FTIR study of the adsorption of chromium carbonyl complexes on silica

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IR spectra are reported of $Cr(CO)_6$, $(C_6H_6)Cr(CO)_3$ and $(Me_4C_6H_2)Cr(CO)_3$ adsorbed on silica which had been pretreated in vacuum at temperatures in the range 250-800 °C or in H₂O or D₂O vapour at 700 °C. Surface isolated silanol groups formed hydrogen bonds with arene rings in Cr complexes which also interacted with the surfaces *via* ligation involving carbonyl groups. The generation of active adsorption sites was promoted by increasing pretreatment temperature. Several types of site were involved and resulted from dehydroxylation of the silica surface. Adsorbed bridging carbonyl species resulted from interactions with active $Si^{\delta+}O^{\delta-}$ surface sites. There was negligible evidence for the loss of CO ligands from adsorbed molecules and the supported complexes were inactive for the polymerisation of ethene. However, some loss of benzene occurred for $(C_6H_6)Cr(CO)_3$ on silica pretreated at 800 °C. Pretreatment of silica in H₂O or D₂O at 700 °C promoted hydrothermal surface reorganisation of silica and destroyed a high proportion of the active adsorption sites generated at 700 °C on silica in vacuum.

The polymerisation of alkenes over heterogeneous catalysts is well established, the structure of the catalysts having significant effects on the structure and properties of the polymeric products.1 Catalysts with active chromium-containing sites are particularly important for the generation of high molecular weight and highly linear polyethene from ethene.² The typical preparation of Phillips catalyst involves impregnation of high surface area silica or silica-alumina with a precursor chromium salt followed by calcination in air to generate a supported chromium(vI) oxide material which is subsequently activated by reduction in CO or ethene to a lower oxidation state of chromium at the active site.³ Different precursor salts have recently been shown to generate identical oxidised catalysts after calcination,⁴ and hence the final active catalyst behaviour is not affected by the precursor salt. However, sensitivity of catalyst performance to the structure of the precursor chromium compound is observed for supported organo-chromium complexes which in the activated form retain some of the constituent ligands at the active site.5-7

Organo-chromium complexes on oxide supports generate highly active catalysts for alkene polymerisation.⁵⁻¹⁰ One proposal is that the complexes bind to the support via intergroups.6,11,12 hydroxy surface actions with Hexacarbonylchromium(0) has been shown to be physically adsorbed on silica¹³ and silicalite.¹⁴ However, O-ligation to A1³⁺ surface sites occurs on dehydroxylated alumina.¹⁵ Some decarbonylation probably occurred on adsorption¹⁵ and this ligand displacement may be important in the generation of active catalytic sites.⁵ For example, chromocene is deposited on silica with the liberation of cyclopentadiene to give catalysts with increasing activity as the pretreatment dehydration temperature of the support was increased.¹¹ Despite the potential importance of these systems as polymerisation catalysts there has been surprisingly little effort to characterise the interactions between organo-chromium compounds and oxide supports, apart from an IR study of arenetri-carbonylchromium(0) compounds on silica¹⁶ and the more detailed studies of $Cr(CO)_6$ on silica, silicalite¹⁴ and alumina.15 The present work set out to characterise the adsorption of η^6 -benzenetricarbonylchromium(0) and related compounds on silica, alumina and silica-alumina and to relate the results to catalytic behaviour for ethene polymerisation. The results for adsorption on silica are reported here.

Experimental

Silica (Crosfield EP10) had surface area 300 m² g⁻¹ and pore volume 1.75 cm g⁻¹. (η^{6} -Benzene)tricarbonylchromium(0) [(C₆H₆)Cr(CO)₃] was prepared by refluxing hexa-carbonylchromium (Fluka, 2 g) with benzene (10 cm³) in di-*n*-butyl ether (60 cm³) and tetrahydrofuran (5 cm³) under nitrogen, followed by rotary evaporation under vacuum at 60 °C. The product was recrystallised from dichloromethane and stored in the dark. (1,2,4,5-tetramethylbenzene)tricarbonylchromium(0) [(Me₄C₆H₂)Cr(CO)₃] was similarly prepared from 1,2,4,5-tetramethylbenzene and Cr(CO)₆.

Transmission FTIR spectra at 4 cm⁻¹ resolution of compressed self-supporting silica discs mounted in a vacuum IR cell fitted with fluorite windows were recorded using a Perkin-Elmer 1710 spectrometer coupled to a Perkin-Elmer 7300 dedicated computer. Initially each disc studied was heated in vacuum for 18 h at a temperature in the range 250-800 °C to give, after cooling to ambient temperature, silica designated silica(t). A typical experimental cycle subsequently involved sublimation of chromium compound onto the disc, otherwise under vacuum, followed by desorption by evacuation. Experiments involving adsorption or desorption stages at temperatures other than ambient temperature (ca. 25 °C) are specifically described in the Results section. Hydrothermal pretreatment of discs involved heating in saturated water or deuterium oxide vapours at 700 °C for 18 h before simultaneous cooling and evacuation. All spectra were recorded with discs at ca. 27 °C and are presented as either the absolute spectra (e.g. in the OH-stretching spectral region) or after subtraction of the initial spectrum of the disc before adsorption took place (e.g. in the v_{CO} region).

X-Ray fluorescence spectroscopy was used to analyse the chromium content of discs at various stages of treatment using a Phillips PW1540 spectrometer calibrated with physical mixtures of oxide support and known masses of $(C_6H_6)Cr(CO)_3$.

