

Infrared spectra of $(\eta^6\text{-C}_6\text{H}_2\text{Me}_4)\text{Cr}(\text{CO})_3$ adsorbed on silica and silica–alumina

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Abstract

Durene $\text{Cr}(\text{CO})_3$ adsorbed on silica which had been preheated at 973 K either by H-bonding between surface silanol groups and the π -electrons of durene rings or by O-ligation of carbonyl ligands to electron-deficient Lewis acidic Si atoms in the silica surface. Lewis acidic sites were generated during high temperature pretreatment by condensation of surface silanol groups forming exposed strained siloxane bridges. Heat treatment of silica in water vapour at 973 K removed strained surface sites and subsequent adsorption of durene $\text{Cr}(\text{CO})_3$ at 298 K primarily involved only H-bonding interactions. In contrast, the adsorption of durene $\text{Cr}(\text{CO})_3$ on silica–alumina which had been preheated at 773 K was dominated by O-ligation to Lewis acidic sites with little evidence for H-bonding. Ligand loss from molecules adsorbed at Lewis acidic sites led to sub-carbonyl surface species and bicarbonate anions.

Keywords: Durene; Silica; Alumina; Acid sites; Adsorption

1. Introduction

The usefulness of organometallic compounds as catalysts in homogeneous systems makes their transfer to heterogeneous catalysis a potentially desirable objective. Organometallic compounds adsorbed on suitable solid supports may themselves act as catalysts, or they may act as precursors of surface structures containing catalytically active sites. A detailed review has emphasised the importance of these systems and how in particular infrared spectroscopy gives information about surface structures derived from transition metal carbonyl and metallocene complexes adsorbed on oxidic substrates [1].

Organo–chromium complexes supported on oxides lead to catalysts for the polymerisation of alkenes [2–4]. Both metallocenes and carbonyl complexes give active catalysts [1,5,6] and bis-arene chromium complexes are active on silica–alumina [6]. The benzenechromiumtricarbonyl complex has been shown to generate active catalysts when supported on silica–alumina but inactive catalysts on silica under the same experimental conditions [7]. Ligand loss accompanying adsorption promoted catalyst activity. The present study was aimed at assessing differences between the adsorption behaviour of durenechromiumtricarbonyl on silica and silica–alumina. Dodonov et al. [8] previously reported infrared spectra of arenechromiumtricarbonyl complexes adsorbed on silica.

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2. Experimental

Silica (EP10, Crosfield) had pore volume $1.75 \text{ cm}^3 \text{ g}^{-1}$ and surface area $300 \text{ m}^2 \text{ g}^{-1}$. Silica–alumina (grade 135, Aldrich) with 13% alumina had pore volume $0.77 \text{ cm}^3 \text{ g}^{-1}$ and surface area $475 \text{ m}^2 \text{ g}^{-1}$. Durenechromiumtricarbonyl (here designated $\text{DuCr}(\text{CO})_3$) was prepared by refluxing a mixture of $\text{Cr}(\text{CO})_6$ (Fluka, 2.21 g), durene (1,2,4,5-tetramethylbenzene, Sigma–Aldrich, 1.37 g), di-*n*-butyl ether (60 cm^3) and tetrahydrofuran (5 cm^3) for one week under nitrogen. Solvent was removed by rotary evaporation under vacuum at 333 K and the product was recrystallised from dichloromethane.

Transmission spectra of self-supporting discs of oxide mounted in a vacuum cell fitted with fluorite optical windows were recorded at 4 cm^{-1} resolution using a Perkin-Elmer 1710 spectrometer coupled to a Perkin-Elmer 7300 computer for data manipulation. Before spectra were recorded silica was preheated at 973 K either in vacuum or in saturated water vapour (followed by evacuation as the disc was cooled) and silica–alumina was heated at 773 K in

vacuum. All spectra were recorded with discs at ca. 298 K.

