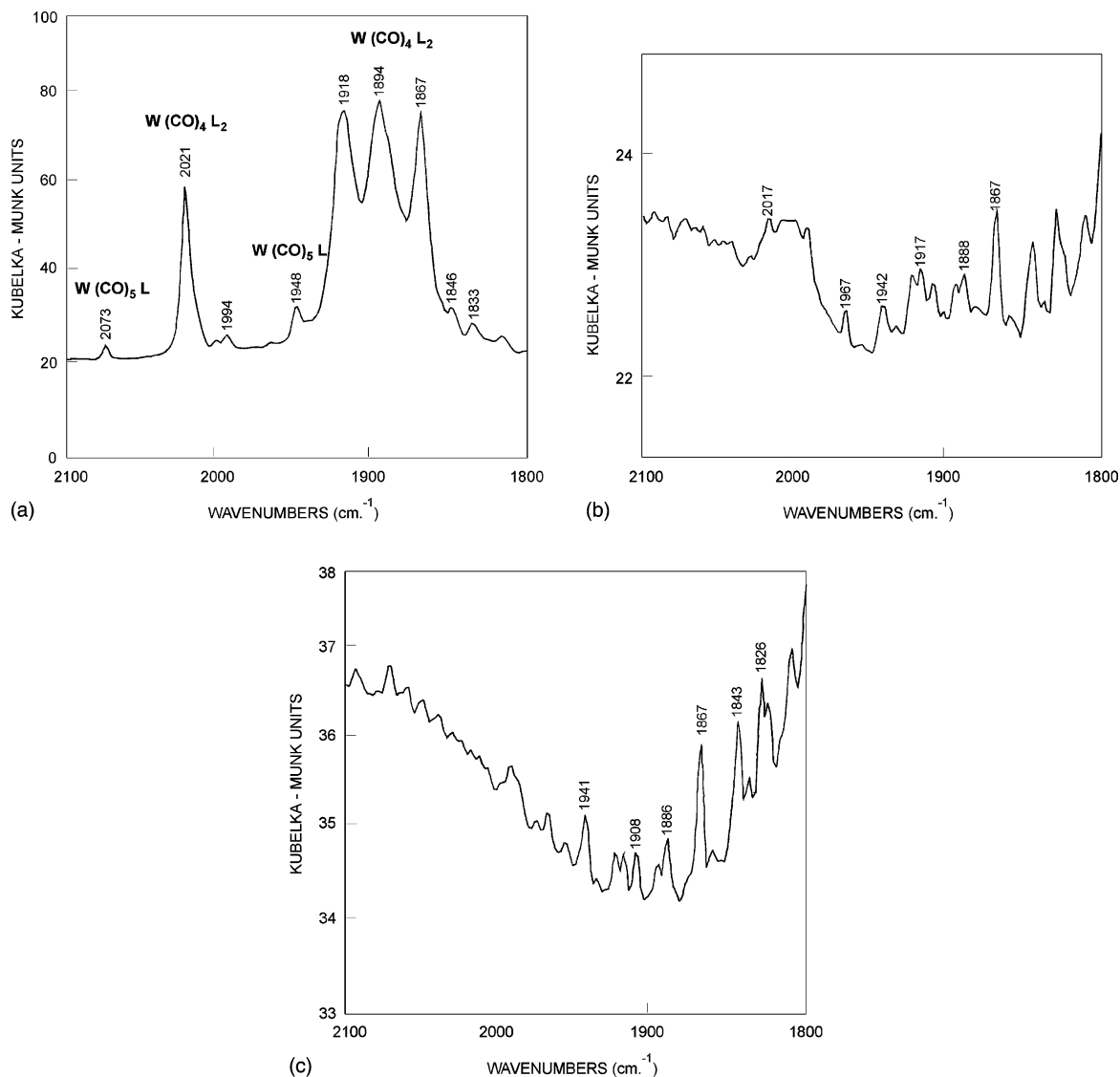


Fig. 1. DRIFTS IR spectrum in the $\nu(\text{CO})$ region of $\gamma\text{-Al}_2\text{O}_3$ after 6 h UV irradiation; reaction of $\gamma\text{-Al}_2\text{O}_3(\text{I})$ with $\text{W}(\text{CO})_6 + \text{PPh}_3$ (a); reaction of $\gamma\text{-Al}_2\text{O}_3(\text{I})$ with $\text{W}(\text{CO})_6$ (b); reaction of $\gamma\text{-Al}_2\text{O}_3(\text{II})$ with $\text{Mo}(\text{CO})_6$ (c).