Results

The IR spectrum of $(C_6H_6)Cr(CO)_3$ in a KBr disc exhibited three weak bands in the CH-stretching region, two dominant maxima at 1967 and 1860 cm⁻¹ due to the A₁ and E vibra-

absorbance

2000

1900

tional modes involving carbonyl groups, and a band at 1450 cm⁻¹ ascribed to a deformation mode of the benzene ring. The molecule has C_{3v} symmetry and therefore in accordance with the spectrum only the A and E vibrational modes should be active in the IR.^{17,18}

Adsorption of (C₆H₆)Cr(CO)₃ : IR spectra

Spectra of $(C_6H_6)Cr(CO)_3$ adsorbed on silica were extremely complex and in the CO-stretching region exhibited fifteen discernable absorption bands. Factors affecting the relative intensities of the bands were surface coverage during adsorption and desorption at ambient temperature, desorption at elevated temperature, the pretreatment temperature of the silica in vacuum, and hydrothermal pretreatment of the silica in H₂O or D₂O at high temperature. The analysis of the results has concentrated on the CO-stretching region of the spectrum as the spectra in the v_{CH} region were much less sensitive to the particular modes of adsorption and could not therefore be used to distinguish different surface structures. The intensity of the maximum at 1450 cm⁻¹ was used to assess the surface concentration of benzene rings remaining ligated to Cr atoms in adsorbed complexes. Results are given for each of six pretreatments of the silica before the adsorption and subsequent desorption of $(C_6H_6)Cr(CO)_6$. In some cases the absence of a band does not necessarily mean that the species responsible for the band was not present, but may have arisen because the existence of the band was completely obscured by overlapping more intense maxima.

Spectra of $(C_6H_6)Cr(CO)_3$ on silica (250) contained three main bands at 1982, 1906 and 1878 cm⁻¹ [Fig. 1(A)] which can be ascribed to adsorbed molecules which were weakly perturbed by interactions with the silica surface leading to a distortion of the C_{3v} symmetry and hence a slight splitting of the E vibrational mode. Weak shoulders at 1998 and 1805 cm⁻¹ which were initially present became swamped by bands due to the dominant adsorbed species as surface overage was increased. The involvement of surface hydroxy groups in the adsorptive interactions was shown by the growth of a broad maximum at 3650 cm^{-1} attributable to silanol groups which were perturbed by hydrogen-bonding interactions with $(C_6H_6)Cr(CO)_3$ molecules. Desorption by evacuation was slow at ambient temperature although the dominant species was removed by 70 °C (Fig. 1). Desorption was accompanied by the disappearance of the band at 3650 cm^{-1} due to perturbed silanol groups. Residual weak bands at 1998, 1922, 1845 and 1742 cm^{-1} suggested that a small amount of a more strongly adsorbed species had been retained on the surface. This species was completely desorbed at 95 °C.

Adsorption of $(C_6H_6)Cr(CO)_3$ on silica (500) gave dominant bands at 1986, 1913 and 1888 cm⁻¹ [Fig. 2(A)], the appearance of which was accompanied by growth of a broad band at 3650 cm⁻¹. However, there was greater evidence than for

0.54

0.24

1700



1700

2000

wavenumber/ cm

1900

1800

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1800



Fig. 2 Decrease of IR bands for $(C_6H_6)Cr(CO)_3$ on silica (500) after contact times of (A) 8, 21 and 24 h, then 1 h at 30 °C and 30 min at 60 °C; (B) 30 min at 60 °C, 30 min at 70 °C, 30 min at 75 °C, 1 h at 80 °C, 1 h at 90 °C, and 30 min at 100 °C

silica (250) for other modes of adsorption. This was confirmed by the desorption spectra which showed more intense bands at 1998, 1931, 1845 and 1735 cm^{-1} than for silica (250) under similar desorption conditions [Fig. 2(B)], together with additional bands at 1952, 1893, 1788 and 1757 cm⁻¹ not recognisable for silica (250). Desorption of the dominant species was accompanied by the disappearance of the band at 3650 cm^{-1} . The additional effects for silica (500) were further enhanced for silica (600) for which bands at 1998, 1850 and 1811 cm^{-1} became particularly noticeable during adsorption and a very weak band at 2024 cm⁻¹ grew in intensity at low surface coverages but then remained constant. Subtraction of a spectrum at intermediate coverage from spectra at higher coverage showed that the dominant growth at high coverages involved the three bands [Fig. 1(A)] characteristic of weakly perturbed $(C_6H_6)Cr(CO)_3$ species together with an additional pair of bands at 1998 and 1760 cm⁻¹, the latter appearing as a broad maximum.

The gradual changes in the spectra with increasing silica pretreatment temperature led for silica (700) to spectra for low to moderate surface coverages which were significantly different [Fig. 3(A)] from the results for silica (250) (Fig. 1). Dominant bands initially were at 1998 cm^{-1} with a shoulder at 1987 cm⁻¹, a triplet of bands at 1947, 1924 and 1897 cm⁻¹ and a doublet at 1845 and 1810 cm^{-1} with shoulders at 1796 and 1762 cm⁻¹. Weakly perturbed $(C_6H_6)Cr(CO)_3$ [Fig. 1(A)] only constituted a minor mode of adsorption, a result which apparently correlated with the appearance of a much weaker band at 3650 cm⁻¹ due to perturbed silanol groups on silica (700) than the corresponding band for silica (250). At high coverages of silica (700) the major growth was for bands at 1985 and 1906 cm^{-1} . This behaviour is emphasised by the difference spectra in Fig. 4 which are dominated by a pair of maxima which may be attributed to the A, and E modes of $(C_6H_6)Cr(CO)_3$ molecules which were sufficiently weakly



Fig. 3 Growth of IR bands for $(C_6H_6)Cr(CO)_3$ on silica (700) after (A) 3-60 min and (B) 1-10 h



Fig. 4 Growth of IR bands for $(C_6H_6)Cr(CO)_3$ on silica (700). The spectrum after 5 h subtracted from spectra after 6, 7, 8, 9 and 10 h.

adsorbed to retain their C_{3v} symmetry. These molecules were readily desorbed by evacuation at 60 °C leaving a spectrum with a strong band at 2025 cm⁻¹ and additional prominent bands at 1956, 1894, 1845 and 1791 cm⁻¹.