The $\text{DuCr}(\text{CO})_3$ was sublimed onto discs at ca. 298 K under dynamic vacuum. Spectra were recorded as a function of time as increasingly more $\text{DuCr}(\text{CO})_3$ was adsorbed and subsequently as infrared bands due to adsorbed species weakened in intensity. In the later stages of each experiment, the impregnated discs were heated ($< 378 \text{ K}$) for $\frac{1}{2} \text{ h}$ in vacuum before being rapidly recooled to ca. 298 K for spectroscopic examination. Spectra presented here in the carbonyl region ($1550\text{--}2100 \text{ cm}^{-1}$) are difference spectra from which the initial spectrum of the oxide disc before modification with $\text{DuCr}(\text{CO})_3$ has been subtracted.

3. Results

3.1. Adsorption on silica

Spectra recorded during the adsorption of $\text{DuCr}(\text{CO})_3$ on silica exhibited ten bands at 2005, 1998, 1981, 1968, 1925, 1893, 1865, 1832, 1790 and 1748 cm^{-1} (Fig. 1) all of which

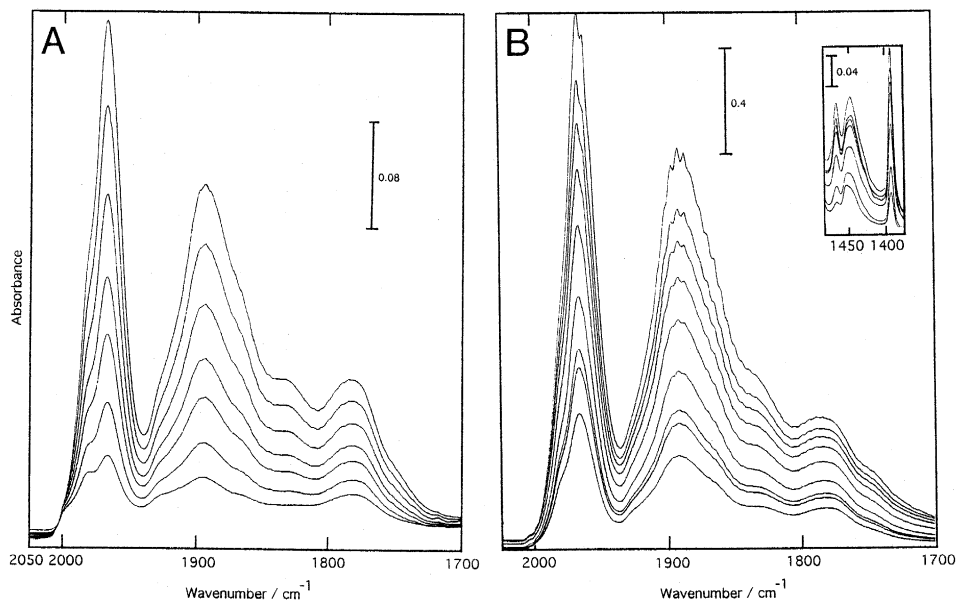


Fig. 1. Growth of IR bands for $\text{DuCr}(\text{CO})_3$ on silica after (A) 15–60 min, (B) 80 min–6 h.

are ascribed to ν_{CO} vibrations of adsorbed molecules. The large number of bands and variations in their relative intensities as a function of coverage suggest that at least four forms of adsorbed $\text{DuCr}(\text{CO})_3$ existed on the silica surface. The growth of a broad band at 3620 cm^{-1} due to perturbed silanol groups (Fig. 2A) showed that one mode of adsorption involved hydrogen bonding interactions between surface silanol groups and the π -electrons of aromatic durene rings in $\text{DuCr}(\text{CO})_3$ molecules [8]. The carbonyl groups in hydrogen bonded $\text{DuCr}(\text{CO})_3$ molecules remain unperturbed by direct interaction with the surface and gave infrared bands at 1968 , 1893 and $1865(\text{sh})\text{ cm}^{-1}$ (Fig. 1) similar to those reported for $\text{DuCr}(\text{CO})_3$ in solution [9]. Dodonov et al. [8] reported bands at 1960 and 1885 cm^{-1} for this species on an Aerosil silica.

