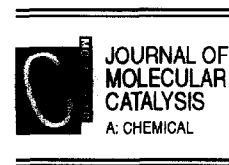




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# An EXAFS investigation of chromocene on silica using empirical, semi-empirical and ab initio methods

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## Abstract

The average chromium environment on the surface of a chromocene/silica ethylene polymerisation catalyst has been determined by Cr-EXAFS to be  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\mu\text{-OSi=})(\text{OSi=})_2]$ .

**Keywords:** EXAFS; Ethylene polymerisation; Chromocene

## 1. Introduction

One of the most potent catalysts for ethylene polymerisation is obtained by reacting partially dehydrated silica with chromocene [1–17]. The catalyst is thought to be formed by a chemical reaction between chromocene and the hydroxyl groups of the silica surface, during which cyclopentadienyl ligands are released [18]. This catalytic system has been studied in great detail since it was first reported by Karol et al. in 1972 [5]. The polymerisation characteristics were found to be strongly dependent on the nature and dehydration temperature of the silica support (i.e. surface morphology, surface silanol concentration) [2,9,10]. However, there is still only a limited understanding of (a) the active

site(s) and (b) the average chromium surface environment. Thus, the chromium oxidation state has variously been assigned as being from Cr(0) to Cr(VI) [9]. The number of cyclopentadienyl ligands evolved during the loading of the chromocene onto the silica has been reported as one or two, depending upon the surface pretreatment. Different infra red spectra have been reported following exposure of the catalyst to CO and a variety of structures has been proposed to account for the active site. A common, often unstated, assumption underpinning most of these spectroscopic investigations is that the spectroscopic response is that of the active catalyst, i.e., that the active catalyst is the only, or at least predominant, surface species and that the active site is sensitive to the spectroscopic probe.

Several investigations have probed the catalyst by CO poisoning experiments [1–4,14,18]. Structural assignments based on interpretations

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of the infrared spectra of CO-poisoned catalysts in the CO stretching region can only be valid if the poisoning can be shown to be reversible and the contribution to the spectrum of the poisoned active site can be established. These tests are seldom applied. It is significant that the careful work of Lunsford and Fu [2] has been interpreted as indicating that the catalytically active species accounts for only some 1% of the surface confined chromium (the interpretations of these experiments were restricted to establishing the relative amount, but not the structure, of the active species). Although this conclusion is based on evidence from a single technique and has not yet received independent confirmation, it has not been incorporated into the interpretations of other investigations.

There is some disagreement as to the existence and identity of the non-catalytically active chromium species which account(s) for the bulk of the surface confined chromium. The main surface species have been variously assigned as monomeric  $(\eta^n\text{-C}_5\text{H}_5)\text{Cr}(\text{OSi}\equiv)_n$  complexes, stabilised by (physisorbed or chemisorbed) chromocene [12] or as surface confined  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{OSi}\equiv)]_m$  clusters which vary in their degree of aggregation according to the silica pretreatment [1–3]. These clusters are believed to be made up of dimeric sub-units. When the system is exposed to carbon monoxide, infrared absorptions consistent with the presence of  $\text{Cr}(\mu\text{-CO})\text{Cr}$  moieties are observed. These chromium carbonyl fragments have been postulated to be derived from the direct interaction of carbon monoxide with preformed  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{OSi}\equiv)]_m$  clusters or by carbon monoxide-induced oligomerisation of the monomers.

In view of the foregoing, it is perhaps not surprising that ‘modelling’ experiments using homogeneous organometallic species have not been successful in establishing the likely structure of the active species. In most, if not all, of the few examples where model compounds have exhibited catalytic activity, the activity is generated by the addition of a co-catalyst, which is

not required by the chromocene/silica catalyst. Moreover, the activities of the homogeneous ‘models’ are generally lower than that of the heterogeneous catalyst, an observation contrary to simple expectations.

It is of interest, therefore, to establish the nature of both the catalytically active and the bulk chromium species. We report here a Cr-EXAFS investigation of the material produced by the interaction of chromocene with partially dehydrated silica.