The highest pretreatment temperature used was 800 °C. At low coverages the spectra for silica (800) were similar to those for silica (700) although, relative to the intensity of the band at 1998 cm⁻¹ for silica (800) bands at 1987, 1934, 1897 and 1845 cm⁻¹ were less intense and bands at 2027, 1956, 1947, 1810, 1796 and 1762 cm^{-1} were more intense than for silica (700) [Fig. 3(A) and Fig. 5(A)]. These differences between the adsorption characteristics were further accentuated at higher surface coverages [Fig. 3(B) and 5(B)]. The band at 3650 cm^{-1} due to perturbed silanol groups was weaker for silica (800) than for silica pretreated at lower temperatures. The growth of absorbance at the 3650 cm^{-1} band maximum for silica (800) was only ca. 5% of the absorbance of the band maximum at 3750 cm^{-1} before adsorption occurred showing that only a small proportion of the total number of available silanol groups were perturbed by adsorbate molecules.

Fig. 6 shows the relationships between the growth in band intensity at 3650 cm^{-1} and the intensity of the maximum at 1450 cm^{-1} ascribed to a ring deformation vibration of benzene ligated to Cr in adsorbed complexes. With increasing pretreatment temperature there was an increasing proportion of adsorbed species which were not involved in interactions leading to a perturbation of surface silanol groups. Spectra of



Fig. 5 Growth of IR bands for $(C_6H_6)Cr(CO)_3$ on silica (800) after (A) 1–30 min, (B) 40 min–5 h



Fig. 6 Relationship between the integrated intensities (arbitrary units) of the IR bands at 3650 and 1450 cm⁻¹ for $(C_6H_6)Cr(CO)_3$ on silica preheated in vacuum at (\blacklozenge) 250, (\blacksquare) 500, (\bigtriangleup) 700 and (\times) 800 °C

 $(C_6H_6)Cr(CO)_3$ in the early stages of adsorption on silica (800) exhibited a band at 1480 cm⁻¹ which disappeared at higher coverages [Fig. 5(B)]. Free benzene has an IR band at 1480 cm⁻¹ and therefore it is implied that loss of the benzene ligand had occurred from some adsorbed molecules and the resulting adsorbed benzene molecules were displaced by further adsorption of $(C_6H_6)Cr(CO)_3$.

Desorption of $(C_6H_6)Cr(CO)_3$ from silica (800) finally led (Fig. 7) to a similar spectrum to the result for silica (700). However, spectra at earlier stages of desorption confirmed that the band at 1987 cm⁻¹ was more intense for silica (700) than silica (800) but that for the later bands at 2027, 1998, 1810, 1796, 1775 and 1762 cm⁻¹ were more intense.



Fig. 7 The desorption of $(C_6H_6)Cr(CO)_3$ from silica (800) after (1) 9 h, (2) 24 h, (3) 30 min at 55 °C, (4) 30 min at 75 °C, and (5) 30 min at 85 °C

Accurate recording of small changes in absorbance at 3750 and 3650 cm^{-1} was hampered by bands due to water vapour in the spectrometer. Experiments involving H/D exchange of silanol groups were designed to obviate this problem and also to test whether there was any H/D exchange between acidic CH groups in benzene molecules ligated to chromium atoms. Attempts to exchange OH groups by repeated exposure to saturated D₂O vapour at ambient temperature were only partially successful. Even after heating discs in saturated D_2O vapour at 700 °C ca. 10% of the OH groups were not exchanged suggesting that these groups were inaccessible to gas-phase molecules. In support of the results for $(C_6H_6)Cr(CO)_3$ on silica (700), the adsorption on the deuteriated surface led to a ca. 5% decrease in the intensity of a band at 2763 cm⁻¹ due to isolated SiOD groups and a corresponding increase in absorbance of a broad band centred at 2690 cm⁻¹ due to OD groups perturbed by interactions with (C₆H₆)Cr(CO)₃ molecules. There was no evidence for any H/D exchange on adsorption. However, spectra in the carbonyl region of the spectrum were appreciably different for the D_2O -treated discs, designated silica (700, D_2O) than for silica (700). Subsequent treatment of new discs in water vapour at 700 °C showed that the results for silica (700, H₂O) and silica (700, D_2O) were identical in the 1700-2100 cm⁻¹ spectral region. The spectra were dominated by bands at 1986, 1913 and 1888 cm⁻¹ with much weaker shoulders at 1998, 1850 and 1810 cm⁻¹, the general form of the spectrum resembling the result for silica (250) [Fig. 1(A)] much more closely than the result for silica (700) [Fig. 3]. Hydrothermal treatment of silica apparently had a profound effect on the characteristics of the silica surface vis-à-vis its interactions with $(C_6H_6)Cr(CO)_3$ molecules. The desorption spectra for silica (700, H_2O) were also more similar to the results for silica (250) rather than silica (700).

Adsorption of (Me₄C₆H₂)Cr(CO)₃ : IR spectra

Previous IR data for $(Me_4C_6H_2)Cr(CO)_3$ adsorbed on silica¹⁶ showed significant differences from the present data for $(C_6H_6)Cr(CO)_3$. The adsorption of $(Me_4C_6H_2)Cr(CO)_3$ on silica (700) and silica (700, H₂O) has therefore been studied to gain an unambiguous comparison with the $(C_6H_6)Cr(CO)_3$ data.

Spectra of $(Me_4C_6H_2)Cr(CO)_3$ were also complex after adsorption on silica (700). The spectra for adsorption and desorption could, as for $(C_6H_6)Cr(CO)_3$, be deconvoluted into fifteen bands. Similarities between the sets of spectra for $(Me_4C_6H_2)Cr(CO)_3$ and $(C_6H_6)Cr(CO)_3$ adsorption strongly suggested that the two compounds were involved in similar modes of adsorption. The results in the OH-stretching region of the spectrum for $(Me_4C_6H_2)Cr(CO)_3$ adsorption were also consistent with the results for $(C_6H_6)Cr(CO)_3$. However, the band due to perturbed silanol groups was at 3620 cm⁻¹ for $(Me_4C_6H_2)Cr(CO)_3$ and had an intensity at high overall surface coverages which was slightly higher than that for the 3650 cm⁻¹ band appearing after $(C_6H_6)Cr(CO)_3$ adsorption. These data suggest that the electronic effect of the Me groups in 1,2,4,5-tetramethylbenzene strengthened the interactions between silanol groups and adsorbed (Me₄C₆H₂)Cr(CO)₃ molecules. This effect would be as expected for the formation of hydrogen bonds between silanol groups and the aromatic rings in the adsorbate molecules.

