On the Active Site of the Phillips Catalyst for Ethylene Polymerization

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The FTIR spectra of CO adsorbed on the chromium(II)-A surface compound (the active site of the Phillips catalyst) before and after short polymerization with ethylene have been reexamined. No difference in the CO spectra of the room temperature triplet at 2190, 2185, and 2179 cm^{-1} was found for that part of chromium which reacts with ethylene compared to the CO spectra of the unreacted surface compound. The same result was observed with the low temperature CO IR triplet at 2120, 2100, and 2035 cm^{-1}. After low temperature polymerization with ethylene a new CO IR band at 2176.82 cm^{-1} was observed. After high temperature reaction with ethylene a symmetrical and rather sharp CO IR band at 2171.52 cm^{-1} was noted at room temperature instead. It is concluded that in both cases rather well-structured chromium surface compounds are formed. The CO IR bands of the room temperature triplet shifted from 2190.79, 2184.74 and 2178.69 cm^{-1} to 2192.28, 2185.03, and 2180.76 cm^{-1} after seven oxidation (800°C, O$_2$)/reduction (350°C, CO) cycles. The CO IR bands of the low temperature triplet (-145°C) separated into two triplets with higher (2121.12, 2102.06, and 2040.37 cm^{-1}) and lower (2117.12, 2098.47 and 2031.34 cm^{-1}) positions than the original one. It is concluded that the surface structure of the support has a rather large influence on the electronic density of the chromium(II) surface ions. © 1989 Academic Press, Inc.

INTRODUCTION

The hydrocarbon group connecting the growing polymer to the catalytically active site of the Phillips catalyst (*1*) for the polymerization of ethylene was identified some years ago by Ghiotti *et al.* (*2*). These authors assigned a band at 2750 cm^{-1} to a carbene group bonded to the chromium surface compound. It was also noticed that this band disappears on adding CO. Recently, the present author showed that this polymer in the case of low temperature polymerization (below 100°C), is connected to the chromium(II)-A metal ion by a methylene group (Cr–CH$_2$–R) (*3*), because its deformation vibration is observed at 1448 cm^{-1}. Furthermore, no end-groups of the polymer (R) such as methyl (–CH$_3$) or vinyl groups (–CH=CH$_2$) could be observed although very short polymer chains were investigated: 20 CH$_2$ units in Ref. (*2*) and 4 to 14 CH$_2$ units per active chromium site in Ref. (*3*).

The structure of the coordinatively unsaturated chromium(II) surface compound, first proposed to be the catalytic center of the Phillips catalyst by Krauss and Stach (*4*), has been investigated by several research groups (*5–19*). Krauss *et al.* (*5–8*) concluded that two chromium(II) surface species exist (named **A** and **B**), where the **A** species has only two oxygen ions as ligands at the chromium(II) and **B** an additional oxygen from a surface silanol group as a third ligand. At the same time Zecchina *et al.* (*9, 10*) described an active and a deactivated chromium(II) surface compound with IR bands from adsorbed CO at 2186 and 2181 cm^{-1}, respectively. A band at 2191 cm^{-1} was assigned to CO adsorbed on a chromium(III) surface compound (*10*). Later members of this research group adopted the **A**/**B** notation and added two **C** species (*11*),

which are deactivated **A** species. A year later the present author assigned a band near 2200 cm^{-1} to CO on a chromium(III) surface compound (*12*). An IR band at 2191 cm^{-1} was assigned to CO on the high temperature deactivated chromium(II) surface species. A model was proposed for this surface species with oxygen from a surface siloxane group as a third ligand on the chromium(II) ions (*12*). The three bands of the room temperature triplet were assigned to a dinuclear surface compound with one chromium(II) ion in a *cis* configuration (CO IR bands: 2190 and 2179 cm^{-1}) and another in *trans* configuration (CO IR band: 2184 cm^{-1}) (*12, 13*). All the above assignments refer to terminally bonded CO molecules. Recently, the Turin group (*14*) proposed models where species **B** included the former Krauss species **B** and the one with the oxygen from a siloxane group. Species **C** was modeled with two oxygen ligands from siloxane groups. This classification is rather inconsistent because the two **B** species have quite distinct preparation procedures and should react quite differently, for example in the polymerization of ethylene.

