

Short Communications

IR Studies of Coordinatively Unsaturated Surface Compounds on Silica Gel. VI. CO Adsorbed on Surface Allyl Chromium

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On the basis of IR CO adsorption studies, we have recently put forward the idea that both the Phillips ($\text{CrO}_3/\text{SiO}_2$)¹ and the Union Carbide (Chromocene/ SiO_2)² polyethylene catalysts consist of dinuclear catalytic centres.^{3,4} We further concluded that the failure to find homogeneous analogs to the two catalysts was caused by investigating only mononuclear compounds. A system with both homogeneous and heterogeneous activity is, however, available as tris(allyl)chromium^{5–8} and tris(allyl)chromium on silica gel.^{9–12} An IR CO study should possibly reveal if the latter catalytic centres are related to those of the two commercial chromium catalysts.

Experimental. Tris(allyl)chromium(III) was synthesized following Ref. 13 and stored at -40°C . One must note that, according to Ref. 12, a bis(allyl)chromium(II) dimer is always present in the pentane solution of allyl chromium. This allylchromium compound is, however, not active as a polymerization catalyst.⁸

Silica gel "Merck 7733"¹⁴ was pressed to a disc and placed in a previously described IR cell.¹⁵ The allyl chromium solution was splashed on to the silica gel disc with the help of a syringe and a 1 mm PVC hose. This procedure was performed under argon (exclusion of oxygen and water). The chromium content of the silica gel disc was not determined analytically, but conversion to chromium(II) with the help of O_2 at 800°C and CO at 370°C followed by measuring the CO IR absorption³ showed that the chromium content was in the range of 0.5 to 1%. The IR spectra were recorded on a Perkin-Elmer 580 B spectrophotometer con-

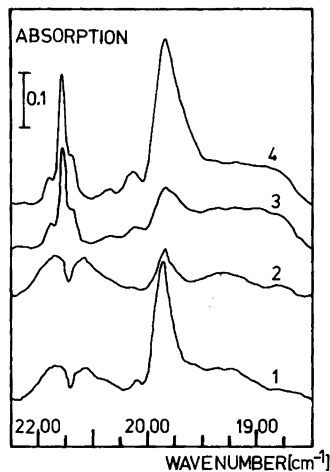


Fig. 1. IR spectra of CO adsorbed on allyl chromium/silica gel. Spectrum 1: Vacuum heat treatment at 600°C and recorded at 20°C with 80 Torr CO. Spectrum 2: As 1 but vacuum heat treatment of the silica gel at 300°C . Spectrum 3: As 2 but 1 Torr CO at -145°C . Spectrum 4: As 3 but after 16 h.

nected to the IR data station from the same manufacturer.

Results and discussion. Fig. 1 shows the IR spectrum of CO adsorbed on reaction products between allyl chromium and the silica gel surface. Only the band at 1984 cm^{-1} has a noteworthy intensity. A shoulder at 2024 cm^{-1} is coupled to this band and two weak bands at 1920 and 1875 cm^{-1} merge at low temperature (spectra 3 and 4, Fig. 1) to one very broad absorption. The small shoulder at 2184 cm^{-1} in the low temperature spectra is assigned to single bonded CO adsorbed on chromium(II).³ The two broad bands at 2170 and 2115 cm^{-1} at room temperature (spectra 1 and 2, Fig. 1) are due to CO gas and the band at 2158 cm^{-1} , together with its shoulder at 2136 cm^{-1} , arises from CO adsorbed at surface silanol groups or CO clusters.¹⁶

The band at 1984 cm^{-1} was found to be air insensitive. This excluded the possibility that this band could be due to an allyl chromium surface compound. In view of recent investigations on the

adsorption of $\text{Cr}(\text{CO})_6$ on silica gel^{17,18} it was concluded that the band at 1984 cm^{-1} and the shoulder at 2024 cm^{-1} belong to $\text{Cr}(\text{CO})_6$ physisorbed on the silica gel surface.

Heating the silica gel in vacuum to either 300 or 700°C prior to admission of allyl chromium had only a minor effect. After relatively low pretreatment temperature (300°C) the formation of $\text{Cr}(\text{CO})_6$ was slower by a factor of at least ten. This might be explained by the assumption that the allyl chromium surface compound, that forms the $\text{Cr}(\text{CO})_6$, coordinates with nearby silanol groups.

Fig. 2 shows the CO IR spectrum of chromium(II) CO surface complexes (spectrum 2) obtained after treatment of allyl chromium/ SiO_2 with O_2 at 800°C and CO at 370°C . The three bands at 2120 , 2100 and 2035 cm^{-1} have been assigned previously^{3,4} to a dinuclear chromium(II) surface complex with three bridging CO molecules adsorbed. These three bands are not present in spectrum 1 (Fig. 2), which shows the IR spectrum of CO adsorbed on allyl chromium/ SiO_2 . It becomes clear that with allyl chromium on the silica gel surface no dimers are detectable with CO, *i.e.* no coordinatively unsaturated dimers are formed. The small band at 2184 cm^{-1} in spectrum 1, Fig. 2 and the absence of the bands at 2120 and 2100 cm^{-1} in this spectrum (at low temperatures) show that also this chromium(II) CO complex is a mononuclear one. Treatment with H_2 at 600°C according to Ref. 11 did not give a

stronger CO band at 2184 cm^{-1} . The same was the case with heating in vacuum to 300°C .

