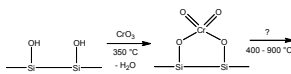


# Evidence for a metallasiloxane ring size effect in metal oxides dispersed on silica

## Introduction

Dispersed metal oxide catalysts are commonly activated by calcination in dry air or O<sub>2</sub>. The calcination temperature is one of the most influential variables determining catalytic activity. The requirement for elevated temperatures is often justified in terms of the need to dehydrate the support, as well as to anchor the metal oxide on its surface via bridging oxygens. The widely-used Phillips' catalyst for ethylene polymerization is made by calcining a Cr precursor (e.g., CrO<sub>3</sub>) in the presence of silica. Polymerization activity increases with calcination temperature above 400 °C, to a maximum at 800 °C just prior to sintering of the support. However, dehydration of the material and anchoring of the chromate as a silyl ester on silica is complete by 350 °C. Scheme 1.



Scheme 1. Proposed stages in the thermal activation of the Phillips' catalyst

The nature of the surface transformation(s) occurring at higher temperatures is not known, although it is speculated that extensive removal of surface hydroxyl groups is essential to avoid poisoning the active sites. The heterogeneity of the Phillips' catalyst, and dispersed metal oxides in general, makes it difficult to study the activation process at a molecular level. We hypothesize that the active sites are embedded in metallasiloxane rings, whose size (and strain) depend on thermal treatment. To investigate this hypothesis, we prepared uniform grafted chromate sites by a molecular route.

## Grafting CrO<sub>2</sub>Cl<sub>2</sub> onto silica

In order to create uniform chromate sites on silica, we started with a molecular precursor. CrO<sub>2</sub>Cl<sub>2</sub> is a volatile liquid that reacts with the surface hydroxyl groups at room temperature to release HCl(g). On fully hydroxylated silica (pretreated at 200 °C), only one equiv. HCl is liberated; no chloride-free chromate sites are formed. On highly dehydroxylated silica (pretreated at 800 °C), ca. 30% chromate sites are formed, presumably by opening strained siloxane rings (Scheme 2).

Scheme 2. Proposed reactions of CrO<sub>2</sub>Cl<sub>2</sub> with hydroxyl groups associated on unstrained silica surface (top) and on strained silica surface (bottom).

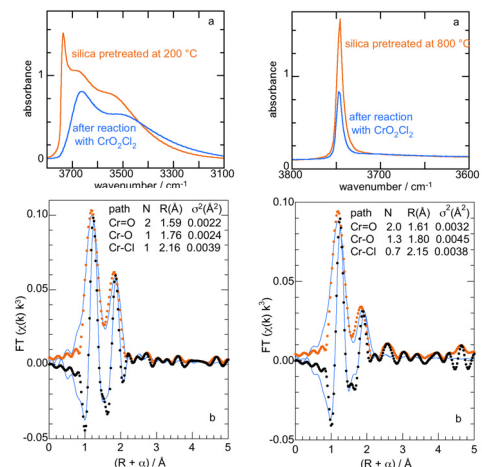
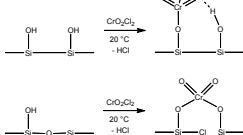
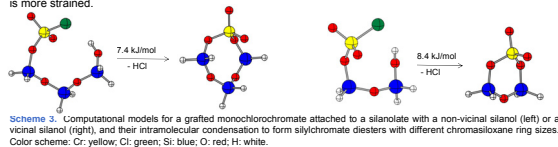


Figure 1. (a) Transmission IR spectrum in the O-H stretching region, for a mesoporous silica (Sylpop 952) after evacuation (10<sup>-4</sup> Torr) for 4 hr at 200 °C, and after reaction with excess CrO<sub>2</sub>Cl<sub>2</sub> (b) Cr K-edge EXAFS of the CrO<sub>2</sub>Cl<sub>2</sub>-modified silica, showing curve-fit to a single-site model of a monochlorochromate monosilyl ester, (eSiO)CrO<sub>2</sub>Cl. Figure 2. (a) Transmission IR spectrum in the O-H stretching region, for a mesoporous silica (Sylpop 952) after evacuation (10<sup>-4</sup> Torr) for 4 hr at 800 °C, and after reaction with excess CrO<sub>2</sub>Cl<sub>2</sub> (b) Cr K-edge EXAFS of the CrO<sub>2</sub>Cl<sub>2</sub>-modified silica, showing curve-fit to a two-site model consisting of 70% monochlorochromate monosilyl ester, (eSiO)CrO<sub>2</sub>Cl, and 30% silylchromate diester, (eSiO)<sub>2</sub>CrO<sub>2</sub>.