From IR spectra of CO adsorbed at low temperatures it is now clear that the active site consists of a pair of chromium(II) ions on the silica gel surface (*9–13*), although reaction of chromium compounds with the silica gel showed no evidence for dinuclear chromium surface compounds (*15–19*). The only explanation for the low temperature triplet of CO adsorbed at the chromium(II) surface compound at 2120, 2100, and 2035 cm^{-1} (*10, 12*) is that of bridging CO molecules and the author proposed previously that only dinuclear chromium species can be catalytically active in the polymerization of ethylene (*20*).

However, it is known that only a small part of the chromium (*21*) or even of the chromium(II)-**A** centers (*3, 22*) are polymerization-active and that this active part increases with lower chromium content of the catalyst. One aim of the present investi-

gation was to examine the IR bands of CO adsorbed on the polymerization active chromium(II)-**A** surface compound and compare them with those for the part of chromium(II)-**A** that is polymerization-inactive.

EXPERIMENTAL

The experimental conditions have been described previously (*3*). In short, a self-supporting disk from silica gel 60 (Merck 7733) with 0.5% Cr was heated in an IR cell to 800°C, while changing between vacuum and oxygen. Thereafter the chromium(VI) was reduced by CO at 350°C. The CO was evacuated at 300°C and a spectrum was recorded. The cell was filled with 10 kPa CO and spectra were recorded at room temperature and at −145°C (100 Pa CO). The cell was again evacuated at 300°C and cooled to the polymerization temperature. Ethylene was then reacted with the catalyst for 15 s (30 s in the case of 50°C polymerization) and removed again in vacuum at the polymerization temperature for 15 min. The fourth spectrum was then recorded at room temperature. Again 10 kPa CO was added and the fifth and sixth spectra were recorded at room temperature and at −145°C (100 Pa CO). After this the cycle was started again by heating the IR cell to 800°C changing between vacuum and oxygen.

The above procedure gave several series of differences spectra, namely (1) CO IR spectra on reduced chromium surface compounds after a number of preparation cycles, (2) by subtracting the CO IR spectra after short polymerization from those taken before, CO IR spectra of that part of chromium that had reacted with ethylene, and (3) with double difference spectra (subtracting adjusted spectra of the first series from inverse spectra of the second series) the CO IR spectra of CO adsorbed on "living" polymerization site were obtained.

The IR spectra were recorded on a Nicolet FTIR spectrometer 20 SXC with a resolution of 4 cm^{-1} and 512 scans were accumulated. The second derivative of the
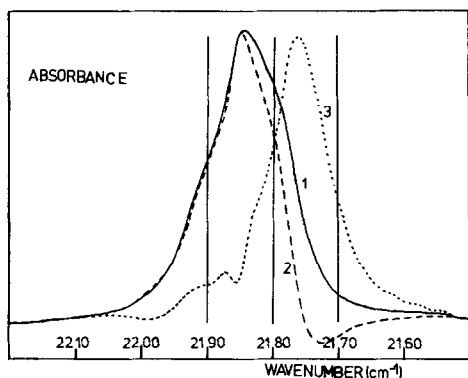
FIG. 1. FTIR spectra of CO adsorbed on chromium(II)-A at room temperature (spectrum 1) and CO adsorbed on that part of the chromium which has reacted with ethylene at 50°C (spectrum 2, difference spectrum). Spectrum 3 is the difference spectrum from spectrum 2 minus spectrum 1.

spectra has been used to determine the exact position of bands and shoulders. As shown below a reproducibility of 0.02 cm^{-1} was achieved on certain spectra of the third series after different preparation cycles.

