Acta Chemica Scandinavica A 39 (1985) 133–141

UV/Vis Investigation of the Polymerization Center of the Phillips Catalyst

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UV/Vis diffuse reflectance spectra have been recorded of the chromium(II)/silica gel system with low chromium concentration (0.074 %) after polymerization of C_2H_4 at 373 K. From the decrease of the UV band on the CO (at 10^5 Pa) complex with the chromium(II) surface ion at 34 000 cm^{-1}, it was estimated that roughly 50 % of all chromium is polymerization active at this concentration. The difference spectra of the polymerization active chromium show two bands at 16 000 and 31 500 cm^{-1} with absorbed CO or C_2H_4. After removing CO or C_2H_4 by evacuation, a difference spectrum with four bands at 13 500, 27 500, 31 500 and 35 700 cm^{-1} was obtained. These bands are interpreted as arising from a chromium(III) surface compound formed by reaction of the chromium(II) with C_2H_4 and thus creating the Cr–C bond, which is essential for the polymerization active center of the Phillips catalyst.

Recent investigations on the chromium/silica gel system for the polymerization of ethylene (Phillips catalyst[1]) have shown that two different catalytic centers exist, either with chromium(II) or with chromium(III).[2–7] It was found that chromium(III) on silica gel is over a hundred times more active in the polymerization of ethylene than chromium(II).[7]

Nevertheless, on the basis of ESCA measurements[8] and the determination of turnover numbers[7] it was concluded that chromium(II) on silica gel is most likely the catalytically active center of the Phillips catalyst. However, because chromium(III) on silica gel has a much higher activity, relatively small amounts of this species can improve the performance of the Phillips catalyst considerably.

For the Phillips catalyst[9] and the chromium(II) on silica gel[7] it was found that with low chromium concentration the ratio of the polymerization active chromium to the overall chromium is strongly improved, so that at 0.07 % chromium per silica gel roughly 50 % of all chromium is active.[7] This ratio is sufficient for an investigation of the conversion of the chromium(II) (without a Cr–C bond) to the polymerization species (with the Cr–C bond). While other investigation methods like ESCA or IR spectroscopy are difficult to use in the case of low chromium concentrations, UV/Vis diffuse reflectance spectroscopy has such a good signal to noise ratio, that difference spectra can be used successfully on such samples.

EXPERIMENTAL

The chromium content of all samples was 0.074 % (aftere heating to 1073 K, after drying at 393 K: 0.056 %). Chromium was analyzed by colorimetric determination.[10] The silica gel

0302-4377/85 $2.50

("Merck 7733") was impregnated with chromic acid. The samples were heated to 1073 K in vacuum and O_2 intermittently and reduced to chromium(II) with CO at 643 K. Three different samples were investigated: 1) The chromium(II) on silica gel was treated with C_2H_4 at 373 K and 66 kPa pressure, so that only 30 % of the maximum possible amount of polyethylene was formed. 2) The chromium(II) on silica gel was reacted with C_2H_4 at room temperature for five minutes. 3) The standard chromium(II) on silica gel sample.

The samples were filled under nitrogen into cylindrical quartz tubes with Schlenk attachment. The diffuse reflectance spectra were recorded on a Hitachi (Perkin-Elmer) UV/Vis/NIR spectrophotometer 330 with an integrating sphere. The spectra were stored in a Perkin-Elmer IR data station 3500, transferred to a Tektronix 4051/4662 table computer and recalculated according to the Kubelka-Munk function.[11]

In order to show at the same time in the figures the *d-d* bands (between 4000 and 26000 cm^{-1}) and the at least ten times more intense charge transfer bands (between 30000 and 50000 cm^{-1}), the scale of the reflectivity (recalculated according to the Kubelka-Munk function) was changed at 26000 cm^{-1} from 0–1.5 to 0–15. Sharp bands at 4700, 5900, 7100 and 8200 cm^{-1} are first overtones or combination vibrations from stretching vibrations of O–H, Si–O or C–H bonds.

RESULTS

Figs. 1. and 2 show the diffuse reflectance spectra of sample 1 (polymerization of C_2H_4 at 373 K). The evacuated sample (spectrum A, Fig. 1, peaks at 13300, 40000 and 47500 cm^{-1}) reacts only very weakly with N_2 (spectrum B, peak shift to 13500 cm^{-1}). When treated with CO (10^5 Pa), however, a strong reaction is observed (spectrum C, peaks at 19000 and 33800 cm^{-1}). This adsorbed CO can be removed by vacuum to a high extent (spectrum D, Fig. 1, peaks at 14000, 38500 and 47500 cm^{-1}). It should be noticed that the absorbed CO (10^5 Pa) shows a strong band in the UV region at 33800 cm^{-1}. This band will be used later to estimate the percentage of the polymerization active chromium.