Spectra of $(Me_4C_6H_2)Cr(CO)_3$ on silica (700, H_2O) contained fewer bands in the v_{CO} region than the corresponding spectra for silica (700). In particular silica (700, H_2O) gave predominantly maxima which are attributable to CO vibrations of weakly perturbed $(Me_4C_6H_2)Cr(CO)_3$ molecules. As for silica (700), $(Me_4C_6H_2)Cr(CO)_3$ on silica (700, H_2O) gave a bigger shift ($\Delta v_{OH} = 130 \text{ cm}^{-1}$) in the band due to silanol groups perturbed by hydrogen-bonding interactions than did $(C_6H_6)Cr(CO)_3$ and also gave a more intense band at 3620 cm $^{-1}$ than the band at 3650 cm $^{-1}$ for $(C_6H_6)Cr(CO)_3$.

Adsorption of Cr(CO)₆ : IR spectra

Octahedral $Cr(CO)_6$ gas gives a single C–O stretching mode of T_{1u} symmetry with an IR band at 2000 cm⁻¹.¹⁹ Spectra of $Cr(CO)_6$ on silica (500) were dominated by an intense band at 1992 cm⁻¹ [Fig. 8(A)]. Weaker bands were also present at 2118, 2038(sh), 2003 and 1924 cm⁻¹ and became more obvious with increasing desorption [Fig. 8(B)]. The adsorption of $Cr(CO)_6$ gave no change in the OH-stretching region in contrast to the results for $(C_6H_6)Cr(CO)_3$ and $(Me_4C_6H_2)Cr(CO)_3$ which gave changes consistent with hydrogen-bonding interactions between surface silanol groups and adsorbate molecules.

Adsorption of $Cr(CO)_6$ on silica (800) gave a dominant band at 2017 cm⁻¹ with a band of about half the intensity at 1994 cm⁻¹, and a maximum at 1875 cm⁻¹ with a prominent shoulder at 1915 cm⁻¹. These, together with additional bands at 2123, 2080, 2038, 1840(sh), 1800 and 1609 cm⁻¹ corresponded to an overall spectrum which contained more bands than that for silica (500). Removal of Cr(CO)₆ by evacuation reduced the intensities of all the bands (Fig. 9) with the bands at 1994 and 1915 cm⁻¹ giving the greatest percentage loss. The bands at 2050, 2017, 1875, 1840 and 1800 cm⁻¹ shifted to 2062, 2021, 1860, 1820(sh) and 1790 cm⁻¹ after desorption for 2 h. However, some adsorbed species were not desorbed at 25 °C even after prolonged evacuation. A weak band at 1609 cm⁻¹ grew in intensity as evacuation was continued [Fig. 9(B), inset]. There were no spectroscopic changes involving silanol groups for Cr(CO)₆ on silica (800).



Fig. 8 Spectra of $Cr(CO)_6$ on silica (500) (A) adsorption after 5 min, (B) desorption for 5 and 10 min



Fig. 9 Spectra showing the loss of IR bands for $Cr(CO)_6$ on silica (800) after (A) 10-30 min (B) 30-120 min

Adsorption of $(C_6H_6)Cr(CO)_3$: exposure to ethene

Silica (500) and silica (800) were both exposed to $(C_6H_6)Cr(CO)_3$ and subsequently evacuated at either 25 or 50 °C before exposure to ethene gas. Similar catalysts involving alumina and silica-alumina supports were active for ethene polymerisation.²⁰ However, the silica-supported catalysts were completely inactive.

Adsorption of (C₆H₆)Cr(CO)₃ : XRF Cr analyses

Table 1 contains band intensities A for the maximum at 1450 cm^{-1} due to a vibration of benzene rings in $(C_6H_6)Cr(CO)_3$ molecules and B for the total band envelope due to v_{CO} vibrations for $(C_6H_6)Cr(CO)_3$ on silica (500) and silica (800) after adsorption, thermal ageing at 25 or 45 °C in a static vacuum, and subsequent evacuation at 25 °C. The ratio of B to A is a quantitative measure of the extent to which the adsorbed molecules retained both the benzene and carbonyl moieties of the parent $(C_6H_6)Cr(CO)_3$ molecules on adsorption. The resulting ratios (Table 1) were remarkedly constant. XRF gave Cr analyses for the discs at the end of the experiments. The relative wt.% values for the three discs are of no significance other than perhaps showing that $(C_6H_6)Cr(CO)_3$ was more strongly adsorbed on silica (800) than on silica (500). The similarity between the A/[Cr] ratios for the three discs and also the agreement between the B/[Cr] ratios for silica (500) and silica (800) held at 25 °C throughout the treatments further suggest, together with the constant B/A ratios, that the majority of the adsorbed $(C_6H_6)Cr(CO)_3$ molecules had retained their integrity on the silica surfaces.

Discussion

Surface silanol groups were involved in forming hydrogen bonds with the arene rings in $(C_6H_6)Cr(CO)_3$ and $(Me_4C_6H_2)Cr(CO)_3$. Simultaneous weak perturbation of at least one CO group in each adsorbed molecule occurred, the strength of perturbation, as detected by the band splitting for the E vibrational mode, depending on the chemical character of the adsorbing surface. However, stronger perturbations of CO-group vibrations became increasingly significant with increasing silica pretreatment temperature and involved adsorbate molecules for which the CO-groups provided the primary bonding mechanism with the surface. Morrow and Cody²¹ proved the existence of Lewis acidic sites on silica which had been heated at elevated temperature. These sites may be electron deficient trivalent surface silicon atoms. Low²² argued for a silicon atom in a favourable geometric configuration to accept an extra pair of electrons achieving greater than four-fold coordination. However, Chiang et al.² showed that IR bands associated with the sites coincided with bands for edge-shared tetrahedral surface defects. Earlier Zecchina and co-workers²⁴ had suggested that the migration of hydroxy groups at high temperatures into vicinal positions was followed by condensation reactions introducing extra strain which was not balanced by further surface rearrangements. Extremely distorted structures are formed and probably consist of uncoupled Si—O oscillators containing weakly or non-bridging oxygen atoms. Surface defect sites of differing reactivity exist on the thermally activated silica surfaces.²⁵

