Interaction of Group 6 Metal Carbonyls with Sulfated Zirconium Dioxide: IR Studies

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Received May 12, 1993®

The interaction of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with dehydroxylated active zirconia (prepared by thermolysis of a zirconium sulfate) has been studied by *in situ* IR spectroscopy. Adsorption of the three metal carbonyls takes place via O-bonding between a CO ligand and Lewis acid sites on the zirconia surface. Two kinds of these sites (with different Lewis acid strength) have been identified using CO as a spectroscopic probe. Formation of surface adducts between the zirconia support and the metal carbonyls was found to labilize CO ligands. Reversible decarbonylation of the adsorbed metal carbonyls was observed when pumping at room temperature. Subsequent admission of CO into the IR cell regenerates the hexacarbonyl surface adducts. The stability of these adducts (toward decarbonylation) was found to follow the order $W(CO)_6 > Cr(CO)_6 > Mo(CO)_6$.

Introduction

There is current interest on supported transition metal carbonyls as heterogeneous catalysts or catalyst precursors. It is believed that such systems can potentially combine advantages from both homogeneous and heterogeneous catalysis.[1-3] They also provide a convenient route to highly dispersed low-valent metals, without the need for strong reduction treatments.[4-6] Several high surface area inorganic materials (*e.g.* alumina, magnesia, zeolites) have been used as supports, and the interaction with the metal carbonyl was found to be mainly of the Lewis acid–base type.

Zirconium dioxide can easily be prepared in the high surface area form,[7-9] and it shows good thermal stability and resistance to chemical attack, which are desirable properties for a catalyst support. A few studies have appeared on zirconia-supported cobalt,[6] molybdenum,[10] and rhodium[11] carbonyls as catalysts for CO hydrogenation and for olefin metathesis and hydrogenation. However, the primary interaction between metal carbonyl and support is not known in detail. We report here an IR study of Lewis adduct formation between group 6 metal carbonyls and ZrO_2. Lewis acidity of the support was characterized by using CO as a probe molecule. Related work on group 6 metal carbonyls supported on active alumina has been reported by several workers.[12-15]

Experimental Section

Mesoporous ZrO_2 with a BET surface area of 90 $m^2\ g^{-1}$ was prepared by thermolysis, at 1000 K in a free atmosphere, of $Zr(SO_4)_2{\cdot}4H_2O$ (BDH, analytical grade). X-ray diffraction showed the material to be basically in the monoclinic form. Chemical analysis showed a residual sulfur content of 1.1%, and a most frequent pore radius of 8 nm was inferred from the corresponding nitrogen adsorption–desorption isotherm at 77 K. Further characterization of this ZrO_2 support was reported elsewhere.[16]

For IR studies, the zirconia sample in the form of a self-supporting wafer was placed inside a vacuum cell (similar to that described by Boccuzzi *et al.*[17]) which allowed in situ activation prior to dosing of CO or metal carbonyls, by vacuum sublimation from an adjacent reservoir. For activation, the zirconia wafer was fired for 30 min at 873 K under a dynamic vacuum. $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were obtained from Strem Chemical Co. and used without further purification. CO (99.9%) was from Air Products. IR transmission spectra were recorded, at room temperature, by using either Perkin-Elmer 881 or Bruker 66 instruments, both equipped with the corresponding data station.

Results and Discussion

The zirconium dioxide prepared by thermolysis of the sulfate, and activated in a vacuum at 873 K, gave the typical IR spectrum for a highly dehydroxylated material, as shown in Figure 1. Very weak OH stretching bands were observed at 3644 and 3667 cm^{-1}. A strong IR absorption was found at 1394 cm^{-1}, which can be assigned[18] to the S=O double bond of sulfate groups retained from the oxide precursor (zirconium sulfate). Weaker bands, from single S–O bonds, were also observed in the 1100–800-cm^{-1} range. Adsorption of the metal carbonyls did not significantly alter the OH and S=O bands (see insets in Figure 3).

CO Adsorption. Figure 2 shows the IR spectra, in the CO-stretching region, after dosing increasing amounts of CO to the zirconia sample. At low CO doses, two weak IR absorption bands are observed at 2212 and 2202 cm^{-1}. When the CO equilibrium pressure is increased, the 2212-cm^{-1} band changes very little while the 2202-cm^{-1} band grows and shifts to lower frequency, reaching 2198 cm^{-1} in the most intense spectrum. Both bands were found to disappear when CO was pumped out.