RESULTS

Figure 1 contains three FTIR spectra of CO adsorbed on chromium(II) on silica gel. Spectrum 1 (first series of spectra) shows the typical room temperature triplet of CO (10) with bands at 2190.87, 2184.86, and 2178.82 cm^{-1}. When this adsorbed CO is removed in vacuum at 300°C and the sample is brought into short contact with ethylene at 50°C for 30 s (short polymerization) 23% less CO is adsorbed at room temperature than before (3). Subtracting the IR spectrum of the latter CO spectrum from that of the CO adsorbed on the original chromium(II)-A (spectrum 1) one obtains spectrum 2 (second series of spectra), which is normalized to the same height as spectrum 1. Again three bands can be noted at nearly the same positions as before: 2190.74, 2184.93, and 2179.36 cm^{-1}. These three bands are now from the CO which was adsorbed before at the part of the chromium(II) that has been converted by the ethylene to the active polymerization sites.

One should especially note that the band at 2190.8 cm^{-1} has not been changed in any way. On the low wavenumber side a negative band appears.

Subtracting now spectrum 2 from spectrum 1 one obtains spectrum 3 in Fig. 1 (third series of spectra) again normalized to the same height. One band can be noted in the new spectrum at 2176.83 cm^{-1} with perhaps a small shoulder at 2182.94 cm^{-1}. The shoulder is tentative because here the two original spectra overlap too heavily. With a polymerization temperature of 100°C the band appears at 2176.81 cm^{-1}, which is within the limits of error, exactly the same position as above.

In a slight change of the experimental procedure the IR cell was once evacuated after short polymerization and CO addition. It was observed that the adsorbed CO with the band at 2176.8 cm^{-1} can be removed by evacuation and that the CH_2 band at 2750 cm^{-1} (2, 3) will be restored. This proves that this CO is only *adsorbed* on the active chromium(II) and that no chemical reaction with the polymer chain occurs.

The author has previously identified two different polymerizing species originating from chromium(II)-A on silica gel via reaction with ethylene at different polymerization temperatures (22). Therefore, corresponding experiments were carried out at a polymerization temperature of 225°C; the spectra are shown in Fig. 2. In spectrum 1
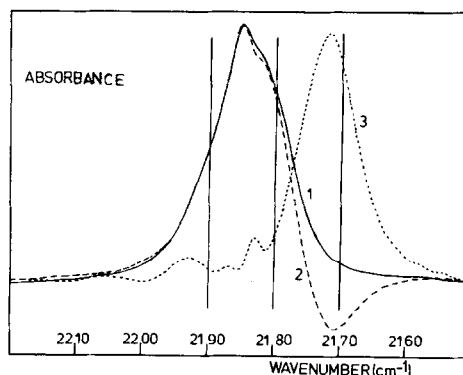

FIG. 2. FTIR spectra after reaction with ethylene at 225°C. Nomenclature as in Fig. 1.
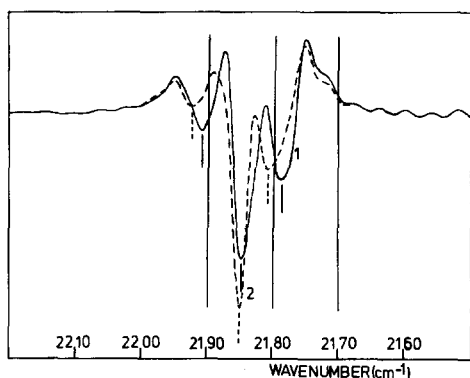
FIG. 3. Second derivative of FTIR spectra of CO adsorbed on chromium(II)-**A** at room temperature after the first preparation (spectrum **1**) and after seven preparation cycles (spectrum **2**) (first series spectra). Observe the shift of the (negative) peaks.