In the present study, where there is no suitable ligand to stabilize the carbonyl species, exposing the samples to ambient air after the photochemical reaction leads to either weak bands or broad bands in the IR $\nu(\text{CO})$ region; 1800–2000 cm^{-1} . Fig. 1b and c display the DRIFTS spectra obtained for $\text{W}(\text{CO})_6 + \text{Al}_2\text{O}_3(\text{I})$ and $\text{Mo}(\text{CO})_6 + \text{Al}_2\text{O}_3(\text{II})$, respectively. They are quite similar despite the large difference in W and Mo uptake; 0.70 wt.% versus 0.16 wt.%, respectively (see

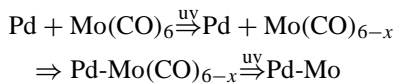
Table 1). The high tungsten loading relative to that of molybdenum is surprising, taking into account that $\text{Mo}(\text{CO})_6$ presents a higher photolability. It is important to realize that the alumina support, initially dehydroxylated at 773 K ($\text{Al}_2\text{O}_3(\text{I})$) or 973 K ($\text{Al}_2\text{O}_3(\text{II})$), was only treated at 573 K in H_2 prior to reaction. Consequently, one should expect a partial dehydroxylation of the support leading to low molybdenum and tungsten loadings. These conditions were chosen in

order to minimize the uptake by the alumina support and to favor the interaction of the hexacarbonyls with the palladium particles. In our case, the high tungsten loading is attributed to the large particle size of the γ -Al₂O₃(I) support, that allows the retention of tungsten hexacarbonyl and carbonyl species in the pores, despite the hexane washing step.

When the reaction was carried out in the presence of Pd/ γ -Al₂O₃(I) or Pd/ γ -Al₂O₃(II), the DRIFTS spectra again did not reflect the increased tungsten and molybdenum uptake determined by AA or the formation of new adsorbed species. In fact, they were quite similar to those obtained with the pure supports. This result may suggest that carbonyl species adsorbed on the metal particles are also sensible to the presence of air, or that they migrate to the metal during the subsequent thermal treatment. Another more likely interpretation is that these carbonyl species react and decompose very rapidly upon adsorption on the metal surface. It is relevant to mention that a few studies have been published on the interaction of hexacarbonyls with clean metal surfaces. Xu and Zaera [15] have studied in detail the adsorption and thermal decomposition of Mo and W hexacarbonyls on a clean Ni(100) surface. When the thermal decomposition was investigated by temperature programmed desorption, it was found that W(CO)₆ or Mo(CO)₆ desorption takes place at <250 K and only occurs on a fully saturated surface. A subsequent peak due to CO desorption from the nickel surface appears at around 450 K which indicates that the decomposition of hexacarbonyls adsorbed on the metal takes place rapidly at a lower temperature. By XPS analysis the growth of a W film on the nickel surface was observed to start at around 300 K. On the other hand, the decarbonylation of tungsten and molybdenum hexacarbonyls adsorbed on Al₂O₃ occurs at higher temperatures and it depends on the metal loading and the pretreatment temperature [16,17].

Based on these results, we propose that the adsorption and decomposition of molybdenum and tungsten hexacarbonyls with Pd/ γ -Al₂O₃ may follow two different reaction paths; one on the alumina support and another on the metal particles. Interaction with the palladium particles is facilitated by the photochemical process, because the removal of CO ligands leads to partially decarbonylated species that adsorb and decompose rapidly on the palladium surface. This

process, which leads to the formation of bimetallic particles, may be described by the following reaction scheme:



Although not investigated in detail, we have found that a necessary condition for this reaction to occur is the presence of relatively large palladium particles; >1.8 nm. Using a Pd/ γ -Al₂O₃ catalyst with a high metal dispersion, H/Pd_{irr} = 0.65, the deposition of tungsten was found to occur mainly on the alumina support. This requirement will be addressed again in the following section.