The presence of two IR absorption bands for adsorbed CO reveals two types of Lewis acid centers on the zirconia surface. The 2212-cm^{-1} band (which saturates at low CO equilibrium pressure) must be assigned to strong, and less abundant, Lewis

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® Abstract published in *Advance ACS Abstracts,* February 15, 1994.

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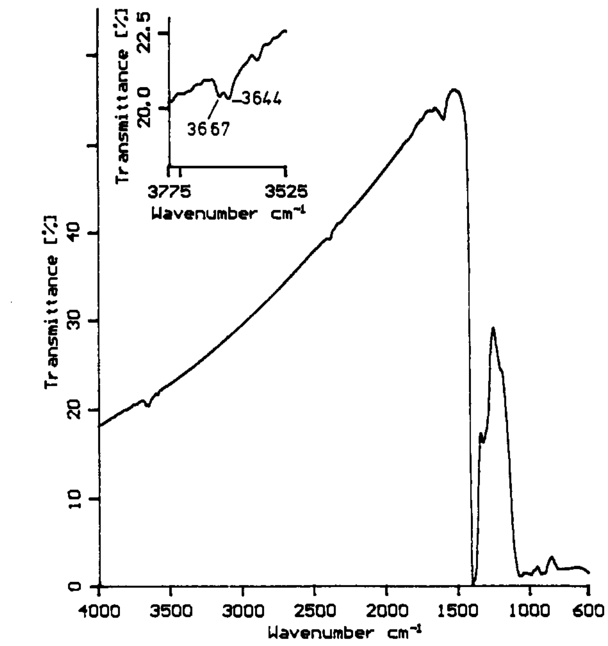

Figure 1. IR spectrum of the ZrO_2 wafer, activated in vacuo at 873 K.

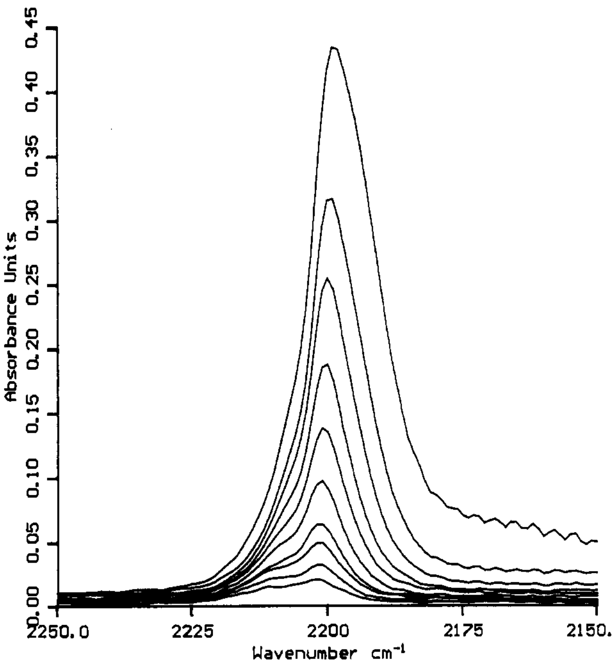

Figure 2. IR spectra of increasing doses (0.5, 1, 1.5, 2, 4, 6, 10, 15, 20, 30 Torr) of CO on ZrO_2. The blank spectrum of the zirconia sample has been subtracted.