## 2. Experimental

All manipulations were carried out under an inert atmosphere. Chromocene (Aldrich) was used as received,  $[(\text{cyclo-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2]$  and  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$  were prepared by literature methods [19,20]. Silica (Merck, mesh 60, 25.1 g) was dehydrated at 390°C under high vacuum (0.1 Torr) for 24 h. Chromocene (1.1 g) was stirred over the dehydrated silica for 1 h. During deposition the white silica became very dark and the red solution turned colourless. The solvent was decanted, the solid washed with hexane and the catalyst dried (room temperature) and sealed under vacuum. Sufficient chromocene was used to give a loading of 1.18%. EXAFS experiments were performed at the Australian National Beamline Facility in the Photon Factory, Japan, and at station 7.1 of the Synchrotron Radiation Source (SRS) at the SERC Daresbury Laboratory. At the Australian National Beamline Facility the ring was held at 2.5 GeV and the ring current after each injection was 360 mA, decaying nearly linearly to 280 mA (i.e. 78%) over a period of 23.5 h. The scans took about 45 min, thus the flux difference between the beginning and end of each scan is estimated to be around 0.7%. The EXAFS were recorded in transmission mode using an external standard (nickel foil) to calibrate the energy range for each scan. At least two scans were collected for each sample. Three ion

chambers were used in a linear arrangement. The samples were in powder form diluted with sufficient BN (Fluka) to give an anticipated X-ray absorption ( $\ln(I_0/I_1) = \mu\rho x$ ) of  $\approx 0.8$  (where  $\mu$  and  $\rho$  are the X-ray absorption coefficient and density, respectively). Published X-ray absorption coefficients [21] and densities taken from published crystal structures were used. The cell consisted of a 1 mm thick aluminium base with a hole covered by KAPTON™ tape. The white beam was passed through a set of primary slits, a monochromator and a set of secondary slits. The monochromator was a single cut Si[111] crystal with a  $d$ -spacing of 3.135625 Å at operating temperature. The baseline drift was estimated to be on average  $\pm 0.2$  eV between consecutive scans. All edge jump ratios lay in the interval of  $0.5 < \ln(I_0/I_1) < 1.2$ . Data were collected to  $15 \text{ \AA}^{-1}$ . The value of  $E_0$  was set to be 6005 eV for all compounds. Experiments at the SERC Daresbury Laboratory were similar and used a Si[111] order-sorting double crystal monochromator at 50% harmonic rejection and a platinum focusing mirror. The SRS operated at 2 GeV with beam currents in the range 200–300 mA and data were collected at the Cr K-edge. Data were acquired in fluorescence mode using a single TlI/NaI scintillation counter with a cobalt foil filter. The experiments used a series of catalyst wafers ranging in thickness from 0.5 to 1.5 mm which were sealed under an inert atmosphere between two sheets of KAPTON™ film. A variety of chromium-containing species was used as model compounds to determine the phase shifts or phase shift corrections and to examine the oxidation state dependence of the pre-edge. The background subtraction was performed using SPLINE [22] and the modelling process was carried out with three independent programs: XFPACK [23–26], EXCURV90 [27–31] and FEFF 4.06 [32,33] in which the amplitude and phase functions are derived by empirical, semi-empirical and ab initio methods, respectively. A common graphical user interface and improved fitting procedures were provided for XFPACK

and FEFF 4.06 via the program XFIT [22]. Multiple scattering calculations were carried out using FEFF5.05 in combination with XFIT<sup>1</sup>.

### 3. Results and discussion

The shape of the absorption edge is compared with those of a variety of representative model compounds in Fig. 1. The comparison conclusively confirms that the bulk of the surface chromium is not present as Cr(VI) nor as Cr(V), since the EXAFS of model compounds with these oxidation states exhibit distinctive 1s to 3d pre-edge features. Similarly, the distinctive profiles of the absorption edges of the EXAFS of Cr(0) model compounds are not observed in the EXAFS of the chromocene/silica sample. The shape of the absorption edge in the present data is best approximated by those of Cr(III) and/or Cr(II) model compounds, suggesting that most of the surface chromium is present as Cr(III) or Cr(II). It was not possible to accurately determine the relative edge positions for the various oxidation states because of the difficulty in finding a common reference point on the different edge profiles.