3.2. The effect of tungsten and molybdenum uptake on the fraction of exposed palladium atoms

In Table 1 the main physicochemical properties of the mono and bimetallic catalysts are presented. It is observed that both Pd/ γ -Al₂O₃ samples have a similar BET surface area, palladium content and dispersion, which indicates a negligible influence of the alumina calcination temperature or particle size on this preparation. Taking into account that the metal dispersion is about 50%, the average palladium particle size should be around 2.2 nm ($d_p = 1.12/(\text{H/Pd})_{\text{irr}}$). On the other hand, a comparison of the W/ γ -Al₂O₃ and Mo/ γ -Al₂O₃ samples reveals a large difference in uptake, already attributed to the retention of W(CO)₆ in the pores of the γ -Al₂O₃(I) support. The reaction of W(CO)₆ or Mo(CO)₆ with the Pd/ γ -Al₂O₃ catalysts under UV radiation, produces a 35% increase in the W uptake, while the Mo uptake increases by a factor of 3. In addition, a marked decrease in the fraction of exposed Pd atoms is observed, as shown by the (H/Pd)_{irr} or CO/Pd values. The large decrease in the H/Pd ratio by the addition of molybdenum, indicates that the dissociative adsorption of hydrogen, that requires a pair of neighboring Pd atoms, is strongly affected.

This behavior is a clear indication of a specific and preferential interaction (mainly for molybdenum) of the metal particles with the hexacarbonyl compounds and subcarbonyl species, despite the much larger surface area of the alumina support. Assuming hemispherical palladium particles of about 2.2 nm a metal surface area of approximately 1.6 m² g⁻¹ of

catalyst should be expected. In other words, only 2% of the alumina surface is covered by palladium. Consequently, under the present reaction conditions, the interaction between the tungsten and molybdenum hexacarbonyls and the palladium metal surface is enhanced.

3.3. Adsorption of CO and NO on Pd/ γ -Al₂O₃, Pd-W/ γ -Al₂O₃(I) and Pd-Mo/ γ -Al₂O₃(II)

The CO adsorption spectra corresponding to the two basic Pd/ γ -Al₂O₃ catalysts is shown in Fig. 2. The bands displayed are typical of CO adsorption on Pd; they exhibit two strong bands due to multiple coordinated species at 1965–1978 and 1924–1928 cm⁻¹ and also a band at 2082 cm⁻¹ due to linear adsorbed CO. The small differences in intensity were expected, because of the close metal loadings and the similar H/Pd ratios.

The complete absence of CO and NO adsorption bands was verified on W/ γ -Al₂O₃(I) and Mo/ γ -Al₂O₃(II). It is important to recall that all samples

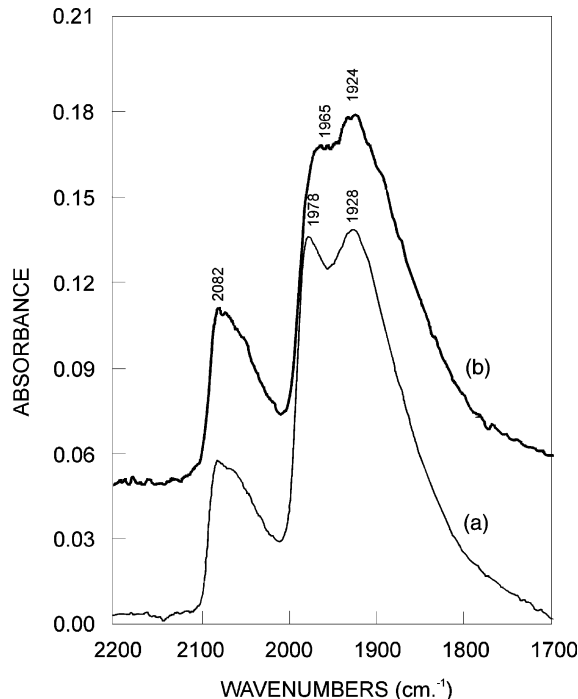


Fig. 2. FT-IR spectra of CO adsorbed on Pd/ γ -Al₂O₃(I) (a) and Pd/ γ -Al₂O₃(II) (b).