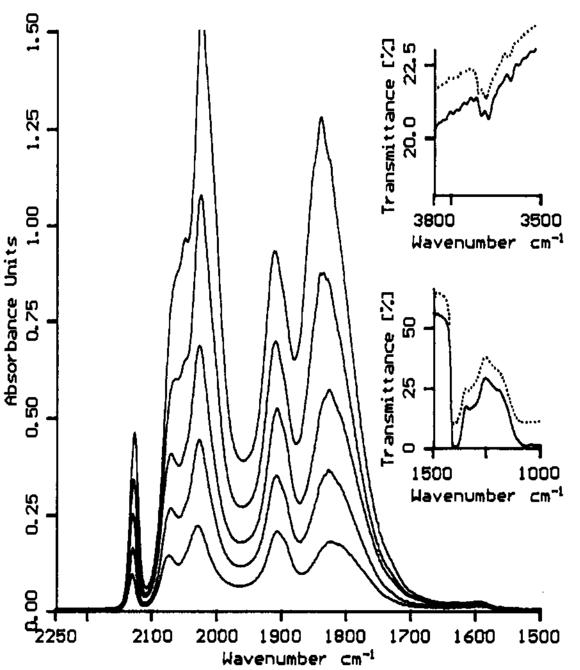

Figure 3. IR spectra (ZrO_2 blank subtracted) of increasing doses of $Cr(CO)_6$ on the zirconia sample. Insets show the OH and S=O bands prior to (—) and after (···) dosing the metal carbonyl. For clarity the dotted line has been vertically displaced.

Table 1. IR Frequencies (cm^{-1}) of Cr, Mo, and W Carbonyls Adsorbed onto ZrO_2

bands	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
X_1 (O-bonded)	1910–1913	1904–1908	1897–1902
X_2 (E)	2005	2006	1996
X_3 (A_1)	2050	2050	2047
X_4 (A_1)	2128	2132	2136
Y_1 (O-bonded)	1824–1842	1822–1837	1810–1823
Y_2 (E)	2031	2026	2024
Y_3 (A_1)	2075	2070	2070
Y_4 (A_1)	2131	2136	2138

acid sites while the 2202-cm^{-1} band corresponds to surface sites with weaker electron-acceptor character. According to Morterra *et al.*,[19,20] these two types of Lewis acid sites are assigned to different sets of coordinatively unsaturated Zr^{4+} cations. The CO-stretching frequencies reported by Morterra *et al.* (who prepared their zirconia from a hydroxide precursor) change slightly with the firing temperature of the zirconia sample, but they are in the range 2198–2190 cm^{-1} (high-frequency band) and 2186–2180 cm^{-1} (low-frequency band). The higher frequencies found for our zirconia sample reveal a higher acidity of the surface sites. This enhanced acidity is a consequence of the remaining sulfate groups which withdraw electron density from Zr^{4+} ions.[21] A similar effect was found by Bensitel *et al.*[22] for a sample of sulfated zirconia.

Adsorption of Metal Carbonyls. Figure 3 shows the IR spectra (in the CO-stretching region) of increasing amounts of $Cr(CO)_6$ adsorbed onto the zirconia wafer. Several bands are observed, all of which grow with increasing $Cr(CO)_6$ equilibrium pressure. A parallel experiment with $W(CO)_6$ gave entirely similar spectra, while $Mo(CO)_6$ showed some differences (see later). Band frequencies for the three adsorbed metal carbonyls are summarized in Table 1.

$M(CO)_6$ molecules (M = Cr, Mo, W), which have O_h symmetry, give in the gas phase a single (T_{1u}) IR-active band at about 2000 cm^{-1}. However, the Raman-active modes (A_{1g} and E_g) become IR-active when the molecular symmetry is slightly perturbed: $M(CO)_6$ in solution or physisorbed. Coordination to a Lewis acid site through a single CO ligand results in considerable lowering of the stretching frequency of the implied CO, which is thus decoupled from the remaining ligands.[23] The C_{4v} moiety should then give a $2A_1 + E$ triplet, as shown in Figure 4.

The IR absorption bands in Figure 3 can be divided into two quartets, which are assigned to $Cr(CO)_6$ molecules O-bonded to Lewis acid sites of different strength on the surface of ZrO_2. This is in agreement with the foregoing discussion on CO adsorption.