Fig. 2 illustrates a typical EXAFS spectrum and its associated radial distribution function for the chromocene on silica sample obtained using a  $k^3$  weighting of the EXAFS function,  $X(k)$ . The feature at  $R \approx 2.6 \text{ \AA}^{-1}$  can to a first approximation be fitted by the presence of a single adjacent chromium atom at a Cr–Cr distance of  $2.95 \pm 0.08 \text{ \AA}$ . The presence of obvious oscillations out to  $> 10 \text{ \AA}^{-1}$  in the EXAFS is indicative of a chromium atom in the second shell in addition to co-ordination of chromium by low  $Z$  elements [34]. Such a Cr–Cr distance is consistent with the presence of a bridging ligand(s) (vide infra). A similar feature, emphasised by

<sup>1</sup> Details of the window functions, fitting routines, phase shift calculations, SPLINE and XFIT can be obtained from P.E.

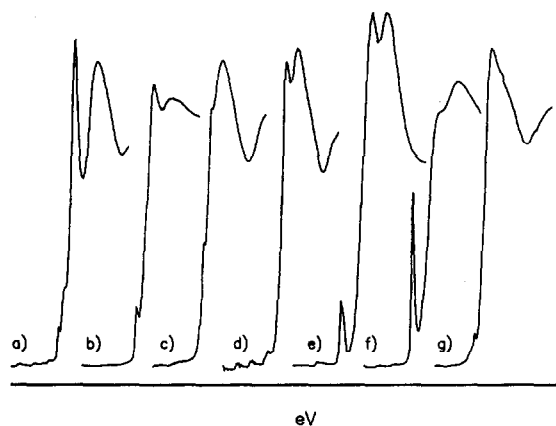


Fig. 1. Representative K-edges of (a) Cr(0), (b) Cr(I), (c) Cr(II), (d) Cr(III), (e), Cr(V), (f) Cr(VI) compounds and of (g) silica-supported chromocene.

multiple scattering contributions, is observable in Fig. 3, the radial distribution function of the Cr–Cr bonded dimer,  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ , and is clearly absent from Fig. 4, the radial distribution function of  $[(\text{cyclo-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2]$ , which does not have a Cr–Cr bond. The additional parameters used to fit the data for the silica-supported chromocene were five carbon atoms at an average Cr–C distance of  $2.02 \pm 0.04$  Å, and two to three oxygen atoms at an average Cr–O distance of  $2.16 \pm 0.06$  Å. The presence of the five carbon atoms, and their distance from the chromium atom is consistent with the presence of a single ( $\eta^5\text{-C}_5\text{H}_5$ ) ligand on each chromium, which in turn,

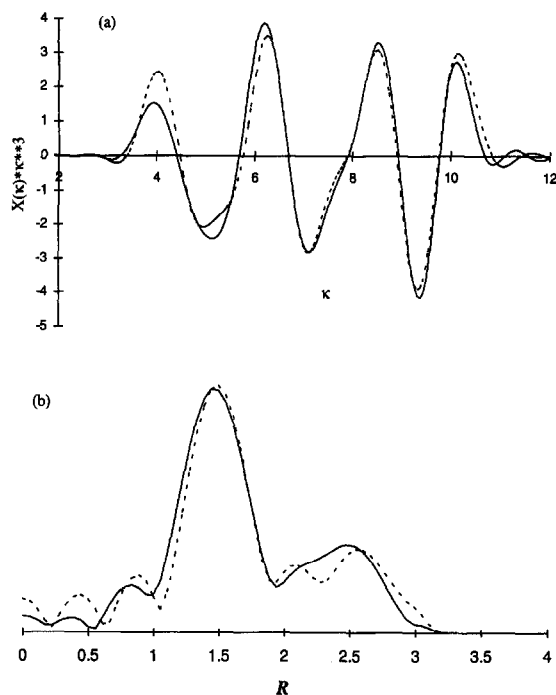


Fig. 2. Fit to (a) Cr K-edge  $k^3$  weighted EXAFS of silica-supported chromocene (b) radial distribution function calculated from (a) (solid line, experimental; dashed line, calculated using XFPACK).

is consistent with the reported loss of a cyclopentadienyl ligand during the loading of the chromocene onto the support.