Our samples were active for polymerization of ethylene. This can be seen from the spectra in Fig. 3. Bands at 3080 and 1640 cm^{-1} in spectra 2 and 3 are assigned to C–H and C=HO vibrations in olefins, respectively. They may arise from ethylene bonded to surface allyl chromium compounds. These two bands were stable up to 200°C and vacuum. The band at 1985 cm^{-1} in spectrum 3, Fig. 3, shows that the formation of $\text{Cr}(\text{CO})_6$ was not prevented by ethylene.

The colour change of the red allyl chromium solution to light gray on contact with the silica gel is evidence that allyl chromium reacts with silanol groups to form the following surface compound as proposed previously:^{8,11} $(\text{C}_3\text{H}_5)_2\text{Cr}(\text{O}-\text{Si}-)_2$. A similar complex with the cyclopentadienyl ligand is known to be a stable and rather inert surface compound, which does not adsorb CO.¹⁹ This would explain why we found only relatively weak CO IR bands. In contrast to the cyclopentadienyl ligand the allyl ligand is more reactive and can start the polymerization of ethylene. This can be exemplified by chromocene and tris(allyl)chromium(III), where the former is inactive and the latter is, as noted above, an active polyethylene catalyst.

The preparation of $\text{Cr}(\text{CO})_6$ is normally performed by reduction of a chromium salt with a reactive metal and under high CO pressure.²⁰ We were

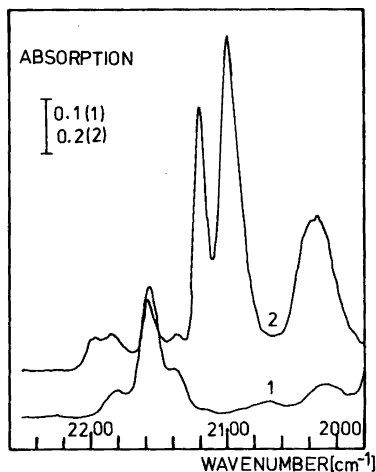


Fig. 2. IR spectra of CO adsorbed on allyl chromium/silica gel and on the dinuclear chromium(II) surface compound. Spectrum 1 is a part of spectrum 4 (Fig. 1). Spectrum 2: Allyl chromium/silica gel converted to chromium(II) with O_2 at 800°C and CO at 370°C . Recorded at -145°C with 1 Torr CO.

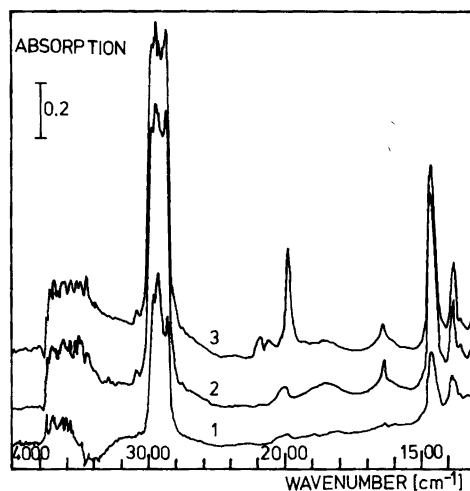
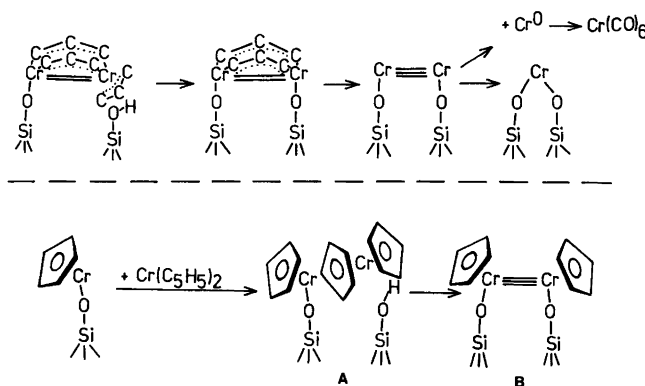


Fig. 3. IR spectra of allyl chromium/silica gel before (spectrum 1) and after polymerization with ethylene (spectrum 2, 650 Torr C_2H_4 , 10 min, 100°C) and evacuation. Spectrum 3: As 2 but addition of 80 Torr CO, 20°C , 16 h. The silica gel spectrum was subtracted in all three spectra shown.



Scheme 1.

unable to find a low pressure process with or without allyl chromium in the literature. In the upper part of Scheme 1 we propose a mechanism for the formation of $\text{Cr}(\text{CO})_6$ and of a chromium(II) surface compound from the bis(allyl)chromium(II) dimer.²¹ The most important reaction step here is the disproportionation of a chromium(I) surface dimer. Whether chromium metal atoms are really formed as intermediates is not quite clear.

Why should then chromocene give dinuclear surface compounds? The lower part of the scheme shows a possible mechanism on how this can come about. The cyclopentadienyl chromium surface oxide is highly coordinatively unsaturated (a 12 electron system) and may coordinate to a yet unchanged chromocene molecule *via* a cyclopentadienyl ligand to form a "double" sandwich²² (A). The coordinated chromocene molecule can thereafter react with the nearby silanol group and form the dimer B shown in Scheme 1. This dimer B can then in turn coordinate four (or three) CO molecules as proposed previously.⁴

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