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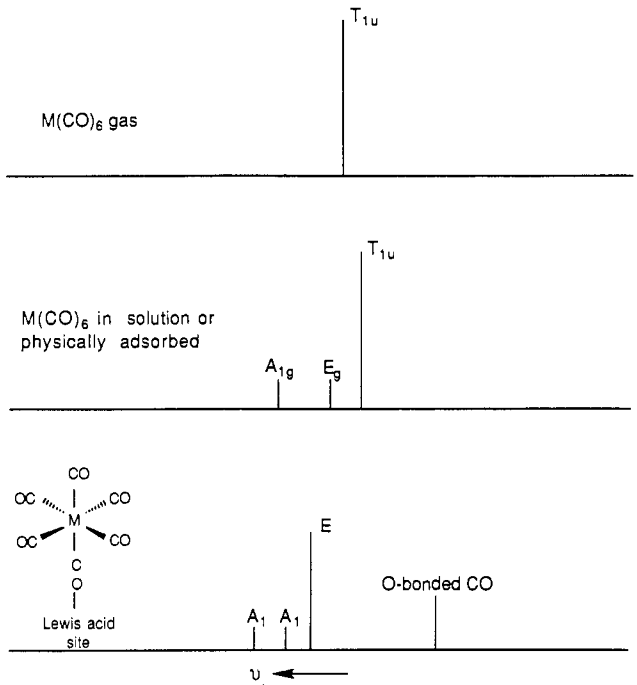

Figure 4. Scheme showing the IR-active modes of free $M(CO)_6$ and the adsorbed hexacarbonyl.

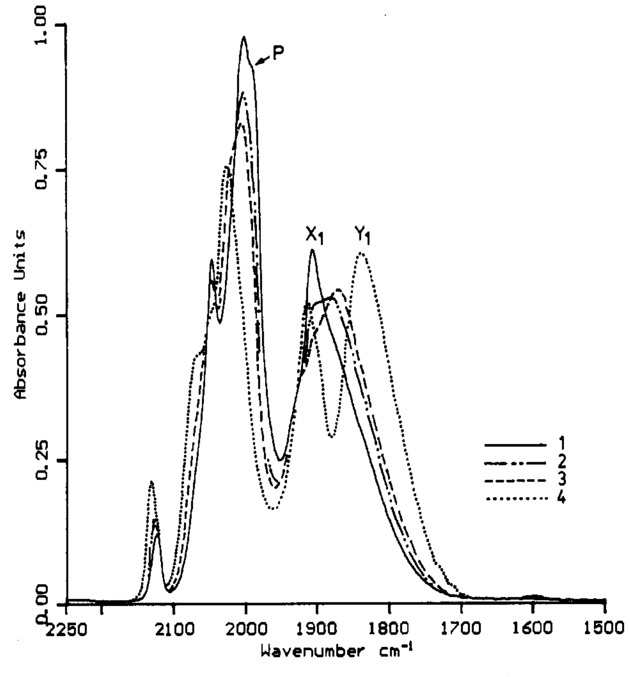

Figure 5. IR spectra of $Cr(CO)_6$ on ZrO_2 immediately after dosing (1) and after 1, 2, and 20 min, respectively (2–4).

It is well-known[24] that the downward shift of the O-bonded CO increases with increasing strength of the Lewis acid center, and the same applies to the upward shift of the stretching frequency of the remaining CO ligands ($2A_1$ + E triplet). This allowed a correlation to be made between the two low-frequency bands (X_1 and Y_1, O-bonded CO) and the corresponding high-frequency ones (X_2–X_4 and Y_2–Y_4), as shown in Figure 3.

Further evidence for the formation of two families of surface adducts between $Cr(CO)_6$ and ZrO_2 was obtained by sending a large dose of the carbonyl onto the oxide wafer and taking IR spectra at increasing time periods. The results, which are depicted in Figure 5, show the following. (i) The IR spectrum obtained immediately after dosing with $Cr(CO)_6$ changes with time, until a final spectrum similar to those in Figure 3 is reached. (ii) In the low-frequency region, the initial spectrum shows a strong band (X_1) and a weaker one (Y_1) which appears as a shoulder. In consecutive spectra the intensity of X_1 first decreases and then increases, while that of Y_1 increases continuously. The related high-frequency bands, X_2–X_4 and Y_2–Y_4, follow a similar trend. (iii) The initial spectrum shows a band (P) at 1989 cm^{-1} which disappears in consecutive spectra. This band is assigned to physisorbed (multilayer) $Cr(CO)_6$.