The fit is illustrated in Fig. 2 and the model parameters giving the best fit are shown in Table 1. The model solutions for the EXAFS data contain very similar coordination environ-

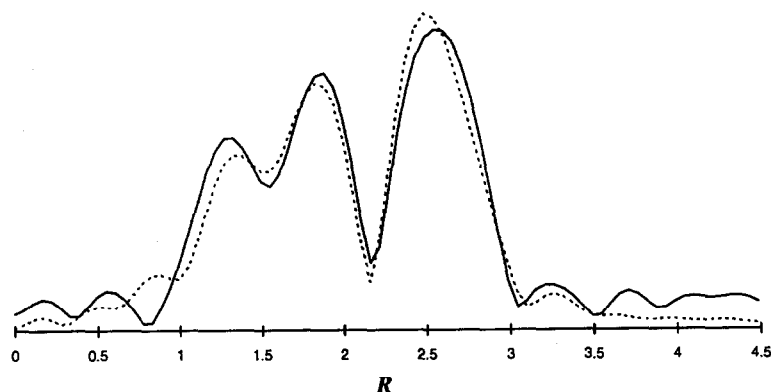


Fig. 3. Fit to radial distributions of the Cr–Cr bonded dimer,  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$  (solid line, experimental; dashed line, calculated using FEFF 5.05).

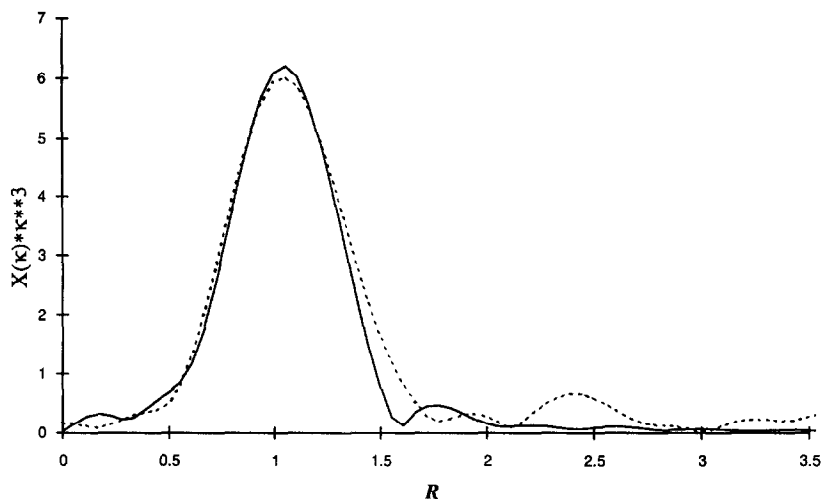


Fig. 4. Fit to radial distribution function of [(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>11</sub>(OSiMe<sub>3</sub>)CrO<sub>2</sub>] (solid line, experimental; dashed line, calculated using FEFF 4.06).

ments for the Cr atom, i.e. approximately one cyclopentadienyl ring, two to three oxygen atoms and one chromium atom each. In light of the introductory comments, it should be emphasised that this model, however, represents only the *average* chromium environment.

Thus, the EXAFS data can be fitted with a model described by adjacent ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Cr(O)<sub>n</sub> (*n* = 2, 3) centres on the surface. The Cr–Cr distance is consistent with a Cr(III) oxidation state (*vide infra*), suggesting the presence of three, rather than two, adjacent oxygen atoms (i.e., *n* = 3). The cyclopentadienyl ring is pre-

sumed to be  $\eta^5$  co-ordinated since the five carbon atoms are equidistant from the chromium atom. This assignment is in agreement with conventional molecular organometallic chemistry and with the necessity to maximize the co-ordination saturation of the chromium. It is possible that in the active species alternative co-ordination modes of any cyclopentadienyl ring may be generated under the conditions of the catalytic reaction. The Cr–Cr distance ( $2.95 \pm 0.08$  Å) is longer than the 2.65 Å separation in the formally Cr(II) dimer, [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cr<sub>2</sub>( $\mu_2$ -OBu<sup>t</sup>)<sub>2</sub>] [35], is also longer than the 2.766 Å