The present data support the previous conclusions^{21,23-25} concerning the availability of active sites on silica. Dehydroxylation involves pairs of hydroxy groups, desorption of water, and a residual O atom left on the silica surface. Unless a fairly stable bridging siloxane group SiOSi is formed the dehydroxylation process must leave a silicon atom which is partly electron deficient with a deficit of up to one electron. The latter would occur when the two condensing silanol groups are too far apart for the remaining O atom to adopt a bridging configuration. In this case an \equiv SiO site would also remain and would be polarised in the sense $\equiv Si^{\delta+}O^{\delta-}$. An intermediate situation would be when the two residual sites $(\equiv$ Si and \equiv SiO) were close enough for a weak bridging interaction to occur. This may be represented as $\equiv Si^{\delta+}O^{\delta-}\cdots Si\equiv$. The strength of interaction between CO groups and activated sites in the surface would depend on the extent of electron deficiency at the Si atom (i.e. the Lewis acidity at the site) and the proximity of a partially bridging O atom. Maximum Lewis acidity would correspond to ≡Si sites with no adjacent O atom. However, the availability of an adjacent O atom in a weakly bridging situation may lead to a μ -bridge-bonded carbonyl complex in which the oxygen atom in a CO group is ligated to an Si site and the C atom in the same CO group is bonded to the O atom in the adjacent $\equiv Si^{\delta^+}O^{\delta^-}$ site. Alternatively an isolated $\equiv Si^{\delta^+}O^{\delta^-}$ site may bond to the carbonyl C atom in an arene Cr(CO)₃ molecule to form an ester-type structure containing a bridging CO group (=CO).¹⁶ Bands in the present spectra below ca. 1800 cm⁻¹ may be ascribed to bridging carbonyl groups.

Adsorption of Cr(CO)₆

Guglielminotti¹³ assigned bands at 1990 (vs) and 2015 (w) cm⁻¹ for Cr(CO)₆ on silica to the T_{1u} and E_g modes, respectively, of physisorbed molecules. An additional band at 2112 (w) cm⁻¹ for Cr(CO)₆ in solution is due to the A_{1g} mode for Cr(CO)₆.¹⁴ The present bands at 2118, 2017 and 1994 cm⁻¹ are similarly ascribed to the A_{1g}, E_g and T_{1u} modes of physically adsorbed Cr(CO)₆ on silica. The band at 1924 cm⁻¹ was not reported before¹³ but could be attributed to the T_{1u} mode of molecules in which one of the carbonyl groups was perturbed.^{26,27} This would constitute a more strongly adsorbed species and should be more resistant to desorption. Bands at 2038, 2003 and 1924 cm⁻¹ in spectra [Fig. 8(B)] after removal

support	Cr loading	$I_{1464-1429} (A)^a$	$I_{2100-1600} (B)^a$	<i>A</i> /[Cr]	<i>B</i> /[Cr]	B/A
SiO ₂ (500) 25 °C						
after adsorption		1.8	91.2			50.7
thermal ageing		1.7	85.4			50.2
evacuated disc	0.15 wt.%	1.2	63.8	8.0	425.3	53.2
SiO ₂ (500) 45 °C						
after adsorption		2.4	115.5			48.1
thermal ageing		1.7	84.0			49.4
evacuated disc	0.21 wt.%	1.6	79.2	7.7	381.7	49.5
SiO ₂ (800) 25 °C						
after adsorption		4.0	198.0			49.5
thermal ageing		4.0	196.6			49.2
evacuated disc	0.44 wt.%	3.7	184.6	8.4	419.6	49.9

Table 1 Correlations of chromium loadings from X-ray fluorescence studies with integrated intensities of IR bands for (C₆H₆)Cr(CO)₃ on silica

" Arbitrary units.

of more weakly bound unperturbed species are ascribed to $Cr(CO)_6$ molecules interacting with the silica (500) surface *via* one of their carbonyl groups. Similar assignments have been given for adsorption on an H-Y zeolite¹⁴ although the band here at 1924 cm⁻¹ was at 1960 cm⁻¹ for the zeolite. The present bands are not attributable to $Cr(CO)_6$ molecules interacting with surface silanol groups *via* hydrogen bonds because the IR band at 3750 cm⁻¹ due to silanol groups was unaffected by the adsorption process. Adsorption may occur at strained siloxane bridge sites which involve silicon atoms exhibiting electron-accepting properties²⁰ and are formed by surface dehydroxylation at high temperatures.

Spectra of Cr(CO)₆ on silica (800) initially contained a band at 1994 cm⁻¹ due to weakly adsorbed unperturbed molecules which were the easiest species to desorb by evacuation. Bands at 2123, 2062, 2021 and 1860/1820 cm⁻¹ for silica (800) are similar to maxima at 2125, 2055, 2020 and 1875–1835 cm⁻¹ attributed to Cr(CO)₆ weakly chemisorbed on Cr²⁺ ions supported on silica.¹³ It is unlikely that Cr²⁺ ions were generated on silica (800) by chemisorption of Cr(CO)₆ and therefore the present result is ascribed to the perturbation of a carbonyl group, giving the complex C_{4v} symmetry and hence four expected IR bands, via interaction with coordinatively unsaturated sites exhibiting Lewis-acidic character. Silica surfaces have been reported²¹ to contain defect sites which possibly involve trivalent electron deficient silicon atoms which have the propensity to act as Lewis-acidic sites.