Silica which has been evacuated at high temperature exhibits surface properties characteristic of the presence of a low surface population

of Lewis acidic sites [10–14]. Transition metal carbonyl compounds are adsorbed at Lewis acidic sites on other oxides such as alumina by ligation via the oxygen atoms of carbonyl groups [1]. Bands at 1832 , 1790 and 1748 cm^{-1} may be ascribed to vibrations of carbonyl groups which were perturbed by O-ligation to electron deficient silicon atoms acting as Lewis acidic sites [10,11]. By analogy to results for benzenechromiumtricarbonyl on silica [7] three types of O-ligation occurred and were weak (1832 cm^{-1}), moderate (1790 cm^{-1}) and strong (1748 cm^{-1}) in terms of their strengths of interaction with Lewis sites. The three infrared bands at 1981 , 1998 and 2005 cm^{-1} may similarly be ascribed to vibrations of non-ligating (to the surface) carbonyl groups in the three types of ligated complex, respectively. The adsorbed complexes would also have given bands in the $1850\text{--}1970\text{ cm}^{-1}$ spectral region but, apart from the band at 1925 cm^{-1} , these were

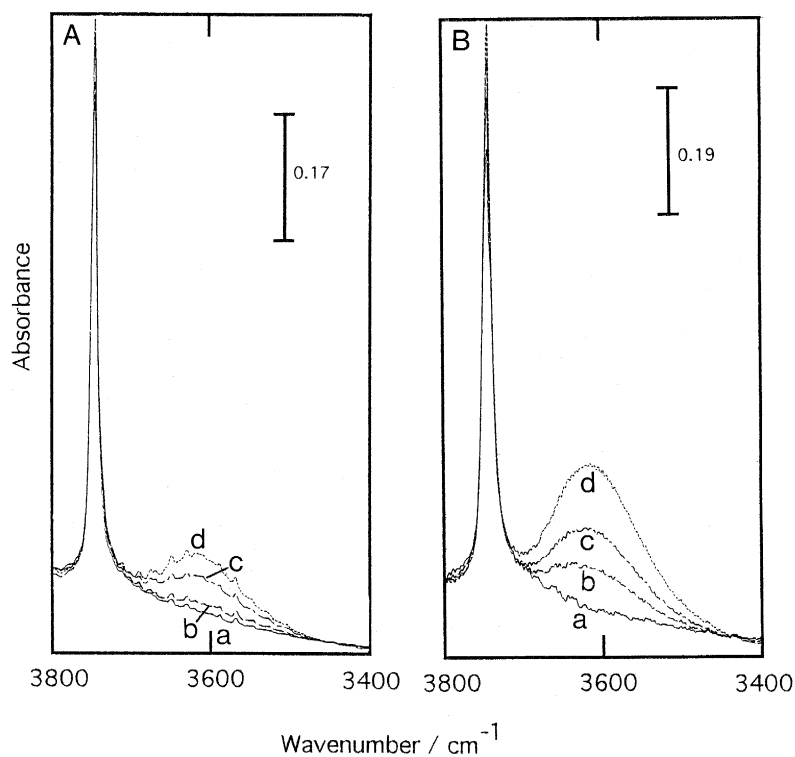


Fig. 2. Spectra of (A) silica exposed to $\text{DuCr}(\text{CO})_3$ for (a) 0, (b) 1, (c) 4 and (d) 7 h, and (B) silica (H_2O) exposed to $\text{DuCr}(\text{CO})_3$ for (a) 0, (b) 1, (c) 2 and (d) $3\frac{1}{2}$ h.

coincident with or obscured by the bands due to H-bonded $\text{DuCr}(\text{CO})_3$ molecules on the surface.

Evacuation of silica treated with $\text{DuCr}(\text{CO})_3$ caused slow desorption which was accelerated by mild heating (Fig. 3). The decreases in intensity of the bands due to H-bonded $\text{DuCr}(\text{CO})_3$ were paralleled by reductions in the maximum at 3620 cm^{-1} due to perturbed silanol groups. The latter band disappeared after evacuation at 398 K. Residual bands in the ν_{CO} region after this treatment (Fig. 3B) resembled bands present during the initial stages of adsorption confirming that O-ligated species were bonded to the surface more strongly than H-bonded species. Increasing prominence of a weak shoulder at ca. 1728 cm^{-1} resembles the appearance of a stronger band at 1717 cm^{-1} in previous work [8].