were subject to a high temperature treatment under vacuum to decompose the carbonyls and were reduced at 573 K prior to CO adsorption. Consequently, bands due to adsorbed carbonyls are not expected to remain on the surface. The probability of regeneration of tungsten or molybdenum carbonyl species upon dosing 1 Torr of CO must be discarded. Using a higher dosing pressure, it has been found that only a small fraction of Mo(CO)₆ undergoes reversible decarbonylation, if decomposition of adsorbed carbonyl is carried out at room temperature [14].

Fig. 3 displays the spectra of CO adsorption on Pd/ γ -Al₂O₃(I) and Pd-W/ γ -Al₂O₃(I). Here, again the bands are assigned to CO adsorption on the palladium surface. The bands due to multiple coordinated species are strongly attenuated by the presence of tungsten. This indicates the tendency of tungsten atoms to interact with palladium atoms located on the surface planes of large particles. Consequently, the adsorption of multiple coordinated CO species that require an ensemble of atoms is prevented.

Fig. 4 compares the adsorption of CO on samples Pd/ γ -Al₂O₃(II) and Pd-Mo/ γ -Al₂O₃(II). In this case, the large amount of molybdenum deposited on the palladium particles changes both the intensity and the

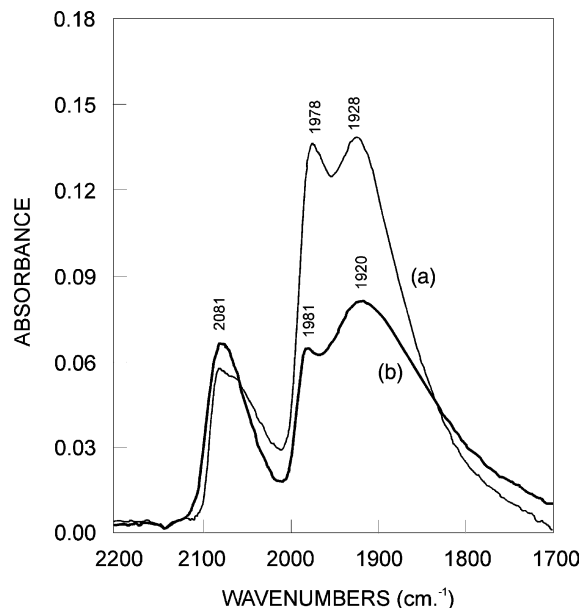


Fig. 3. FT-IR spectra of CO adsorbed on Pd/ γ -Al₂O₃(I) (a) and Pd-W/ γ -Al₂O₃(I) (b).

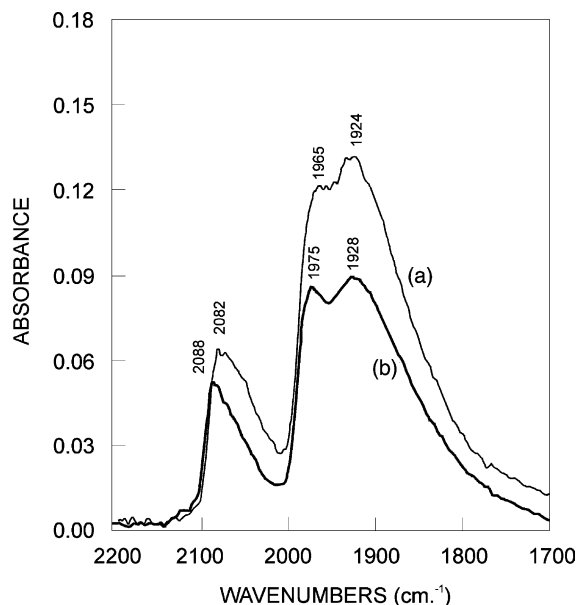


Fig. 4. FT-IR spectra of CO adsorbed on Pd/ γ -Al₂O₃(II) (a) and Pd-Mo(II)/ γ -Al₂O₃ (b).