Bands at 2080, 2037 and 1790 cm^{-1} for $\text{Cr}(\text{CO})_6$ on silica (800) resemble bands for strongly O-bonded $Cr(CO)_6$ on Lewis-acidic sites in H-Y zeolite activated at 800 °C.¹⁴ Morrow and Cody²¹ estimated a surface concentration of 0.15 nm^{-2} for strongly Lewis-acidic defect sites on silica (1200) and ca. half this number for silica (800). This corresponds to 2.25×10^{18} sites in the pressed disc of silica (800) studied here. A Cr loading of 0.44 wt.% (Table 1) corresponds to 5.1×10^{18} adsorbed molecules which indicates that even complete coverage of the strong Lewis-acidic sites allows significant adsorption to occur on other surface sites. The coordination of Cr(CO)₆ to strong Lewis-acidic sites can lead to destabilisation of the molecules with CO elimination and the formation of subcarbonyl species on the surface.²⁹⁻³¹ Zecchina et al.¹⁵ reported bands at 2075, 2010, 1922 and 1605 cm⁻¹ assigned to a partially decarbonylated Cr(CO)₆ species Obonded to Al^{3+} sites on alumina. The growth of a band at 1609 cm⁻¹ [Fig. 9(B), inset] and the residual band at 1930 cm⁻¹ after prolonged evacuation observed here could be attributed to a low level of decarbonylation. The band at 1609 cm^{-1} has also been observed in spectra of $Cr(CO)_6$ on silicaalumina and was ascribed to surface bicarbonate generated from displaced CO ligands.²⁰

Overall four main modes of adsorption of $Cr(CO)_6$ on silica have been identified in terms of the strengths of interaction between the silica surface and $Cr(CO)_6$ molecules. Weakly physisorbed unperturbed molecules give bands at 2118, 2017 and 1994 cm⁻¹. Adsorbed $Cr(CO)_6$ molecules with one weakly perturbed carbonyl group gave bands at 2118(?), 2038, 2003 and 1924/1915 cm⁻¹. Moderate strength O-bonding to electron-deficient silicon sites resulted in bands at 2123, 2062, 2021 and 1860/1820 cm⁻¹. Bonding via oxygen to stronger Lewis-acidic silicon sites gave maxima at 2080, 2038 and 1790 cm⁻¹. Dehydroxylation of silica at 800 °C generated several types of electron deficient surface silicon atom which constituted Lewis-acidic sites of differing strengths and hence led to different strengths of adsorption of $Cr(CO)_6$ molecules.

Adsorption of (C₆H₆)Cr(CO)₃

The lower the pretreatment temperature of silica before admission of $(C_6H_6)Cr(CO)_3$ the more intense were the three bands at *ca.* 1985, 1906 and 1878 cm⁻¹ (Fig. 1) due to

adsorbed molecules which were perturbed sufficiently to lose their C_{3v} symmetry and hence to give splitting of the E vibrational modes which are degenerate for unperturbed $(C_6H_6)Cr(CO)_3$ molecules. The parallel growth of a band at 3650 cm⁻¹ due to perturbed silanol groups together with the absence of a similar band for $Cr(CO)_6$ suggests that hydrogen bonding between silanol groups and benzene rings in adsorbed molecules constituted an important adsorptive interaction.¹⁶ The preferred surface-adsorbate interactions involving benzene rings rather than carbonyl groups is further evidenced by the greater strength of adsorption of $(C_6H_6)Cr(CO)_3$ rather than $Cr(CO)_6$ on partially dehydroxylated surfaces. The hydrogen-bonding interaction would require that on average the plane of the benzene ring would be tilted at $ca. 60^{\circ}$ to the surface plane and that at least one CO carbonyl group would be sufficient close to the surface to experience a perturbation. Hence, C_{3v} symmetry is lost and splitting of the E modes to give two IR bands (1906, 1878 cm^{-1}) would occur.

Consideration of the intensity data in Fig. 6, typical Cr loadings for the present samples and estimated silanol group surface concentrations on silica³² suggest that nearly all the $(C_6H_6)Cr(CO)_3$ molecules adsorbed on silica (250) were involved in hydrogen-bonding interactions with surface silanol groups. The v_{CO} spectra [Fig. 1(A)] supports this conclusion. Increasing pretreatment temperature of silica, however, caused surface dehydroxylation³² and generated several types of high energy site involving either strained siloxane bridges or coordinatively unsaturated silicon atoms. These constituted stronger adsorption sites for $(C_6H_6)Cr(CO)_3$. The extent of adsorption at these sites increased with increasing pretreatment temperature and the proportion of adsorbed molecules involved in hydrogen bonding with silanol groups decreased. Again the v_{co} spectra support this conclusion. The one exception is provided by the results for $(C_6H_6)Cr(CO)_3$ on silica (700, H_2O). The hydrothermal treatment led to surface reorganisation which destroyed the high energy sites present on silica (700). The destruction was not complete as the desorption spectra did exhibit bands which were not attributable to hydrogenbonded species. The main v_{CO} bands for silica (250) and silica (700, H_2O) were the same. However, the general shapes of the band envelopes for the v_{co} E mode bands differed slightly suggesting that the loss of degeneracy was not solely a function of the primary hydrogen-bonding surface-adsorbate interaction but also depended on whether the rest of the surface was highly hydroxylated as for silica (250) or dehydroxylated as for silica (700, H₂O). This supports the contention that the orientation of $(C_6H_6)Cr(CO)_3$ molecules is such that at least one but not all three groups are perturbed by weak interactions with the surface. There was no evidence for the involvement of adjacent interacting silanol groups on silica (250) in hydrogen bonding to (C₆H₆)Cr(CO)₃. Lateral hydrogen bonds between vicinal silanol groups would be too favourable to be broken in order to generate the relatively weak hydrogen bonds with benzene rings in $(C_6H_6)Cr(CO)_3$.

For silica pretreated at high temperature the later stages of v_{co} band growth (Fig. 4) resembled the results for silica (250) [Fig. 1(A)] and silica (700, H₂O) although splitting of the E mode band was less obvious. The band growth was accompanied by the concomitant growth of the band at 3650 cm⁻¹ due to silanol groups perturbed by hydrogen bonding to benzene rings. On silica (700) and silica (800) initial adsorption occurred primarily on high energy strained or coordinatively unsaturated sites but weaker adsorption became increasingly important with increasing coverages and involved hydrogen bonding to silanol groups. The orientation of the hydrogenbonded (C₆H₆)Cr(CO)₃ on these surfaces was such that the molecules retained their C_{3v} symmetry or at most suffered only an extremely weak distortion from C_{3v} symmetry. For

this to occur the silanol OH bond should be directed towards the centre of symmetry of the benzene ring and be perpendicular to the plane of the ring and the three CO ligands should be directed away from any possible interaction with the silica surface.