3.2. Adsorption on silica (H_2O)

Hydrothermal treatment of silica in water vapour at 973 K followed by adsorption of $\text{DuCr}(\text{CO})_3$ at 298 K gave spectra in the ν_{CO} region (Fig. 4) which were dominated by bands at 1968 , 1893 and 1865 cm^{-1} due to $\text{DuCr}(\text{CO})_3$ molecules involved in H-bonding interactions with surface silanol groups (Fig. 2B). The only evidence for O-ligated species in the early stages of adsorption was provided by a broad weak

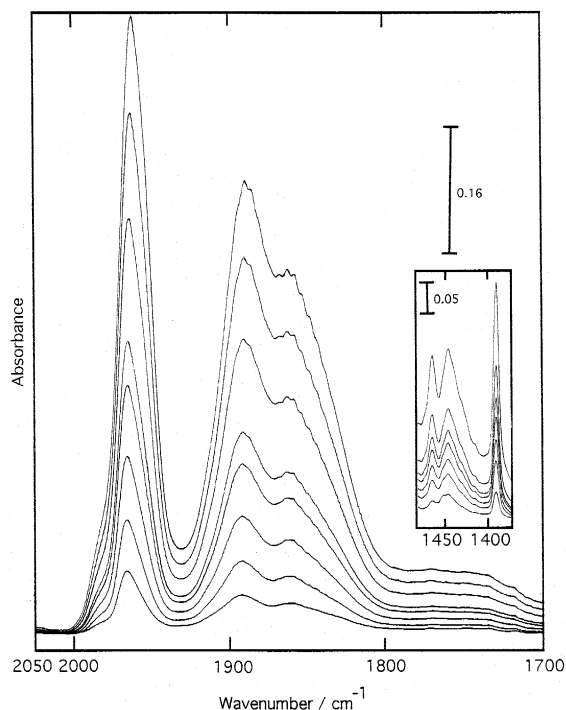


Fig. 4. Growth of IR bands for $\text{DuCr}(\text{CO})_3$ on silica (H_2O) after 10–60 min, and (inset) 30–120 min.

shoulder at $1720\text{--}1800\text{ cm}^{-1}$ and a very weak band at 1983 cm^{-1} . Comparisons of band intensities for the ν_{CO} band at 1968 cm^{-1} and the 3620 cm^{-1} band showed that a much greater total amount of $\text{DuCr}(\text{CO})_3$ was required on the

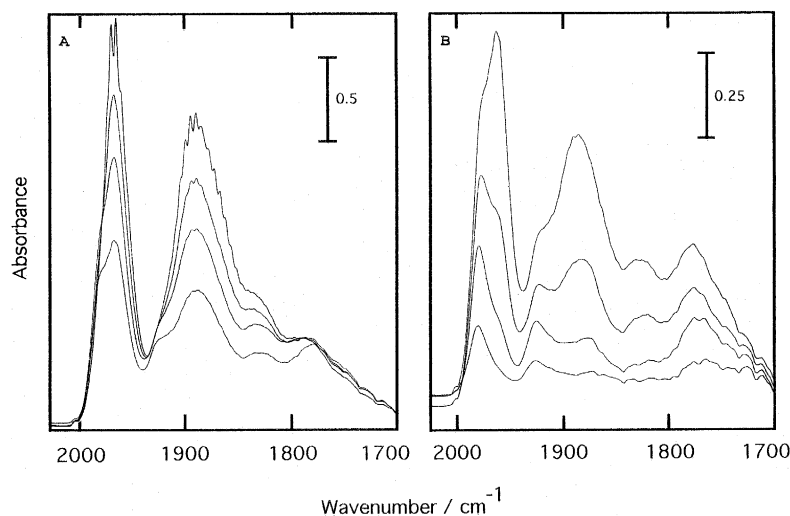


Fig. 3. Decrease of IR bands for $\text{DuCr}(\text{CO})_3$ on silica after (A) 7 h, 24 h, $\frac{1}{2}$ h at 323 K, $\frac{1}{2}$ h at 343 K, (B) $\frac{1}{2}$ h at 343, 358, 378 and 398 K.