On reaction with C_2H_4 (10^5 Pa) the spectrum changes again (spectrum A, Fig. 2, peaks at 16300, 32000, 35500 and 48000 cm^{-1}). The chromium(II) surface compound and the polymerization center are destroyed by O_2 (spectrum B, Fig. 2, peaks at 11000, 16700, 31000 and 41000 cm^{-1}).

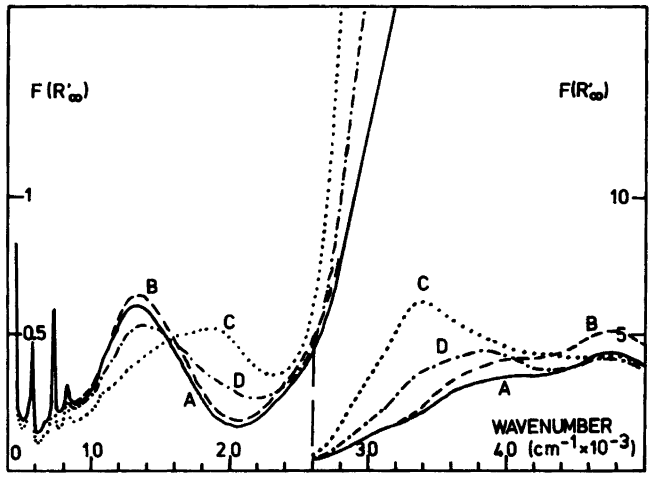


Fig. 1. Diffuse reflectance spectra of chromium(II) on silica gel after polymerization of C_2H_4 at 373 K. Spectrum A: vacuum, B: N_2, 10^5 Pa, C: CO, 10^5 Pa, D: CO, 10 Pa.

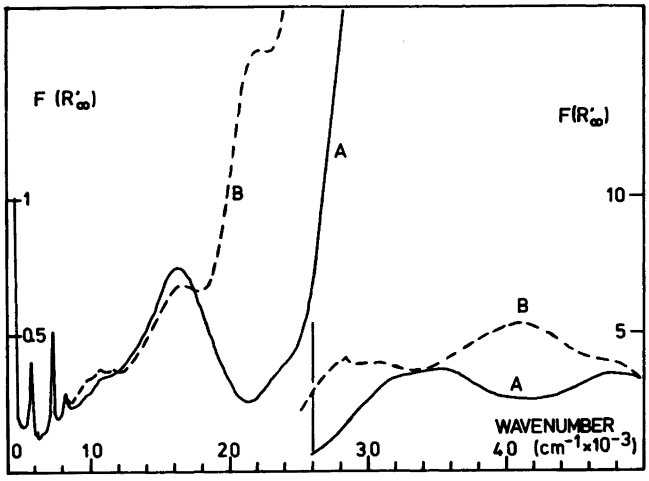


Fig. 2. Diffuse reflectance spectra as in Fig. 1, but spectrum A: C_2H_4, 10^5 Pa, B: O_2, 10^5 Pa.

The above spectra from the polymerization experiment will now be compared with those from a standard chromium(II) on silica gel sample [13] (Fig. 3 and 4). Generally, all spectra from the standard chromium(II) are more intense. This is partly due to a larger specific volume of sample 1, which causes also the first overtone vibration of the OH groups at 7000 cm^{-1} to be weaker for sample 1. In order to reach the same intensity for this vibration the polymerization sample has to be multiplied with 1.4.

