

UV/Vis Investigation of the Polymerization Catalyst Chromium(III) on Silica Gel

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Recent investigations of the chromium/silica gel system have shown that at least three different catalytic centers for the polymerization of ethylene exist, which have large differences in the catalytic activity.¹ These are chromium(II), "chromium(II) repoly" and chromium(III) on silica gel. The chromium(II) on silica gel, which is thought to be the catalytically active center of the commercial Phillips catalyst,^{2,3} has the lowest activity of these catalytic centers. It was found that at low chromium concentration (0.074 % Cr/silica gel) between 50 % [chromium(II) and chromium(III)] and 100 % of the chromium is catalytically active.¹ With such a high content of catalytic centers, it is possible to investigate the change due to polymerization of ethylene with difference UV/Vis reflectance spectroscopy, as has been done for chromium(II) on silica gel.⁴

Experimental. The chromium(III) on silica gel catalyst (0.74 % Cr/SiO₂) was prepared as described previously¹ and the UV/Vis reflectance spectra were recorded and recalculated with the Kubelka-Munk function according to Ref. 4. Semi-quantitative polymerization measurements were performed with 5 g of 0.074 % chromium on silica gel at 273 K and 65 kPa.

Results and discussion. Reflectance spectra of polymerization active chromium(III) on silica gel and with adsorbed CO, C₂H₄ and O₂ have first been recorded by Naumann.⁵ Of special interest is the poisoning of the active center by CO. In Fig. 1 this effect is clarified with the help of reflectance spectra. The coordinatively unsaturated chromium(III) on silica gel (spectrum A) has peaks at 12 900, 23 700 and 42 000 cm⁻¹ and shoulders at 9 500 and 21 300 cm⁻¹.⁵ On adsorption of CO at room temperature (spectrum B) all these bands, except that at 42 000 cm⁻¹, decrease and new bands at 20 000, 29 700 and 33 500 cm⁻¹

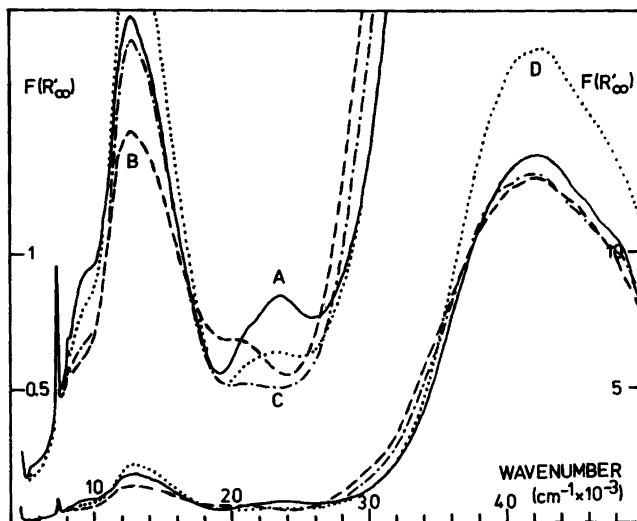


Fig. 1. Reflectance spectra of chromium(III) on silica gel. A: evacuated or under N₂, B: CO, 100 kPa, C: evacuated at room temperature after CO adsorption, D: evacuated at 673 K after CO adsorption.

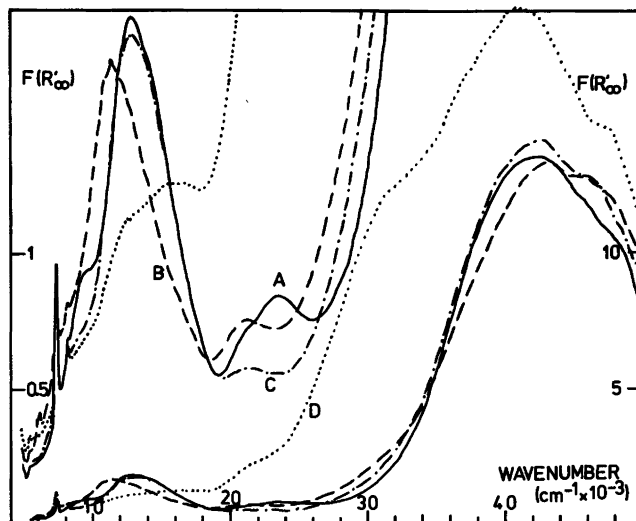


Fig. 2. Reflectance spectra of chromium(III) on silica gel. A: evacuated or under N_2 , B: C_2H_4 , 100 kPa, after CO poisoning, C: evacuated at room temperature after C_2H_4 adsorption, D: O_2 , 100 kPa.

appear. As was already observed by Naumann⁵ the adsorption of CO on chromium(III)/silica gel is not complete at room temperature: the colour change from blueish green to blue (CO at 293 K) continues to pink at 77 K. The latter colour is due to the band at $20\,000\text{ cm}^{-1}$.