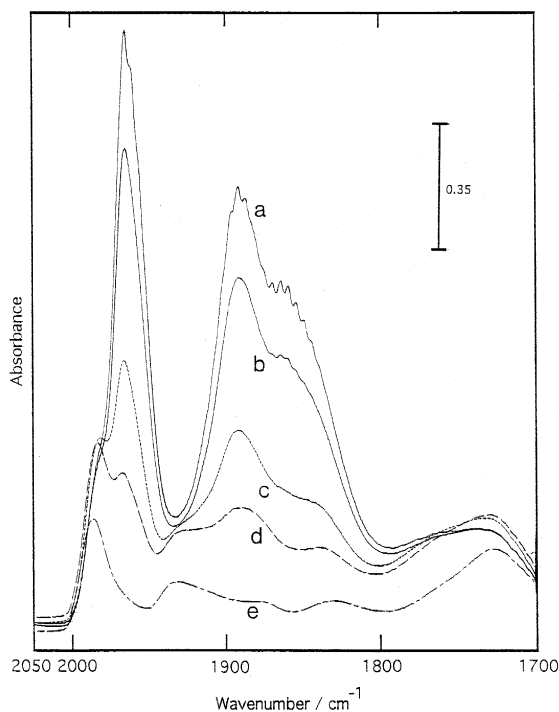


Fig. 5. Loss of IR bands for $\text{DuCr}(\text{CO})_3$ on silica (H_2O): (a) 24 h adsorption, then desorption for (b) 3 h, (c) $\frac{1}{2}$ h at 323 K, (d) $\frac{1}{2}$ h at 343 K, and (e) $\frac{1}{2}$ h at 368 K.

surface of silica to produce the same number of perturbed silanol groups than the amount of $\text{DuCr}(\text{CO})_3$ needed on silica (H_2O). This provides strong evidence for the enhanced proportion of H-bonded rather than O-ligated $\text{DuCr}(\text{CO})_3$ molecules on silica (H_2O), and also confirms for silica that contributions to the band at 1968 cm^{-1} resulted from O-ligated species. The presence of some O-ligated species on silica (H_2O) was shown by the desorption spectra (Fig. 5) which contained bands at 1987, 1937, 1881, 1832 and $1760(\text{sh}) \text{ cm}^{-1}$ in similar positions to the corresponding bands for silica (Fig. 3). Bands at 2005 and 1998 cm^{-1} for silica were absent for silica (H_2O) showing that sites responsible for the moderately strong and strong O-ligation of $\text{DuCr}(\text{CO})_3$ were not present on the silica (H_2O) surface. The weakness of bands at ca. $1740\text{--}1790 \text{ cm}^{-1}$ for silica (H_2O) was consistent with this conclusion. However, a broad maximum at 1728 cm^{-1} (Fig. 5) was much stronger for silica (H_2O) than the corresponding weak shoulder for silica. The in-

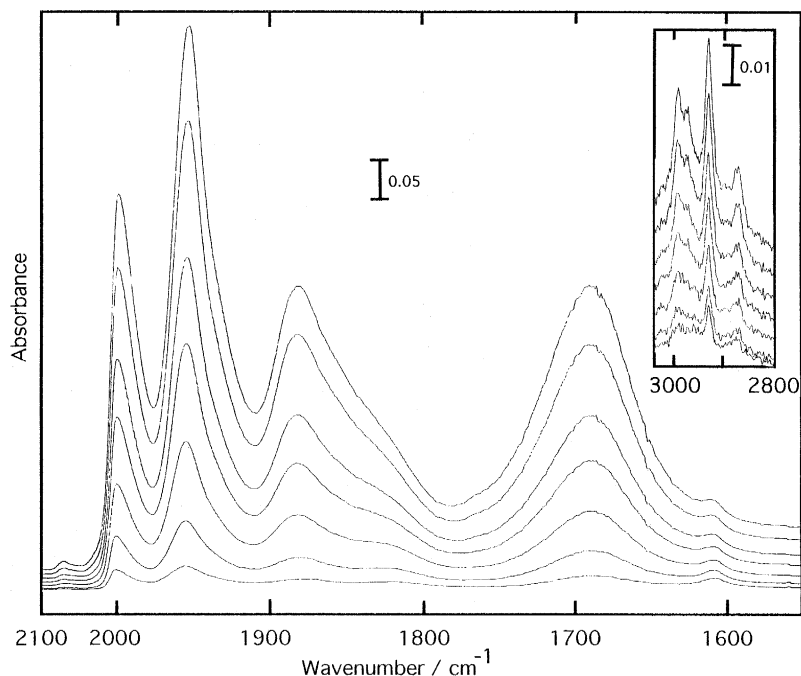


Fig. 6. Growth of IR bands for $\text{DuCr}(\text{CO})_3$ on silica-alumina after 15–90 min.