The second difference that can be noticed is that also the reactions with complexing gases are weaker. The change from the evacuated sample (spectrum A, Fig. 3, peaks at 12000, 31000, 43000 and 47300 cm^{-1}) to that with N_2 (spectrum B, peaks at 13500, 43000 and 47600 cm^{-1}) or CO (10 Pa, spectrum D, peaks at 14000, 19500, 38000 and 48000 cm^{-1}) is

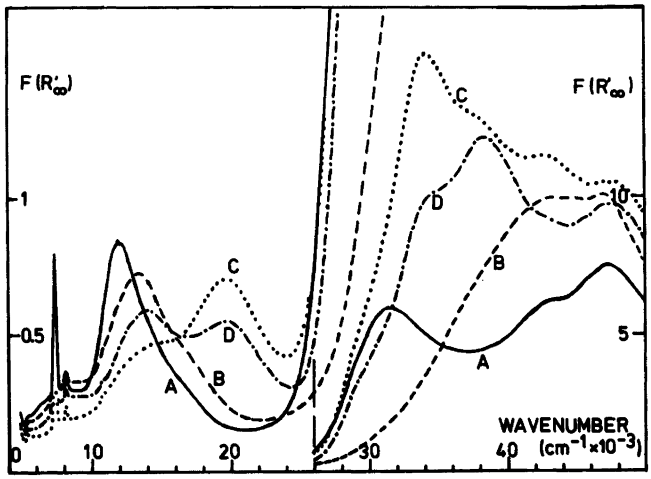


Fig. 3. Diffuse reflectance spectra of standard chromium(II) on silica gel. Spectra A, B, C, D as in Fig. 1.

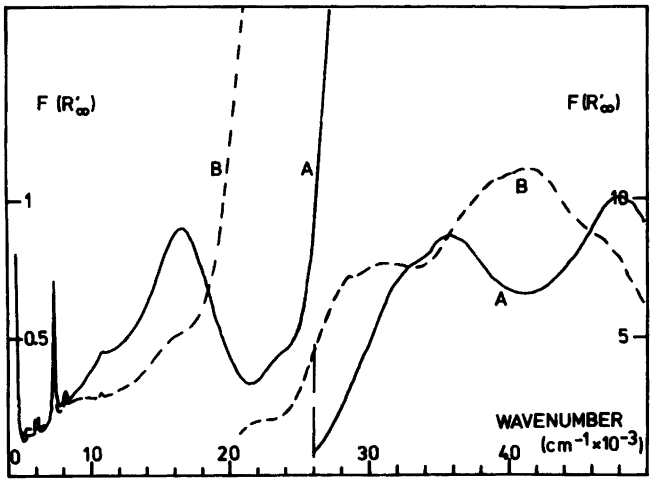


Fig. 4. Diffuse reflectance spectra of standard chromium(II) on silica gel. Spectra A and B as in Fig. 2.

more strongly observed in the spectra of the standard chromium(II) than in those from sample 1 (polymerization with C_2H_4 at 373 K). CO adsorbed at 10^5 Pa on the standard chromium(II) surface compound has peaks (or shoulders) at 14000, 19500, 33700, 38000, 42000 and 48000 cm^{-1} (spectrum C in Fig. 3). The spectrum of C_2H_4 adsorbed on the chromium(II) standard is now very similar to that on polymerization sample 1 (spectrum A in Fig. 4, peaks at 16300, 35800 and 48000 cm^{-1}). The same is valid also for the spectrum after reaction of chromium(II) with O_2 (spectrum B in Fig. 4, peaks (or shoulders) at 9400, 16000, 22000, 31000 and 41000 cm^{-1}).

The weakening of the reactivity in the above spectra from the two samples is most likely caused by the formation of the polymerization species. C_2H_4 adsorbed on inactive

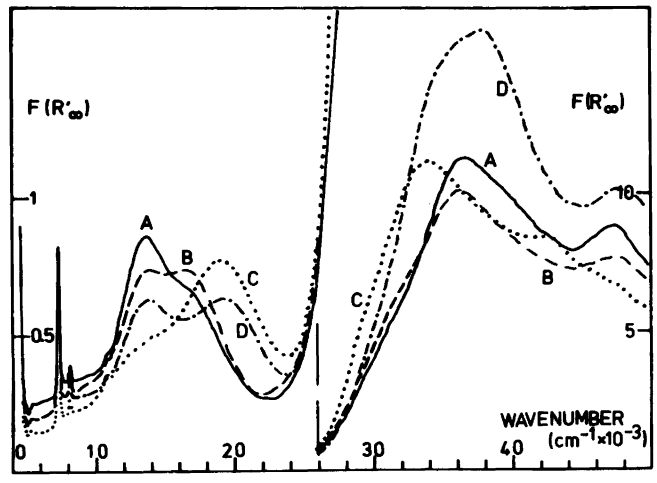


Fig. 5. Diffuse reflectance spectra of chromium(II) on silica gel after contact with C_2H_4 at room temperature (for five minutes). Spectra as in Fig. 1.