Desorbing the CO at room temperature by evacuation reproduces, however, not the original spectrum. The bands in spectrum C, Fig. 1 at $9\,500$, $21\,300$ and $23\,700\text{ cm}^{-1}$ remain very weak, while the main band at $12\,900\text{ cm}^{-1}$ is nearly completely restored. No catalytic activity was observed with this sample. Even evacuation at 473 K did not restore polymerization activity. Only after evacuation at 573 K did weak polymerization activity begin to be observable again, and was comparable to that of the coordinatively unsaturated surface compound after evacuation at 673 K. Spectrum D in Fig. 1 shows the reflectance spectrum of this sample. The bands at $9\,500$, $21\,300$ and $23\,700\text{ cm}^{-1}$ are now restored to roughly half the intensity between spectrum A and C and the main bands at $12\,900$ and $42\,000\text{ cm}^{-1}$ have increased their intensity. Obviously, all these bands are an integral part of the spectrum of polymerization active chromium(III) on silica gel.

IR investigations⁶ and thermodesorption measurements⁷ of CO adsorbed on chromium(III) on silica gel have shown, that CO is only weakly adsorbed at room temperature and that it is completely desorbed below 400 K. Therefore the above effect of CO poisoning even at 473 K cannot be caused by adsorbed CO. The spectra of Fig. 1 seem to indicate, that a subtle structural change has occurred at the chromium(III) surface compound, in order to make it catalytically inactive. The active chromium(III) structure is restored in vacuum at temperatures higher than 573 K. Adsorption of ethylene after CO poisoning (spectrum B, Fig. 2) and evacuation at room temperature (spectrum C, Fig. 2) does not restore the spectrum of the coordinatively unsaturated chromium(III) surface compound. The fact that a reflectance spectrum of chromium(III) on silica gel can be recorded, is again an indication that not adsorbed CO is preventing polymerization. Oxygen (spectrum D, Fig. 2) is adsorbed by chromium(III) on silica gel but can be removed by evacuation.⁵

In Fig. 3 difference reflectance spectra of chromium(III) on silica gel after short polymerization with ethylene are shown. Because only about 50% of the chromium(III) ions are polymerization active,¹ the following procedure was employed to obtain difference reflectance spectra. The spectra from Figs. 1 and 2 were, respectively, divided by two and subtracted from the reflectance spectra of chromium(III) after short polymerization. The results of these calculations are shown in Fig. 3.

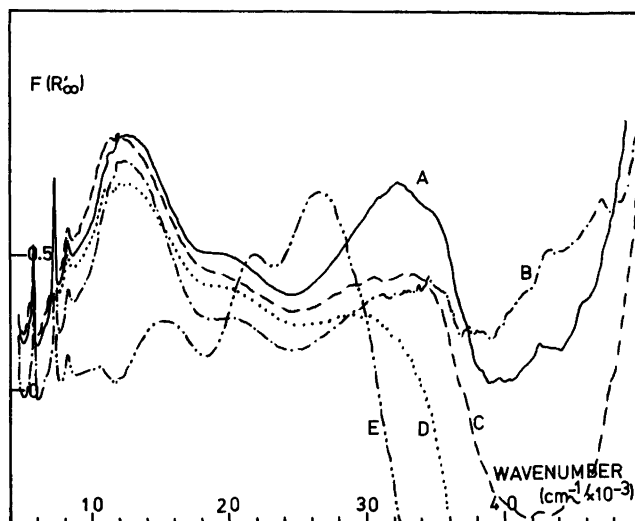


Fig. 3. Difference reflectance spectra of chromium(III) on silica gel. The respective spectra from the previous figures divided by two are subtracted from reflectance spectra of chromium(III) after short polymerization with ethylene. A: CO, 100 kPa, B: evacuated after CO adsorption, C: C₂H₄, 100 kPa, D: evacuated after ethylene adsorption, E: O₂, 100 kPa.

In contrast to a similar study with chromium(II) on silica gel,⁴ no great change is observed between spectra taken before and after short polymerization with ethylene in the case of chromium(III). The peak at 12 800 cm⁻¹ is shifted to 12 100 cm⁻¹ on adsorption of C₂H₄, which is only half the shift observed in Fig. 2, spectra A and B (from 12 900 to 11 300 cm⁻¹). The shoulder at 9 700 cm⁻¹ is very weak, while the second shoulder at 20 000 cm⁻¹ is quite observable for the spectra A to D with only little change of its position. On reaction with O₂ (spectrum E), the chromium(III) reacts by oxidation to chromium(V) (peaks at 15 700, 22 000 and 27 000 cm⁻¹). As can be seen from the large negative absorptions in the UV region in Fig. 3, the method of difference reflectance spectra is in this case obviously unreliable in the UV region above 30 000 cm⁻¹.

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