Table 1  
Comparison of solutions to Cr-EXAFS  $k^3$  weighted data utilizing various methods of calculating phase shifts

Atom	Parameter <sup>a</sup>	FEFF 4.06	EXCURV 90	XFPAKG <sup>b</sup>	Average
C	<i>n</i>	5.1(3)	5.5(1.7)	4.8(4)	5.1(3)
	<i>d</i>	2.03(1)	1.97(3)	2.050(3)	2.02(4)
	<i>D/W</i>	0.0017(4)	0.0014(41)	−0.0028(6)	
O	<i>n</i>	1.9(1)	1.8(1.5)	3.2(4)	2.3(8)
	<i>d</i>	2.18(1)	2.10(1)	2.21(1)	2.16(6)
	<i>D/W</i>	0.006(4)	0.003(18)	−0.003(4)	
Cr	<i>n</i>	0.88(9)	0.6(2)	0.83(9)	0.8(1)
	<i>d</i>	3.01(1)	2.86(1)	2.97(6)	2.95(8)
	<i>D/W</i>	0.009(2)	0.006(4)	0.003(2)	
	<i>R</i>	32.2	18.1	21.4	

<sup>a</sup> *n* = number of atoms; *d* = distance (Å) of these atoms from the Cr atom; *D/W* = Debye–Waller factor (Å<sup>2</sup>); *R* = ((X<sub>0</sub>)<sup>2</sup>/X<sup>2</sup>)<sup>1/2</sup>.

<sup>b</sup> For XFPAKG, *D/W* = difference between calculated and experimental Debye–Waller factors.

separation in the formally mixed-valence Cr(II,III) dimer,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-OBu}^t)_2(\text{OCR})]$ , but is in good agreement with the Cr–Cr distances in the formally Cr(III) dimer  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-OBu}^t)_2(\text{OBu}^t)_2]$ , (3.004 Å) [36,37]. It is much shorter than the 3.281(1) Å distance in the formally Cr(I) dimer,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6]$  [38]. However, this last Cr–Cr bond is considered to be very long as a consequence of substantial non-bonded repulsions in an exceptionally crowded molecule. Thus, the EXAFS experiment implies that most of the chromium exists as dimeric or oligomeric species. The data from this limited collection of structures exhibit the expected correlation between the chromium oxidation state and the Cr–Cr bond distance. By this criterion the present data are more nearly consistent with the surface species being Cr(III)–Cr(III) dimers, the oxidation state deduced from the shape of the absorption edge. Although the presence of the adjacent chromium centres on the surface also accords with the suggestion of chemisorbed chromocene in close proximity to monomeric surface species [12], the Cr–Cr distance is too short to be accommodated by reasonable models of such an interaction. An oligomeric surface species similar to  $(\eta^5\text{-C}_5\text{H}_5)\text{CrO}_4$  is also inconsistent with the fit to the data.

The solutions to the Cr K-edge EXAFS of the structurally characterised complexes  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$  and  $[(\text{cyclo-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2]$  are compared with the crystal structure parameters in Table 2 [19,38] and the fits to the EXAFS data are illustrated in Fig. 3 and Fig. 4. Several features of the EXAFS of these compounds are significant. The prominent pre-edge feature indicative of Cr(VI) (and of Cr(V)) is clearly evident in the EXAFS of  $[(\text{cyclo-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2]$  as expected. The solution does not involve any Cr···Si distances. This contrasts with the detection of Nb···Si distances in the Nb K-edge EXAFS of  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{H}-\mu\text{-}(\eta^5, \eta^1\text{-C}_5\text{H}_4)]_2/\text{SiO}_2$  [39], but is in accord with the absence of Cr···Si distances in the EXAFS of  $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)_2]/\text{SiO}_2$ .