Neither of these materials shows any ethylene polymerization activity below 200 °C.

## Transformation to uniform chromate sites

Mild treatment of the grafted chlorochromate sites at 200 °C results in the elimination of chloride from the coordination sphere of chromium, and the concomitant formation of silylchromate diesters, Figures 3-4. The reactions were modeled with polyoxosilanes terminated with H and OH to represent the silica surface, Scheme 3. Geometry optimizations and energy calculations for DFT models were performed with Gaussian03, using the hybrid exchange functional B3LYP. The Gaussian basis set LANL2DZ was used for Cr, and the basis set 6-311+G(2d,p) basis set for all other elements. The calculations show the smaller ring is more strained.



Scheme 3. Computational models for a grafted monochlorochromate attached to a silanolate with a non-vicinal silanol (left) or a vicinal silanol (right), and their intramolecular condensation to form silylchromate diesters with different chromasiloxane ring sizes. Color scheme: Cr: yellow; Cl: green; Si: blue; O: red; H: white.

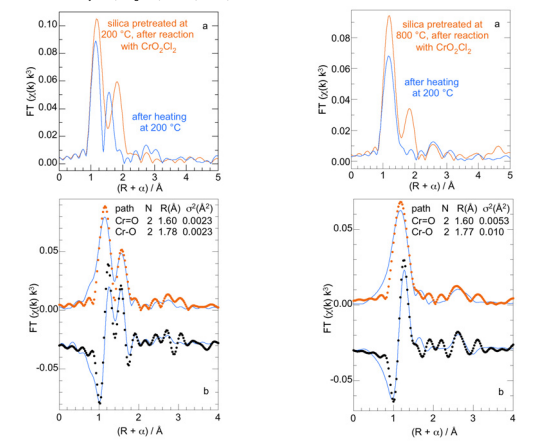
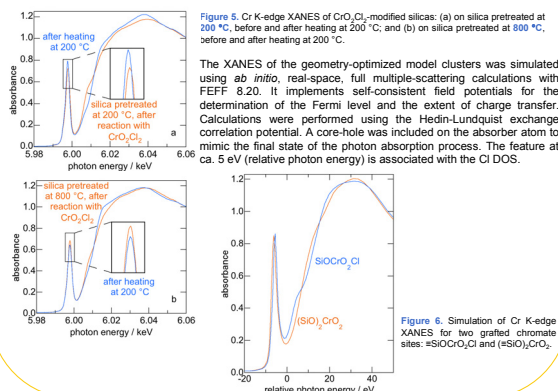


Figure 3. Cr K-edge EXAFS of CrO<sub>2</sub>Cl<sub>2</sub>-modified silica (pretreated at 200 °C): (a) before and after heating at 200 °C; and (b) curvefit of the post-thermolysis spectrum to a single-site model of a silylchromate diester, (eSiO)<sub>2</sub>CrO<sub>2</sub>.

The chromates made on silica pretreated at 200 °C are inactive, while the chromates made on silica pretreated at 800 °C initiate ethylene polymerization spontaneously. Neither the IR nor the EXAFS provide information about the chromasiloxane ring size.

## Cr K-edge XANES

The XANES region contains angular information as well as features dependent on the nature of the ligands. A shoulder superimposed on the edge at 6.01 keV disappears upon thermolysis. The intensity of the pre-edge feature, which is correlated with tetrahedrality, increases for chromate sites on silica pretreated at 200 °C, but decreases for chromate sites on silica pretreated at 800 °C. Figure 5.