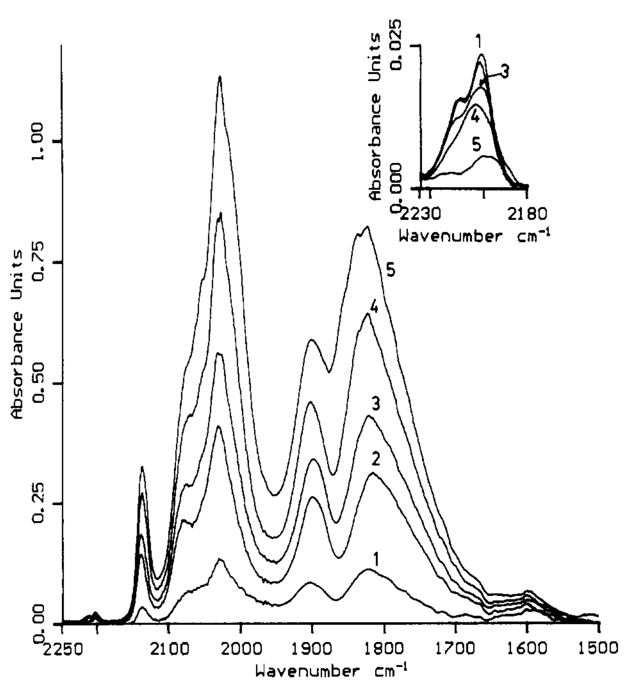

Figure 6. IR spectra (ZrO_2 blank subtracted) of increasing doses (1–5) of $Mo(CO)_6$ on the zirconia sample. Inset shows the corresponding CO bands in the 2200-cm^{-1} region.

The fact that X_1 and Y_1 show different time-dependent intensity changes proves that these two bands correspond to different surface species. $Cr(CO)_6$ molecules interacting with the zirconia surface through two CO ligands would also give an IR spectrum with two low-frequency bands. In this case, however, both bands should change intensity in a parallel way.

The observed time-dependent IR spectra (Figure 5) can be explained in terms of a diffusion-controlled penetration of the metal carbonyl into the oxide wafer. Immediately after arrival, $Cr(CO)_6$ molecules form a penetration front which saturates the exposed surface of the sample and also results in multilayer adsorption (band P). The high intensity of band X_1 (compared with Y_1) in the first spectrum of Figure 5 is a consequence of the higher proportion of weaker Lewis acid sites, as already shown by the CO adsorption experiment (Figure 2). As the penetration front advances through the oxide wafer, $Cr(CO)_6$ molecules coordinate first to strong Lewis acid sites and then to weaker ones. This explains the observed intensity changes of X_1 and Y_1 and of corresponding high-frequency bands.

IR spectra of $Mo(CO)_6$ adsorbed (at increasing dosage) on ZrO_2 are shown in Figure 6. Basically, they show the same general patterns already discussed for $Cr(CO)_6$. However, a distinct feature in these spectra is the presence, at 2212 and 2202 cm^{-1}, of two weak IR absorption bands which must be assigned to adsorbed CO. This shows that, contrary to $Cr(CO)_6$ and also $W(CO)_6$, $Mo(CO)_6$ slightly decarbonylates on interaction with ZrO_2. Decarbonylation, however, must be rather limited, since the spectra of adsorbed $Mo(CO)_6$ are very similar to those of adsorbed $Cr(CO)_6$. The inset in Figure 6 shows that the intensity of bands corresponding to adsorbed CO decreases with increasing doses of $Mo(CO)_6$. This is probably due to increasing saturation of surface sites by metal carbonyl molecules.

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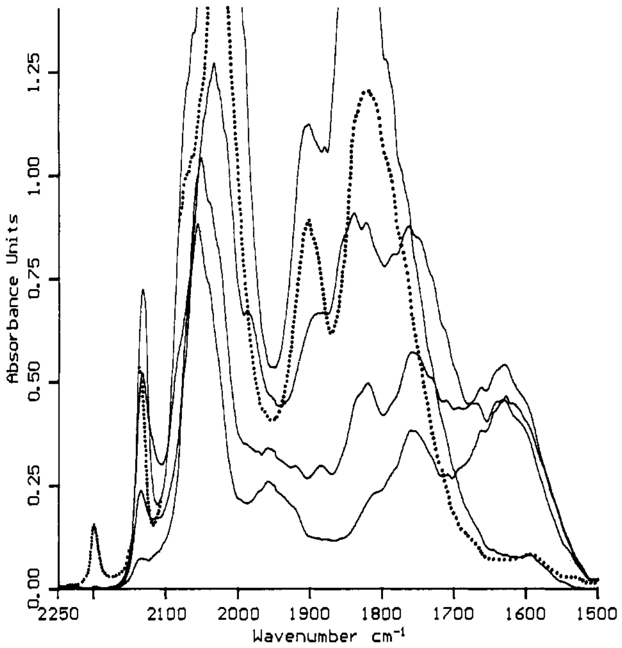

Figure 7. IR spectra of adsorbed $Mo(CO)_6$ at increasing outgassing time at room temperature. The dotted line spectrum shows the effect of dosing with 20 Torr of CO after the last outgassing step (the band at 2200 cm^{-1} corresponds to adsorbed CO).