again three bands, now at 2192.28, 2185.03, and 2180.76 cm⁻¹, can be seen. When these positions are compared with those from the analogous spectrum in Fig. 1 slight differences can be realized (see below). Spectrum **2** in Fig. 2 shows also three bands at 2191.27, 2185.06, and 2180.80 cm⁻¹ for the chromium(II), which has reacted with ethylene. Only the band with the highest wavenumbers has shifted its position compared to spectrum **1** in Fig. 2. However, a similar effect was not observed in other polymerization experiments using higher temperatures and is therefore considered to be of no significance. Spectrum **3** in Fig. 2 shows now a new band at 2171.54 cm⁻¹, which in some five wavenumbers lower than in spectrum **3**, Fig. 1 and is observed in all experiments using higher polymerization temperatures. With polymerization at 150, 175, and 200°C the position of this band was at 2171.53, 2171.50, and 2171.29 cm⁻¹, respectively. The same effect was observed previously (*3*), but for IR spectra of CO adsorbed at low temperature (−145°C).

The results in Figs. 1 and 2 again point to the formation of two different, catalytically active and rather well-structured chromium surface compounds by short reaction of

chromium(II)-**A** with ethylene at different temperatures (*3, 22*).

Above it was already noted that the spectra **1** in Figs. 1 an 2 differ slightly in the position of the bands. A closer examination of the experimental series revealed that this effect is due to the successive preparation cycles. During each activation the sample is heated to 800°C under oxygen and this treatment might change the surface of the silica gel slightly and therefore also the chromium(II) surface compound.

The difference in the spectra due to the reactivation effect can be seen more clearly in Fig. 3 in which the second derivatives of the spectra from the first (spectrum **1**) and the seventh activation cycle (spectrum **2**) have been plotted from first series spectra. One observes that the band with the lowest wavenumbers around 2180 cm⁻¹ is shifted most, while the middle band at 2185 cm⁻¹ is shifted only marginally. Figure 4 reveals that the reactivation effect is increasing with every reactivation step. The band positions of the "zero activation cycle" were extrapolated to 2190.32, 2184.75, and 2178.18 cm⁻¹.

Corresponding IR spectra were run at −145°C, measuring the low temperature IR triplet of CO adsorbed on the chromium(II)-**A** surface compound on silica gel (*10, 12*).
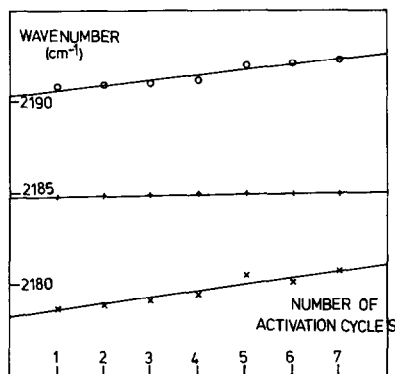

FIG. 4. Shift of the three triplet bands from CO adsorbed at room temperature with successive preparation cycles (first series spectra).
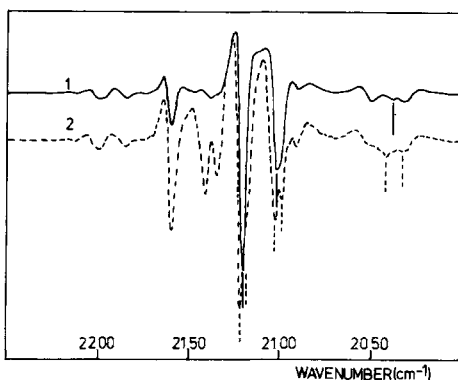
FIG. 5. Second derivative of FTIR spectra of CO adsorbed on chromium(II)-A at low temperature ($-145°C$) after the first preparation (spectrum **1**) and after seven preparation cycles (spectrum **2**) (first series spectra). Note the splitting of the (negative) peaks in spectrum **2**.