tensity of the band at 1728 cm^{-1} was apparently related to the intensity of a maximum at 1987 cm^{-1} as both bands grew in intensity at the same time during thermal activation at 323 K . The latter band differs from that at 1981 cm^{-1} which was present during the early stages of adsorption. Adsorption of $\text{DuCr}(\text{CO})_3$ on silica (H_2O) led primarily to H-bonding interactions, with some O-ligation to weakly Lewis acidic sites and a thermally activated reaction leading to a surface species containing both perturbed (1728 cm^{-1}) and unperturbed (1987 cm^{-1}) carbonyl groups ligated to chromium.

3.3. Adsorption on silica–alumina

The adsorption of $\text{DuCr}(\text{CO})_3$ on silica–alumina initially gave infrared bands in the ν_{CO} region at 2071 , 2003 , 1955 , $1940(\text{sh})$, 1878 , 1822 , 1762 , 1690 and 1609 cm^{-1} (Fig. 6) suggesting the occurrence of at least three distinguishable modes of adsorption. The bands at 1955 and 1878 cm^{-1} were close to bands at

1957 and 1885 cm^{-1} for $\text{DuCr}(\text{CO})_3$ in solution [9] and are therefore assigned to vibrations of physically adsorbed $\text{DuCr}(\text{CO})_3$ molecules. Compared with the result for silica there was little evidence from the OH-stretching region of the spectrum for silica–alumina for H-bonding interactions involving surface hydroxy groups. The intensity of the band at 1955 cm^{-1} was greater than expected [9] for unperturbed $\text{DuCr}(\text{CO})_3$ molecules also giving the band at 1878 cm^{-1} and therefore a contribution to the overall band intensity at 1955 cm^{-1} must have derived from an O-ligated surface species. This was confirmed by the spectroscopic changes immediately after 90 min sublimation (Fig. 7) when the bands at 2003 and 1690 cm^{-1} continued to grow, the band at 1878 cm^{-1} became weaker, and the maximum at 1955 cm^{-1} remained at about the same intensity. Weakly adsorbed $\text{DuCr}(\text{CO})_3$, possibly present as small crystallites condensed on the oxide surface, underwent a structural change and became O-ligated to strongly Lewis acidic Al^{3+} sites in

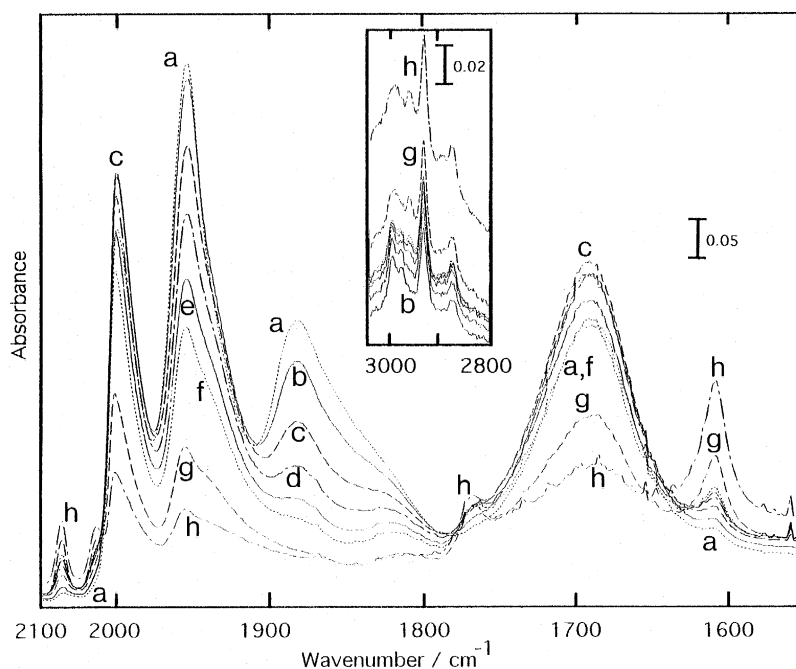


Fig. 7. Spectra of $\text{DuCr}(\text{CO})_3$ on silica–alumina after (a) 3 h sublimation at 298 K , (b)–(h) subsequent desorption or surface reaction for $3\text{--}21\text{ h}$ at 298 K in vacuum.