The question arises which type of surface silanol group was involved in hydrogen-bonding interactions with the benzene rings of adsorbed $(C_6H_6)Cr(CO)_3$ molecules. Spectra for silica (250) gave no evidence for the involvement of vicinal silanol groups. Furthermore, the spectra of silica (600), silica (700) and silica (800) showed no bands attributable to vicinal silanol groups and therefore hydrogen-bonding interactions for these surfaces must have involved either isolated or geminal silanol groups.³³ IR band intensities at 3750 cm⁻¹ before adsorption did not vary by more than ca. 10% for the silica samples preheated at 500-800 °C suggesting, in accordance with measurements of surface silanol concentrations,³³ that after the loss of vicinal silanol groups below 500 °C dehydroxylation declines to some extent before becoming increasingly significant again above 750 °C. However, in contrast the band at 3650 cm⁻¹ due to silanol groups perturbed by (C₆H₆)Cr(CO)₃ molecules became much weaker with increasing pretreatment temperature. From maximum band intensities at 3750 cm^{-1} before adsorption and 3650 cm^{-1} after adsorption the maximum percentages of the total number of isolated plus geminal silanol groups which were perturbed by adsorbed $(C_6H_6)Cr(CO)_3$ molecules were estimated to be 26, 19, 12, 7 and 5% for silica preheated at 250, 500, 600, 700 and 800°C, respectively. An NMR study of silica dehydration up to 800 °C established that the corresponding percentages of geminal silanol groups on dehydrated silica surfaces were in the similar range ca. 12-24%.³⁴ For the silica studied the surface concentration of geminal silanol groups fell with increasing temperature up to ca. 500 °C, then stayed constant up to ca. 600 °C and finally underwent further decreases as the temperature was raised from 600 to 800 °C.³⁴ The present results for the band at 3650 cm^{-1} therefore reflects the behaviour of geminal silanol groups on the silica surface and leads to the tentative conclusion that geminal silanol groups constituted the surface sites for hydrogen bonding interactions with $(C_6H_6)Cr(CO)_3$ and $(Me_4C_6H_2)Cr(CO)_3$ molecules. Two modes of hydrogen bonding interaction occur. Firstly, (structure I) for highly hydroxylated surfaces such as silica (250) molecules involved in hydrogen bonding via benzene rings are tilted to the plane of the surface such that one of the carbonyl ligands in each molecule is weakly perturbed by interaction with adjacent hydroxy groups. This type of interaction gave bands at 1982, 1906 and 1878 cm⁻¹ for $(C_6H_6)Cr(CO)_3$ [Fig. 1(A)]. Secondly, (structure II) on surfaces with no vicinal hydroxy groups hydrogen bonding via benzene rings gives adsorbed molecules in which the carbonyl ligands extend away from the surface and were unperturbed. This mode of adsorption gave bands at 1985 and 1905 cm^{-1} (Fig. 4) for $(C_6H_6)Cr(CO)_3$.



The grouping and assignment of other IR bands due to $(C_6H_6)Cr(CO)_3$ on silica is more difficult because of the considerable overlap which existed between adjacent maxima. Detailed consideration of the data as a function of coverage during adsorption and desorption has led to band groupings which are summarised in Table 2. Band positions are for samples treated at ambient temperature unless otherwise annotated with a higher temperature $(30-75 \,^{\circ}C)$ of desorption which was necessary to reveal the cited bands after the removal of more weakly adsorbed species. In some cases not all the expected bands for a given species are listed if some of the bands could not be clearly identified because of the presence of stronger overlapping bands due to other species.

The species identified in Table 2 by triplets of v_{co} IR bands must have all lost the C_{3v} symmetry characteristic of unperturbed $(C_6H_6)Cr(CO)_3$ molecules and were bonded to the silica surface via interactions involving the carbonyl groups. The species are grouped roughly according to their relative strengths of adsorption as judged by the adsorption and desorption characteristics and the extents of perturbation of the v_{CO} band positions from the positions for $(C_6H_6)Cr(CO)_3$ alone. The heterogeneity of the surface particularly after high temperature pretreatment apparently leads to at least five CObonded surface complexes. One is relatively weakly adsorbed and is characterised by a band at 1844-1850 cm⁻¹. Secondly, two moderately strongly adsorbed complexes gave similar but partly distinguishable triplets of bands and were characterised by one band at ca. $1775-1810 \text{ cm}^{-1}$. Finally, the strongest modes of adsorption gave one band at 2020-2027 cm⁻¹, a second at 1947–1959 cm^{-1} and a third at 1735–1765 cm^{-1} . The broad classification in terms of three strengths of adsorption is consistent with the results for $Cr(CO)_6$ adsorption on silica (500) and silica (800). In general the higher the silica pretreatment temperature the more extensive was the production of strained or incompletely coordinated surface sites

Table 2 Groupings of IR band positions v_{CO}/cm^{-1} for $(C_6H_6)Cr(CO)_3$ on silica

pretreatment	weak ^a			moderate ^a		strong ^a			
250 °C	1982	1906	1845	1998	1922	1775		1742	
				(30 min at 45 °C)			(1 h at 70 °C)		
500 °C	1986	1893	1845	1998	1931	1793–1772	2020	1952	1762-1735
				(1 h at 30 °C)			(30 min at 75 °C)		
600 °C	1986	1893	1850	1998	1935	1811	2024	1760	,
700 °C, H ₂ O	1986	1888	1850	1998	1935	1784	1954		1765-1747
. 1							(30 min at 75 °C)		
700 °C	1985	1894	1845	1996	1924	1810	2025	194 7	1760
				2001	1927	1796-1791	2025	1956	1763-1734
800 °C	1987	1897	1845	1998	1929	1810	2027	1947	1762
				2003	1934	1785	2027	1956	1747

^a Relative strengths of adsorption.