The Cr–O bond lengths are on average longer by about 0.16 Å than expected. However, the elongation of the Cr–O bond distances in complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-OBu}^t)_2(\text{X})_2]$  (X = Cl, Br, I) is suggested to be a consequence of the presence of the electronegative halide ligands [37]. The implication that the silica surface is as electronegative as a  $\text{CF}_3$  group [40] suggests that the elongation observed by EXAFS could be explained analogously. The Cr–C bond lengths are about 0.2 Å shorter than

Table 2

Comparison of parameters derived from the crystal structures and Cr K-edge EXAFS for  $[(\text{cyclo-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2]$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6]$  [19,38]

Compound	Crystal structure			EXAFS		
	R (%)	N	Bond length (Å)	R (%)	N	Bond length (Å)
$[\text{cy}_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2]^a$	6.08			22.00		
Cr=O		2	1.557(5), 1.574(4)		2.1	1.565(9)
Cr–O		2	1.731(4), 1.730(4)		1.9	1.731(12)
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6]$	2.7					
Cr–Cr		1	3.281(1)		1	3.29
Cr–C( $\eta^5\text{-C}_5\text{H}_5$ )		5	2.20 (ave.)		5	2.18
Cr–CO		3	1.86 (ave.)		3	1.86
C–O		3	1.14 (ave.)		3	1.15

<sup>a</sup> cy = cyclo-C<sub>6</sub>H<sub>11</sub>

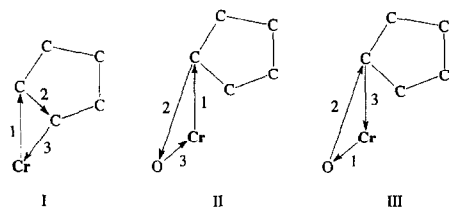


Fig. 5. Principle multiple scattering pathways for silica-supported chromocene.

expected. Alternatively, the differences in the Cr–O and Cr–C bond lengths from the expected values could be due to the emission of multiple scattering contributions from the cyclopentadienyl ring from the analysis.

Two structures consistent with the results of the single scattering analysis were refined using FEFF 5.05 multiple scattering calculations. The parameters used in these calculations were obtained from the known structures of dimeric chromium cyclopentadienyl compounds of the types  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-OR})_2]$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-OR})_2(\text{OR})_2]$ . These model structures were refined using appropriate restraints to preserve the symmetry of the cyclopentadienyl ring.

Table 3  
Multiple scattering solutions for silica-supported chromocene using FEFF 5.05 and XFIT

Atom	Parameter	$[(\text{cp})\text{Cr}(\mu\text{-OR})_2]$	$[(\text{cp})\text{Cr}(\mu\text{-OR})(\text{OR})_2]$
C	<i>n</i>	5	5
	<i>d</i>	2.04	2.03
	D/W	0.006	0.005
O	<i>n</i>	2	2 ( $\mu\text{-OR}$ ) and 1 (OR)
	<i>d</i>	1.93	1.96 ( $\mu\text{-OR}$ ) and 1.86 (OR)
	D/W	0.003	0.003
Cr	<i>n</i>	1	1
	<i>d</i>	3.00	2.96
	D/W	0.002	0.002
	<i>R</i>	25.49	25.49

The results of these analyses are collected in Table 3 and indicate that the multiple scattering contributions of the cyclopentadienyl ring distort the results of the single scattering analysis to the extent that the Cr–O distances are increased by 0.15 Å to 0.25 Å from their expected value. The major multiple scattering contributions are made by the three pathways shown in Fig. 5. The presence of a Cr–Cr vector is also confirmed, the Cr–Cr distance being consistent