The second derivatives of the spectra after one and seven preparation procedures are shown in Fig. 5: the original triplet at 2119.70, 2101.29, and 2036.60 cm^{-1} is split into two triplets, one with bands at higher wavenumber (2121.12, 2102.06, and 2040.37 cm^{-1}) and one with bands at lower wavenumbers (2117.12 (?), 2098.47, and 2031.34 cm^{-1}). While the two bands of the triplet at 2100 cm^{-1} can be well identified, this is not as easily done for the other wavenumber sets because the splitting is small (2120 cm^{-1}) or because the second derivative favors sharp bands (2135 cm^{-1}) even if they have little real intensity.

Figure 6 shows the separation values for the above bands plotted against the arithmetic mean value of the band positions at 2120, 2100, and 2035 cm^{-1}. The continuous line is calculated by the least-squares method with all points in Fig. 6 and has a confidence value of $R = 0.85$. At zero splitting one obtains a value of 2157 cm^{-1}. However, it is quite obvious that there is one point near 2120 cm^{-1} which is rather questionable. The dashed line is drawn through the upper three points and gives a zero splitting value of 2149 cm^{-1}. The dotted line uses only two points from the lower series

and has a zero splitting value of 2142 cm^{-1}. The stretching vibration of gaseous CO is at 2143 cm^{-1}. The zero splitting wavenumbers for the two "corrected" lines are rather close to this value. In other words, the separation of the CO IR bands from the low temperature triplet on the chromium(II)-A surface compound increases linearly with increasing distance from the stretching vibration of gaseous CO. This means that all three bands are connected in some way and should originate from only one surface species. This means also that small differences within the chromium(II)-A species can best be observed on the broad band around 2135 cm^{-1}.

What happens now to these bands after polymerization? The bands of the triplet are broadening even more than without the short polymerization step. The second derivatives of the spectra (Fig. 7) from second series spectra show again that the triplet from the first activation at 2119.55, 2102.10, and 2036.79 (?) cm^{-1} separates into one with higher wavenumbers (2121.70, 2103.38, and 2045.31 cm^{-1}) and one with lower wavenumbers (2117.34, 2096.13, and 2029.61 cm^{-1}).

When the spectra of the CO low temperature triplet taken before and after the short polymerization are compared with ethylene it becomes clear that again the short poly-
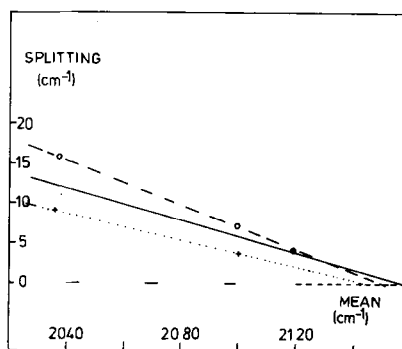

FIG. 6. The splitting of the bands of the low temperature triplet versus the arithmetic mean position of these bands at 2120, 2100, and 2035 cm^{-1}. The stretching vibration of CO_{gas} is at 2143 cm^{-1}.

2200   2150   2100   2050
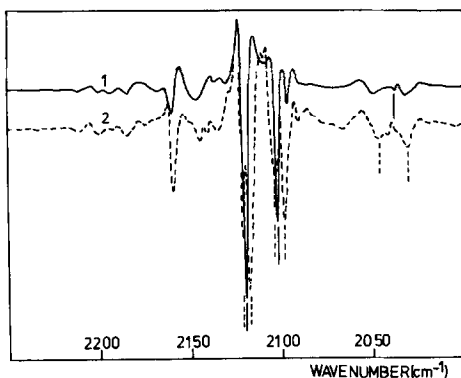
WAVENUMBER(cm⁻¹)

FIG. 7. As in Fig. 5 but now after polymerization in each case (second series spectra).

merization does not discriminate within the CO IR bands of the low temperature triplet. There is no change in the position of these bands after the short polymerization time with ethylene after the first activation (Figs. 5–7, spectra **1**) and after seven activation cycles (Figs. 5 and 7, spectra **1**). If two triplets are found after different preparation cycles, these are also present in both series of spectra. When the high temperature triplet of CO adsorbed on chromium(II) is compared with that at low temperature, one can conclude again that the shift to higher wavenumbers in the former is caused by the same structural change as the splitting of the low temperature triplet.