The structure of active sites for the adsorption of chromium carbonyl complexes will depend on the nature of pairs of surface silanol groups which on thermal activation can undergo dehydration with the elimination of water. The extent of strain or polarity in resulting siloxane bridges will depend on the geometry of the underlying ring system made up of alternating Si and O atoms. Structure III involving a pair of hydroxy groups will dehydrate to give structure IV containing a highly strained four-membered ring with only two Si atoms of which the one designated Si_a, following the nomenclature of Morrow and Cody,²⁵ is electron deficient and therefore will constitute a Lewis-acidic site. Subsequent adsorption of a $(C_6H_6)Cr(CO)_3$ molecule will involve ligation via a carbonyl O-atom to the e-deficient site either without (structure V) or with (VI) disruption of the Si_a...O siloxane bond. Disruption of the latter bond will be promoted by a favourable interaction between the resulting incompletely coordinated O atom and the carbon atom of the already ligating carbonyl group as in VI. Addition of a further $(C_6H_6)Cr(CO)_3$ molecule at the site will lead to a structure with one molecule ligated via a carbonyl group O atom to the electron-deficient Si, atom and one molecule ligated via a carbonyl C atom to the surface Si $-O^{\delta}$ site as in VII. Evidence for the reversal of the adsorption of the second $(C_6H_6)Cr(CO)_3$ molecule on evacuation is provided by the growth of IR bands at 1960 and 1774 $\rm cm^{-1}$ and the concomitant loss of bands at 1937 and 1812 cm^{-1} (Fig. 7) as VII with two moderately strongly bound molecules (Table 2) reverts to the single more strongly perturbed adsorbed molecule in VI.

The strained sites IV were proposed by Chiang *et al.*²³ and can be formed not only from pairs of single adjacent interacting silanol groups but also from pairs of OH groups each of which are components of geminal hydroxy species.³⁵ Geminal silanol groups on adjacent Si atoms can undergo dehydration.³⁵ The further possible mode of interaction VIII of $(C_6H_6)Cr(CO)_3$ with the strained siloxane sites IV involves two carbonyl ligands in each adsorbed molecule perturbed by interactions with the surface.

The surface structure IX in which the ring underlying a pair of silanol groups contains three Si atoms can also dehydrate to give a strained surface siloxane bond.^{36,37} Adsorption of

IV

VIII

٧I

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VII



 $(C_6H_6)Cr(CO)_3$ will lead to similar structures to V-VIII although the different level of bond strain from that in IV will ensure slightly different strengths of interaction and levels of perturbation of carbonyl ligands. In contrast structure X containing four Si atoms in the underlying ring forms an unstrained siloxane structure on dehydration³⁶⁻³⁸ which will be unreactive towards $(C_6H_6)Cr(CO)_3$ and related molecules.

The ease of dehydration of surface silanol groups will depend on the ease with which a stable unstrained siloxane bridge can be formed. Increasing distance between the silanol groups at first (III \rightarrow IX \rightarrow X) favours a less strained siloxane bridge and therefore a less reactive surface site. Adjacent silanol groups involved in hydrogen-bonding interactions are removed from the silica surface by ca. 500 °C and primarily give unstrained unreactive exposed siloxane groups. However, some strained sites have been formed by this temperature [Fig. 2(B)] and will have been derived from structures such as IV or IX. In terms of the nomenclature in Table 2 weak interactions correspond to structure V, moderate interactions to VII and strong interactions to the bridged carbonyl species VI. Structure VIII represents a strong bidentate mode of adsorption but will give smaller shifts in v_{co} than VI, apart possibly for the shift for the carbonyl group which remains not ligated to the surface.

At $T > 500 \,^{\circ}\text{C}$ dehydration continued^{34,35} but now involved isolated and geminal³⁵ silanol groups which were not involved in lateral hydrogen-bonding interactions and therefore contributed to the IR band at 3750 cm^{-1} before dehydration. In the extreme the silanol group pairs would be too far apart to generate a siloxane bond and therefore two separate sites XI and XII result the former having particularly strong (in the present context) Lewis-acidic character and the latter acting as a Lewis base or nucleophilic site. Adsorption of $(C_6H_6)Cr(CO)_3$ leads to structures XIII and XIV which constitute moderately strong (Table 2) modes of adsorption. Structure XII constitutes an electron-deficient silicon atom site^{21,25} and ligation of $(C_6H_6)Cr(CO)_3$ to the site completes the tetrahedral coordination of the Si atom. The similar but weaker mode of adsorption V raises the coordination above four which has been deemed possible at silica surfaces.²²

Adsorption of (Me₄C₆H₂)Cr(CO)₃

The close similarities between the IR results for $(Me_4C_6H_2)Cr(CO)_3$ and $(C_6H_6)Cr(CO)_3$ on silica (700) and silica (700, H_2O) strongly suggest that the patterns of adsorption behaviour were identical for the two chromium complexes. The hydrogen-bonded species gave maxima at 1968, 1893 and 1865 cm⁻¹. The characteristic low wavenumber v_{CO} bands for $(Me_4C_6H_2)Cr(CO)_3$ bonded to the surface via CO groups in three broad strengths of interaction [as given for $(C_6H_6)Cr(CO)_3$ in Table 2] were at 1821–1826 cm⁻¹ for weak interactions, 1759-1795 cm⁻¹ for stronger interactions and 1728-1752 cm⁻¹ for the strongest interactions. The present results resembled those of Dodonov et al.¹⁶ in revealing a hydrogen-bonding interaction between surface silanol groups and the π electrons of the aromatic ring but differed in that no IR bands were previously reported between 1720 and 1880 cm⁻¹. Furthermore, thermal activation (≤ 105 °C) did not here generate the IR bands observed at 3495 and 1717 cm⁻¹ which are attributed to decomposition of (Me₄C₆H₂)Cr(CO)₃



giving a surface complex containing C=O groups (1717 cm^{-1}) which formed hydrogen bonds with surface silanol groups (3495 cm⁻¹).¹⁶ Raising the temperature caused desorption rather than decomposition in the present studies.

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