frequency of the linear and bridge CO bands. The decrease in intensity is more pronounced for the multiple coordinated species. In addition, a clear shift of about 5–10 cm⁻¹ to a higher frequency is observed for all bands, which suggests that the adsorption of CO on palladium is weaker in the presence of molybdenum. This effect is assigned to a change in the electronic properties of palladium induced by the presence of reduced molybdenum species. A plausible explanation is founded on several theoretical studies [18–20] that have analyzed in detail the electronic alterations of Pd monolayers deposited on early transition metals (W, Mo, Ti). The calculations, supported by different experimental measurements (photoemission, work function, L-edge X-ray absorption fine structure and thermal desorption spectra of adsorbed CO) [21,22] have concluded that a small negative charge transfer takes place from the Pd atoms towards the substrate. More important, it has been shown that there is a reduction in the d band electron population of Pd due to a Pd(4d) → Pd(5s, 5p) rehybridization process that moves electrons into the Pd-W interface, making the metal-substrate bond stronger. As a result the Pd(4d) valence band is shifted towards higher binding energies, away from the 2π* CO orbitals. This

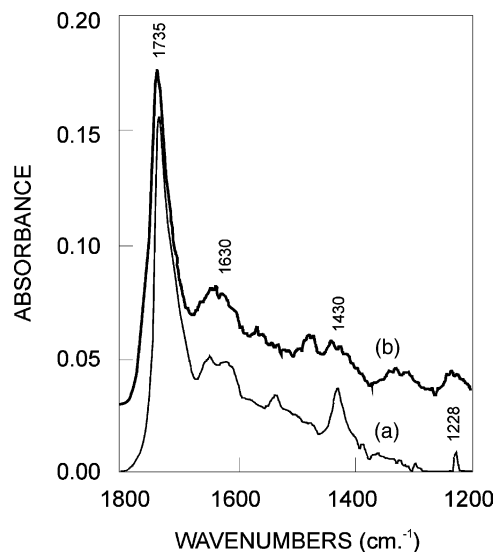


Fig. 5. FT-IR spectra of NO adsorbed on Pd/ γ -Al₂O₃(I) (a) and Pd/ γ -Al₂O₃(II) (b).

behavior mainly affects the back donation processes and weakens the Pd–CO bond.

An electronic influence of this kind may explain the observed frequency shift in the Pd–CO bands observed here, if one takes into account that the preparation method assures that an interaction between Pd atoms and reduced Mo species takes place.

Fig. 5 shows the IR bands for the NO adsorption on the two monometallic palladium catalysts; Pd/ γ -Al₂O₃(I) and Pd/ γ -Al₂O₃(II). They show the same spectrum pattern, with a main band due to linear adsorbed NO located at 1735 cm⁻¹. In addition, a broad and a weaker band at 1630–1650 cm⁻¹ is observed on both samples. A band in this region was assigned to bridged NO by Hoost et al. [23] and tentatively to bent NO on palladium by Almusaiteer and Chuang [24]. The spectra of Pd/ γ -Al₂O₃(I) has two additional bands at 1430 and 1228 cm⁻¹. In our opinion, all these bands are due to the presence of carbonates on the alumina surface, that are formed by an oxidation process that takes place upon addition of NO to a surface contaminated with carbon residuals from previous CO adsorption. The band around 1650 cm⁻¹ is assigned to the stretching frequency of bridged carbonates, the one at 1430 cm⁻¹ to free CO₃²⁻ ions [25] and that at 1228 cm⁻¹ to asymmetric stretching ($\nu_{\text{ass}}\text{COO}$) of bridge carbonates.