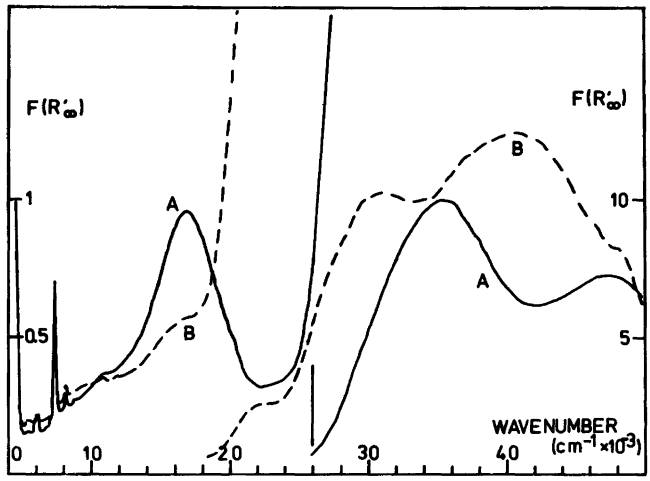


Fig. 6. Diffuse reflectance spectra of chromium(II) on silica gel after contact with C_2H_4 at room temperature. Spectra as in Fig. 2.

chromium(II) and CH_2 groups from the polymer may, however, contribute to the above differences in the spectra. In order to clarify this, spectra of sample 2 (short contact with C_2H_4 at room temperature) are shown in Figs. 5 and 6. From the UV part of the spectra of sample 2, which have similar intensity as those of the standard sample, it becomes clear that adsorbed C_2H_4 does not weaken these bands intensity. From the relatively big difference between spectra A (vacuum) and B (N_2, 10^5 Pa) in Fig. 5 as compared with spectra A and B in Fig. 1, it can be concluded that more than just an adsorption of C_2H_4 has occurred with sample 1. One should also notice that the shoulder at 16000 or 16300 cm^{-1} in spectrum A (Figs. 4 and 6, respectively) is converted into a band with a peak at 16700 cm^{-1} in the case of the polymerization sample (spectrum A, Fig. 2).

The difference between vacuum and adsorbed N_2 is, as was already noticed above, very small for the spectra of sample 1 (polymerization at 373 K), if compared with the difference for a standard chromium(II) sample. The cause of this small difference is most likely an interaction of the produced polyethylene with the catalytically inactive chromium(II) surface compound. This interaction from the polymer, which competes successfully with N_2 for complexing the chromium(II), is however, weaker than the adsorption of CO or C_2H_4. We have no comparison spectrum for the interaction with the polymer to subtract from the spectra of sample 1. Therefore, we start the series of difference spectra with the spectra of CO at 10^5 Pa.

Fig. 7 shows the three reflectance spectra of sample 1, 2 and 3 (spectra A, B and C). Spectrum A from Fig. 1 (here spectrum D) will be used as a baseline for the CO UV band at 34000 cm^{-1}, because it shows the lowest reflectivity at this wavenumber. Spectra A and D in Fig. 7 have been multiplied by 1.4 (see above). By comparing the intensity of the CO UV band at 34000 cm^{-1} in spectrum C to the one in spectrum A, both with respect to the baseline in spectrum D, the intensity of the band in spectrum A is found to be only 46 % of that in spectrum C. The decrease, 54 %, corresponds to the percentage of polymerization active centers formed. This is in good agreement with results from a previous investigation,[7] where roughly 50 % was found. In the case of spectrum B (from sample 2) a percentage of

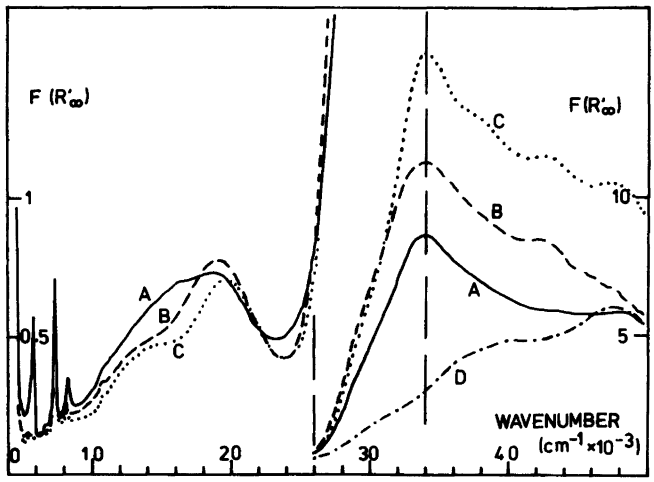


Fig. 7. Diffuse reflectance spectra from the above three chromium(II) on silica gel samples with CO (10^5 Pa). The decrease of the UV and at 34000 cm^{-1} is used to estimate the percentage of polymerization active chromium(II).