The XANES of the geometry-optimized model clusters was simulated using *ab initio*, real-space, full multiple-scattering calculations with FEFF 8.20. It implements self-consistent field potentials for the determination of the Fermi level and the extent of charge transfer. Calculations were performed using the Hedin-Lundqvist exchange correlation potential. A core-hole was included on the absorber atom to mimic the final state of the photon absorption process. The feature at ca. 5 eV (relative photon energy) is associated with the Cl DOS.

Figure 5. Cr K-edge XANES of CrO<sub>2</sub>Cl<sub>2</sub>-modified silica: (a) on silica pretreated at 200 °C, before and after heating at 200 °C; and (b) on silica pretreated at 800 °C, before and after heating at 200 °C.

Figure 6. Simulation of Cr K-edge XANES for two grafted chromate sites: eSiO<sub>2</sub>CrO<sub>2</sub>Cl and (eSiO)<sub>2</sub>CrO<sub>2</sub>.

## XANES simulation of ring size effect

Differences in the simulated XANES for chromates in two chromasiloxane rings (CrSi<sub>2</sub>O<sub>6</sub> and CrSi<sub>3</sub>O<sub>7</sub>) resemble differences observed in the XANES for chromates on silicas pretreated at 200 and 800 °C, Figure 7. The origin of the differences lies in the Si 3d-DOS, Figure 8.

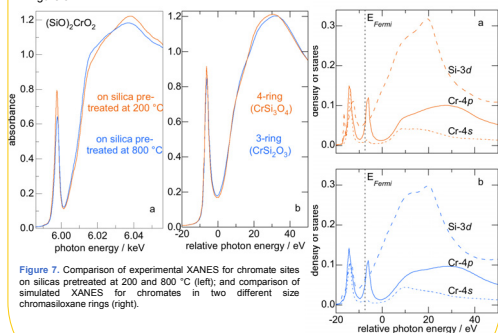


Figure 7. Comparison of experimental XANES for chromate sites on silicas pretreated at 200 and 800 °C (left), and comparison of simulated XANES for chromates in two different size chromasiloxane rings (right).

Figure 8. DOS contributing to the simulated XANES for (a) unstrained chromasiloxane 4-ring; and (b) strained chromasiloxane 3-ring.

## DR-UV-visible spectroscopy

The electronic consequences of ring strain in chromasiloxane rings should be apparent in their electronic spectra. Diffuse reflectance spectra were recorded for CrO<sub>2</sub>Cl<sub>2</sub>-modified silicas before and after thermolysis at 200 °C, Figures 9-10. The low-lying excited states of the closed-shell models were calculated using time-dependent density functional theory (TD-DFT). Models were created with F rather than H termination, Scheme 4, to reproduce the acidity of the silica surface correctly. Vertical excitation energies were computed for the first 50 singlet and triplet excited states for each model. A Lorentzian function with a FWHM of 40 nm was used to simulate a curve for each calculated electronic transition. Peak intensities for singlet-singlet transitions were weighted by their calculated oscillator frequencies. For singlet-triplet transitions, the intensities are arbitrary.

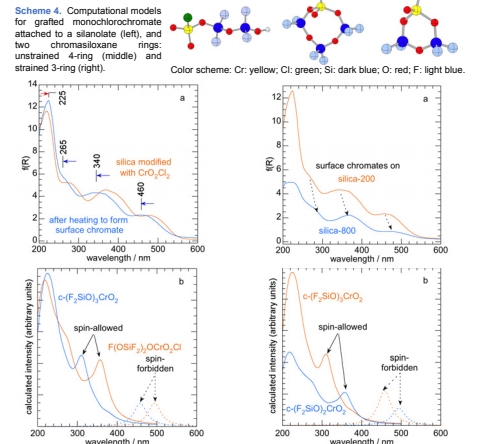


Figure 9. (a) DR-UV-vis spectra of silica pretreated at 200 °C and modified with CrO<sub>2</sub>Cl<sub>2</sub> at room temperature, followed by thermolysis at 200 °C; and (b) calculated electronic spectra for chromate site monosilyl monosilyl ester and strained chromasiloxane 3-ring, including lowest energy singlet-triplet transitions at 400-500 nm.

Both UV-vis and XANES simulations correctly predict the spectral dependence on the silica pretreatment temperature via a chromasiloxane ring size effect.

## Acknowledgements

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