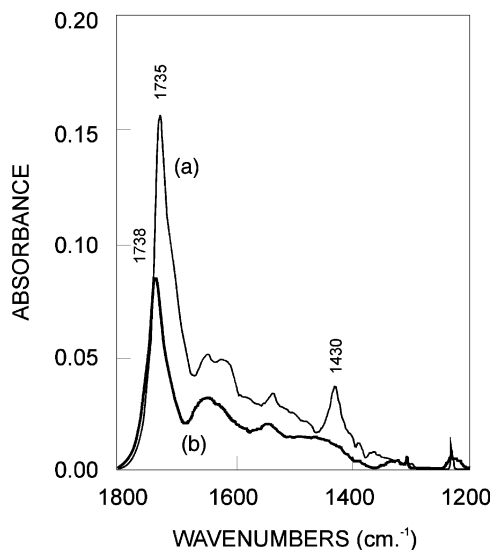


Fig. 6. FT-IR spectra of NO adsorbed on Pd/ γ -Al₂O₃(I) (a) and Pd-W/ γ -Al₂O₃(I) (b).

Figs. 6 and 7 display the change in the spectra of adsorbed NO due to the addition of tungsten and molybdenum to Pd/ γ -Al₂O₃(I) and Pd/ γ -Al₂O₃(II), respectively. Both tungsten and molybdenum decreased the intensity of the NO band, which is in accordance with the reduction in the H/Pd ratios

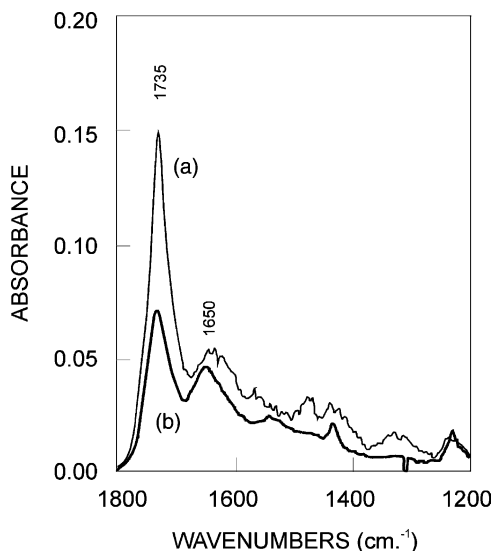


Fig. 7. FT-IR spectra of NO adsorbed on Pd/ γ -Al₂O₃(II) (a) and Pd-Mo/ γ -Al₂O₃(II) (b).

and the change in the CO spectra. In this case, the changes in frequency were less pronounced. On Pd-Mo/ γ -Al₂O₃(II) the bands previously assigned to bridge carbonates are clearly observed.

The marked changes observed in the CO and NO spectra confirm that the palladium chemisorption properties are strongly altered by interaction with tungsten and molybdenum. As mentioned before, the fraction of Mo and W which is deposited on the alumina support may become oxidized due to reaction with surface OH groups, taking into account that the support was not dehydroxylated to a large extent. On the other hand, molybdenum and tungsten atoms in close interaction with palladium more likely remain in a low valence state. Preliminary evidence supporting this interpretation is provided by the frequency upshift of CO adsorbed on Pd-Mo/ γ -Al₂O₃(II) relative to that on Pd/ γ -Al₂O₃(II). A detailed study involving oxygen uptake measurements combined with hydrogen titration and hydrogen adsorption is needed in order to obtain information on the oxidation state of molybdenum after H₂ reduction [7]. However, taking into account that the addition of molybdenum strongly modifies the chemisorption behavior of palladium, changes in the catalytic properties may also be expected.

4. Conclusions

To our knowledge this is the first study to consider the reactivity of hexacarbonyls with supported metal particles without the presence of a ligand. It has been demonstrated that bimetallic catalysts with close palladium–tungsten and palladium–molybdenum interactions could be prepared by the photochemical reaction of tungsten and molybdenum hexacarbonyls with alumina supported palladium particles. The present results suggest that hexacarbonyls and/or partially decarbonylated species adsorb and decompose rapidly on the surface of reduced palladium. On the other hand, the absence of ligands to form stable mono and disubstituted carbonyls as used previously [12] minimizes the adsorption on the alumina surface. The palladium–tungsten and palladium–molybdenum interaction strongly modifies the chemisorption properties of palladium as shown by the reduced H₂, CO and NO adsorption capacity. Moreover, molybdenum

seems to be present in a reduced state in close association with palladium.

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