32 % polymerization active chromium was calculated in the same way. This means that on short contact with C_2H_4 at room temperature, only half the possible number of chromium(II) surface ions is converted to the polymerization active center as would be possible at 373 K.

With the above result of 50 % we now know how much chromium(II) is not converted in Figs. 1 and 2. This inactive chromium(II) should show the same reflectance spectra as in Fig. 3 and 4 for CO and C_2H_4 and can now be subtracted for the first time with safety. So, spectrum C in Fig. 7 was divided by two and subtracted from spectrum A in Fig. 7. The results is shown in Fig. 8 as spectrum A. Only two peaks at 16000 and 31500 cm^{-1} are

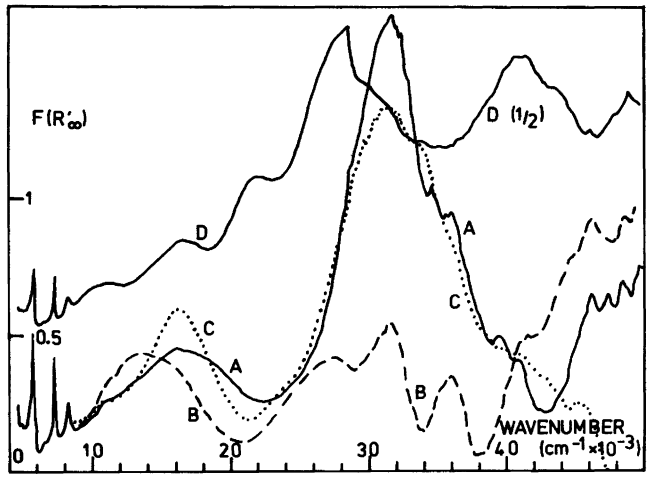


Fig. 8. Difference spectra of the polymerization active chromium surface compound (see text). Spectrum A: CO, 10^5 Pa, B: vacuum, C: C_2H_4, 10^5 Pa, D: O_2, 10^5 Pa.

obtained in the first spectrum of the polymerization active chromium after initiation of the polymerization. Two shoulders at 19300 and 35000 cm^{-1} may indicate that the bands of the polymerization inactive chromium(II) are not subtracted completely.

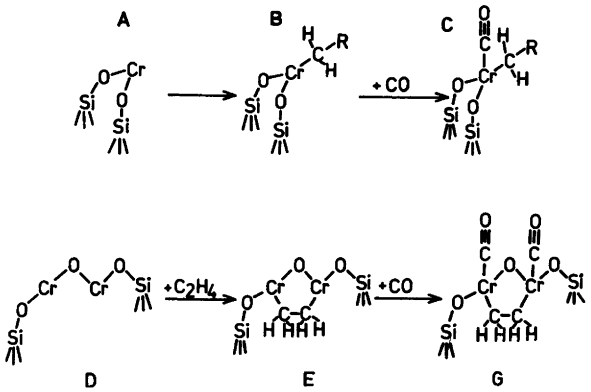
The same subtraction was performed with the spectra CO (vacuum) (evacuation after CO adsorption: spectrum D in Fig 3 subtracted from spectrum D in Fig. 1). The result is spectrum B in Fig. 8. Here we have four peaks at 13500, 27500, 31500 and 35700 cm^{-1}. The band at 31500 cm^{-1} may be an indication, that not all adsorbed CO has been removed from the polymerization active chromium(II) by evacuation.

The third difference spectrum is calculated from the spectra with adsorbed C_2H_4 (10^5 Pa). The resulting spectrum C in Fig. 8 is quite similar to that calculated from the spectra with adsorbed CO (10^5 Pa) with two peaks at 16000 and 31500 cm^{-1}. We can conclude that the polymerization active chromium surface species adsorbs CO and C_2H_4 alike and that, as a result of this reaction, its two d-d bands are shifted to higher wavenumbers by 2200 or 4000 cm^{-1}, respectively. In addition, the intensity of the band at 27500 or 31500 cm^{-1} is increased by a factor of 3 to 4 on reaction with CO and C_2H_4. It should be noticed, that in all three spectra, the wavenumber position of the second band is nearly exactly two times that of the first band.