the silica–alumina surface [15,16]. The O-ligated species gave infrared bands at 2003, 1955 and 1690 cm^{-1} .

After sublimation was complete the infrared spectrum of the impregnated disc standing in a dynamic vacuum underwent changes compatible with the occurrence of surface reactions. Loss of band intensities at 2003, 1955 and 1690 cm^{-1} was accompanied by the growth of bands at 2071, 2026, 1769 and 1609 cm^{-1} (Fig. 7). The growth of the maximum at 1609 cm^{-1} was accompanied by a sharp band at 3615 cm^{-1} and a weaker band at 3680 cm^{-1} . Exposure of silica–alumina to carbon dioxide led to the immediate appearance of these bands which are ascribed to the formation of surface bicarbonate anions. Surface oxide and hydroxide ions on silica–alumina acted as nucleophiles causing loss of CO ligands from $\text{DuCr}(\text{CO})_3$ molecules and the concomitant formation of chromium sub-carbonyl complexes and bicarbonate ions. The overall intensities of bands in the ν_{CH} region of the spectrum (Figs. 7 and 8) only

decreased slightly during the surface reaction showing that durene ligands, and hence by implication Cr atoms, were retained by the surface during the decarbonylation process. The infrared bands at 2071, 2026 and 1769 cm^{-1} are assigned to ν_{CO} vibrations of at least two types of durenechromium sub-carbonyl species, one with a carbonyl group O-ligated to Lewis acidic Al^{3+} sites.

4. Discussion

Dodonov et al. [8] studied an aerosil silica which, before adsorption of $\text{DuCr}(\text{CO})_3$ at 293 K, had been heated in vacuum at 973 K. Hydrogen bonding interactions between surface silanol groups and durene rings in $\text{DuCr}(\text{CO})_3$ molecules were observed in both the previous and present study. However, in contrast to the results here, the earlier study did not provide evidence for O-ligation of adsorbed molecules to Lewis acidic sites in the silica surface. Ratio-

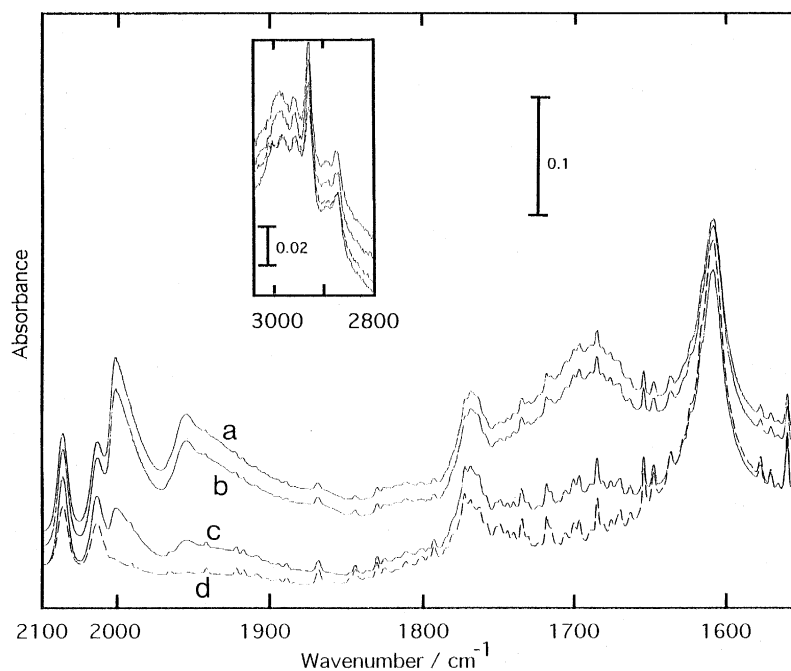


Fig. 8. Spectra of silica–alumina exposed to $\text{DuCr}(\text{CO})_3$ for ca. 3 h followed by evacuation for (a) 21 h at 298 K, (b) 22 h at 298 K, (c) 1 h at 333 K, and (d) $\frac{1}{2}$ h at 358 K.