The observed lower stability of adsorbed $Mo(CO)_6$ is in agreement with the fact[25] that $Mo(CO)_6$ is more reactive toward ligand substitution than $Cr(CO)_6$. It has also been reported[26] that room-temperature chemisorption of $Mo(CO)_6$ on magnesium aluminate (spinel) leads to labilization of CO ligands and partial decarbonylation, whereas $Cr(CO)_6$ is adsorbed without decomposition.

Further decarbonylation of zirconia-supported $Mo(CO)_6$ can be induced by outgassing the IR cell at room temperature. This is shown in Figure 7. Outgassing leads to a progressive decrease of the overall intensity and also to the appearance of new IR absorption bands. The new bands at 1630, 1755, and 2053 and some minor ones at 1975–1925 cm^{-1} can be assigned to subcarbonyl species because the admission of CO into the IR cell erodes these bands and substantially regenerates the original spectrum of adsorbed hexacarbonyl (dotted-line spectrum in Figure 7).

The subcarbonyl species probably remain anchored to Zr^{4+} cations on the support surface *via* the oxygen atom of a CO ligand. Alternatively they could be anchored through the Mo center to a surface anion. The evidence derived from IR spectra supports the first hypothesis for the following reasons:

(i) The 1630-cm^{-1} band is too low to be assigned to a terminal CO. The lowest IR absorption bands observed for molybdenum subcarbonyls in low-temperature matrices[27] are as follows (in cm^{-1}): $Mo(CO)_5$, 1885; $Mo(CO)_4$, 1887; $Mo(CO)_3$, 1862. However, CO stretching frequencies in the 1600-cm^{-1} range have been reported[28,29] for many carbonyl compounds linked through the oxygen atom of one CO ligand to a Lewis acid center.

(ii) Direct interaction of the Mo atom of a subcarbonyl species with an O^{2-} anion at the oxide surface would result in a downward shift of the stretching frequency of the CO ligands, because of increased electron density at the metal center, which favors back-donation to the CO ligands. In fact this was the effect found by Özkar *et al.*[30] for $Mo(CO)_3$ species anchored through the metal center to oxygen atoms of cation-exchanged faujasites. In our case, however, a strong IR absorption band due to subcarbonyl species is observed at 2053 cm^{-1} (Figure 7). An increased stretching frequency of the free CO ligands is precisely the behavior expected for a metal subcarbonyl anchored to a Lewis-acid center through a CO ligand. The simultaneous presence of the 2053- and 1630-cm^{-1} bands can easily be explained on the hypothesis that molybdenum subcarbonyl species interact with the surface acid centers through the oxygen end of a CO ligand.

The presence of two Lewis acid sites with different acid strength on the zirconia surface gives rise to two subcarbonyl anchored species. The CO ligands of the subcarbonyl species are known to be more basic[24,27] than the CO ligands of the holocarbonyls. Therefore, CO ligands interact more strongly with Lewis acid centers on the oxide support, thus lowering the corresponding CO stretching frequency down to 1755 and 1630 cm^{-1}.

The dotted-line spectrum in Figure 7 confirms the assignment of the 1630-, 1755-, 1925-, 1975-, and 2053-cm^{-1} bands to subcarbonyl species and also proves that the decarbonylation process is reversible, at least to a large extent.

Outgassing of zirconia-supported $Cr(CO)_6$ and $W(CO)_6$ was also found to lead to partial decarbonylation but not so pronounced as for the $ZrO_2/Mo(CO)_6$ system. The stability of the supported hexacarbonyls followed the order $W(CO)_6 > Cr(CO)_6 > Mo(CO)_6$.

Acknowledgment. The authors are thankful for the financial support given by the Spanish DGCYT, Project PS90-0214.

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