The fourth spectrum (D in Fig. 8) is the difference spectrum calculated from the spectra with O_2 (10^5 Pa). In order to show this spectrum in the scale of Fig. 8 it was divided by two. Here we have five peaks at 11000, 16500, 22000, 28500 and 41000 cm^{-1}, which arise from different oxidation products from chromium(II) and the polymerization active chromium surface compound. Both surface compounds are destroyed by oxygen.

DISCUSSION

The chromium(II) surface compound on silica gel has been investigated ever since Krauss and Stach[2] stated, in 1968, that this coordinatively unsaturated surface compound is the polymerization center of the Phillips catalyst. It is well known that the chromium(II) in this compound is only two-coordinated (under vacuum) with two oxygen ligands.[12–14] A simple model of this surface compound is structure A in the scheme. In order to become the polymerization center, this coordinatively unsaturated chromium(II) compound has to get a chromium-carbon bond as shown in the scheme by structure B. During this conversion the chromium(II) is formally oxidized to chromium(III). In order to be able to polymerize



ethylene a free coordination site must be available. In structure C this free coordination site is occupied by CO, which can be replaced by C_2H_4 without difficulty.

Replacing the organic rest R in structure B by a methyl group ($-CH_3$) produces a severe problem for an initiation of the polymerization by a reaction of structure A with C_2H_4. One additional hydrogen atom is neccessary. No evidence of a carbene mechanism was found.[17] The problem can be solved, however, very easily by using a dinuclear surface compound[18] as shown in structure D in the scheme. One ethylene molecule produces in this case two chromium-carbon bonds and no additional hydrogen atom has to be created from nothing. The chromium is again oxidised formally to chromium(III) and can adsorb CO or C_2H_4 (structure E and G, respectively).

In order to determine how many bands at which position the polymerization active chromium(III) surface compound should show, a comparison with octahedral chromium(III) complexes gives three bands, for example at 18000, 24600 and 36600 cm^{-1} ($KCr(SO_4)_2 \cdot 12H_2O$).[15] These three bands are interpreted as transitions from the $^4A_{2g}$ ground state to the $^4T_{2g}$, $^4T_{1g}$ and $^4T_{1g}$ excited states. The last two excited states have the same designations. This means that they never cross and that the second transition has not exactly two times the energy of the first one. The first two bands from our example above agree only roughly with the first two bands from spectra A (16000, 31500 cm^{-1}), B (13500, 27500 cm^{-1}) and C (16000, 31500 cm^{-1}) from Fig. 8.

We have, however, in our case a different configuration than octahedral; most likely trigonal planar for the polymerization active chromium(III) without CO or C_2H_4 and trigonal pyramical for that with adsorbed CO and C_2H_4. We try now to fit the bands from spectrum B, Fig. 8 to ligand field energy diagrams for d^3 electronic systems with trigonal symmetry.[16] Fitting our first band to the first transition in the diagram we get a DQ value of 1300 cm^{-1}. The groud state is $^4A_2 2(^4_3F)$ and the excited states are $^4A_1 1(^4_3F)$, $^4E1(^4_3F)$, $^4A_2 1(^4_3F)$, $^4E2(^4_3F)$, $^4A_2 1(^4_3P)$ and $^4E1(^4_3P)$. There are six transitions with 13500, 16000, 19200, 28000, 33000 and 40000 cm^{-1}. Of these six transitions we can point out five (together with the first band) in spectrum B in Fig. 8. The transition at 19200 cm^{-1} is at best a weak shoulder and the band in the spectrum at 31500 cm^{-1} was interpreted above.

Now fitting the band at 16000 cm^{-1} from the spectra A and C in Fig. 8, we get a DQ value of 15300 cm^{-1} and transitions at 16000, 18500, 21800, 31000, 35000 and 46000 cm^{71}. Again the bands at 18500 and 21800 cm^{-1} are shoulders together with that at 35000 cm^{-1}. Only one band at 46000 cm^{-1} is missing in spectrum C. Although the above assignments are tentative, they show that the spectra of the polymerization active chromium can be interpreted as bands from a chromium(III) complex with trigonal symmetry.

Acknowledgement. The author thanks the Swedish Board for Technical Development for financial support.

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Received July 5, 1984.