nalisation of this difference is provided by detailed consideration of the surface structure of silica [17–19]. Strained ring structures at the silica surface [17–19] provide a low surface population of Lewis acidic sites for the adsorption of electron donating molecules [11,12,14]. The existence of strained structures depends on the method of silica synthesis [18,19]. In particular, silicas made by flame hydrolysis, as used by Dodonov et al. [8], contain far fewer high energy strained rings and active adsorption sites than the type of porous silica used here [18,20]. The contrast between the behaviour of the active porous silica and the inactive flame hydrolysed silica towards the adsorption of $\text{DuCr}(\text{CO})_3$ is reminiscent of activity differences for metal catalysts supported on the two types of silica [19,21].

After evacuation at 973 K the silica surface will contain isolated terminal and geminal hydroxy groups [22–24] and strained and unstrained siloxane bridges [17–19]. Strained siloxane bridges contain electron deficient Si atoms which act as Lewis acidic adsorption sites [10–12,14]. The activity of these sites for the adsorption of $\text{DuCr}(\text{CO})_3$ via O-ligation will depend on the extent of strain in the $-(\text{SiO})_n-$ ring structure of which the exposed siloxane bond is a part. Chiang et al. [14] regard two-membered ($n = 2$) ring sites as the most reactive on the silica surface, and they have been shown to exist on the present type of silica [20]. The existence of three-membered strained rings ($n = 3$) in silicas similar to that used here is also well-established [17–20]. Rings with $n = 4$ are unstrained [25] and will not have provided active sites for the adsorption of $\text{DuCr}(\text{CO})_3$.

Gladden et al. [18] reported that the concentration of three-membered rings in a silica xerogel was considerably reduced by contact with water. Here contact with water vapour at 973 K had a related effect and completely removed the highly strained sites responsible for moderate and strong perturbations of CO ligands in $\text{DuCr}(\text{CO})_3$ molecules. The enhancement by hydrothermal treatment of the appearance of the

band at 1728 cm^{-1} (Fig. 5), together with a maximum at 1987 cm^{-1} due to unperturbed carbonyl ligands, may be ascribed to the structure proposed by Dodonov et al. [8], although their band at 3495 cm^{-1} due to H-bonded silanol groups was not observed here. The surface of the present silica after heat treatment in water vapour at 973 K behaved as would be expected [18,20] for silicas prepared by flame hydrolysis rather than for a porous silica xerogel.

The decarbonylation of $\text{DuCr}(\text{CO})_3$ and formation of surface bicarbonate ions on silica–alumina resembles results for the adsorption of $\text{Co}_2(\text{CO})_8$ on silica–alumina [26]. Adsorption of metal carbonyl complexes at strongly Lewis acidic surface sites [15,16] weakens metal–CO bonds and promotes decarbonylation [1]. Loss of one of the unperturbed CO ligands would give a structure involving an incompletely coordinated Cr atom, a CO ligand perturbed by interaction with the Lewis acidic site (infrared band at 1769 cm^{-1} (Fig. 8)), and an unperturbed CO group (2071 or 2026 cm^{-1}). Loss of both unperturbed CO groups would leave a Cr atom with two coordination vacancies which is a desirable requirement for an active ethene polymerisation catalyst. The benzene analogue of $\text{DuCr}(\text{CO})_3$ gives active catalyst on silica–alumina [7]. Decarbonylation of $\text{DuCr}(\text{CO})_3$ may alternatively lead to an Al–O–Cr (or Si–O–Cr) bonding linkage between the adsorbed complex and the oxide surface. The resulting dicarbonyl structure could be responsible for both infrared bands at 2071 and 2026 cm^{-1} . The three bands at 2071 , 2026 and 1769 cm^{-1} must therefore be ascribed to at least two sub-carbonyl species.

Acknowledgements

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