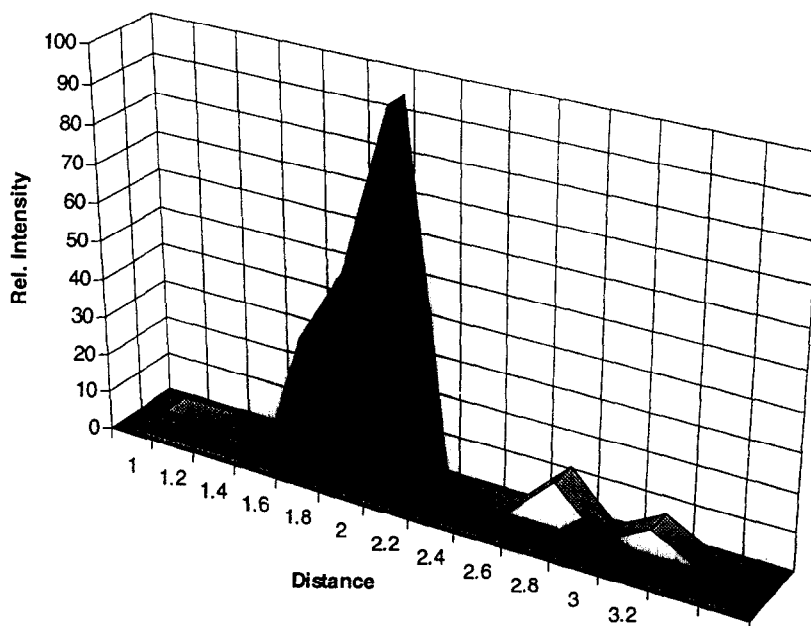
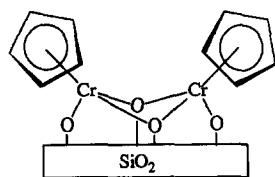


Fig. 6. Individual single and multiple scattering contributions.

with Cr(III) atoms as discussed above. The EXAFS can be fitted with either two or three oxygen atoms around the chromium absorber, as found for the single scattering analysis. A multiple scattering analysis of the EXAFS of the dimer,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6]$ , was performed for comparison. Multiple scattering pathways involving Cr–Cr–CO and Cr–Cr– $(\eta^5\text{-C}_5\text{H}_5)$  were significant and the solution showed similarities in the multiple scattering from the cyclopentadienyl rings.

The multiple scattering analysis shows that the feature at 2.6 Å, which was fitted by the single scattering analysis to only the Cr–Cr vector, is in fact, due to the Cr–Cr vector and several multiple scattering contributions, the most significant of which are illustrated in Fig. 5. The relative contributions of the single and multiple scattering pathways to the EXAFS are illustrated, by consideration of the radial distribution function, in Fig. 6.

Hence, the EXAFS data and chemical considerations taken together indicate that the average chromium environment is represented by the formulation  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{O})_2]_2$ . Given the existence of well characterised molecular species of the composition  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{OR})_2]_2$ , it is likely that surface compounds with a very similar stoichiometry, and possibly structure, exist on the surface.



(I)

These data are then consistent with the representation (I) for the average environment of chromium on the surface. It is inappropriate at this stage to speculate about the bond-order of the Cr–Cr interaction, other than to recognise that the Cr–Cr distance is consistent with a bond order of 1. We note that the Cr– $(\eta^5\text{-C}_5\text{H}_5)$

distances are ca. 0.3 Å shorter than in the analogous molecular species,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\mu\text{-OBU}^t)_2(\text{OBU}^t)_2]$ , (3.004 Å) [36,37]. Although this decrease in the Cr–C bond distance is consistent with the retention of one cyclopentadienyl ligand per chromium in the supported complex, the magnitude of the decrease is surprising. The synthesis and characterization of additional model compounds may clarify this point. The species (I) may react with CO, consistent with the results of CO poisoning experiments. For example, the related dark red  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{OBU}^t)]_2$  dimer reacts with CO to produce a non-volatile, greenish blue hydrocarbon-insoluble compound of empirical formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{OBU}^t)(\text{CO})_2]$  with infrared absorptions consistent with the presence of bridging carbonyls [35].

However, in the context of Lunsford and Fu's interpretation of their data – that only 1% of the surface chromium sites are active for the polymerisation – it is important to emphasise that a surface species such as (I) could represent the bulk surface species, rather than the catalytic active site. Such a conclusion may explain the observations that molecular species of a similar formulation have been shown to be poor models of the supported catalyst [35]. In order to discriminate between proposals of the active sites (i.e. dimeric, monomeric, different oxidation states, etc.) the suggested active sites must be modelled synthetically and their spectroscopic fingerprints and their catalytic activities determined. Some preliminary results of this modelling approach have been published [41].

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