DISCUSSION

As mentioned in the Introduction, the CO IR bands of the room temperature triplet were correlated in previous work by other authors with two different types of surface chromium(II) (*10, 11*). This is not supported by the results presented here. In Figs. 1 and 2, with low and higher temperature reaction with ethylene, all three bands of the room temperature triplet of CO IR bands decrease in the same way, although only between one and two fifths of the whole chromium reacts (*3*). If there were an activity difference of the chromium surface species expressed in the room temperature

triplet, it should have been detected. This conclusion is also valid for the low temperature triplet of CO IR bands.

The accepted model (*23*) of CO adsorption on metals and metal ions contains two different types of bonding: (1) the σ-donation bond from the slightly antibonding and filled 5σ orbital of the CO molecule to the metal ion, and (2) the π back-donation from the metal into the empty, antibonding $2\pi^*$ orbital on the CO. The first type strengthens the bond between C and O and increases the stretching vibration of adsorbed CO, while the back-donation weakens the CO bond and decreases the stretching vibration of CO. In principle the adsorbed CO molecule tests the electron density of the metal ion. In CO bridging between two metals the σ-bond is of much less importance than the π back-donation (the 5σ orbital points just in between the two chromium ions), so that the bond between C and O is weakened compared to terminal bonded CO and the stretching vibration is decreased by more than 100 cm⁻¹ (*23*). Usually, bridging CO is an indication of a metal–metal bond. The above model neatly explains why the room temperature CO IR bands can be converted at low temperature from positions higher than the stretching vibration of gaseous CO (2143 cm⁻¹) to those at lower wavenumbers than gaseous CO: terminal CO at room temperature is converted to CO bridging between two chromium(II) ions. No other explanation for the above effect has been put forward. This implies that the chromium(II)-**A** surface compound on silica gel is built up as a dinuclear surface complex (possibly with a metal–metal bond). The above results suggest that also the catalytically active site of the Phillips catalyst is a dinuclear chromium(II)-**A** surface compound.

However, this surface compound is not as rigid as structures of molecules in crystals. The above results from IR spectra of CO adsorbed at room temperature and low temperature on the chromium(II)-**A** surface compound suggest that the surface of the

silica gel has an effect on its adsorption properties which is by no means small. In our case restructuring of the surface due to several preparation cycles or even sintering of the silica gel may cause this effect.

CO adsorption on the chromium surface compared after short reaction with ethylene at 50 and 225°C showed that the two surface compounds formed are different, with CO IR bands at 2176.8 and 2171.5 cm^{-1}, respectively. The first species is most likely to be a chromium(II)-A alkyl ((-O-)$_2$Cr-CH$_2$-R) (3). It should be noted that the CO IR band is shifted to lower wavenumbers in this case compared with the original chromium(II) surface compound ((-O-)$_2$Cr). After reaction with ethylene at higher temperatures the symmetric and rather narrow CO IR band is shifted to still lower wavenumbers. This means that a well-defined, new chromium surface compound is formed, which has a higher electron density at the chromium metal ion than before. The nature of this compound is not clear at the moment, but the new ligand(s) have to provide more electron density than the -CH$_2$- R group. Whether this effect is due to a weakened σ or a stronger π back-donation bond cannot be decided here.

In conclusion, the above results give no evidence for two chemically different chromium(II)-A surface compounds on silica gel causing the room temperature triplet of adsorbed CO. However, the structure of this chromium(II)-A surface compound is not exactly defined, but will be changed, within certain limits, by the structure of the silica gel surface.

As to the question of why only a part of the chromium(II) surface compound is catalytically active (at low polymerization temperatures 20%, at higher temperatures 40%) (22) and why this percentage is depen-

dent on the chromium surface concentration, the above results provide no answer.

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