

# Synthesis of Chromates in Chromasiloxane Ring Structures as Active Site Models for the Phillips' Catalyst

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## Introduction

The Phillips' catalyst, Cr/SiO<sub>2</sub>, was discovered more than 50 years ago, yet still ranks as one of the most mysterious heterogeneous catalysts. It is used, to this day, in about 40 % of the world's annual production of polyethylene [1]. The active site forms spontaneously in situ, without addition of cocatalyst or activator, upon contact between the precursor chromate sites and ethylene. The onset of polymerization is preceded by a pronounced induction period, during which Cr(VI) is reduced and one or more Cr-C bonds are formed. The nature of the initiation process has been widely-debated and experimental evidence is scarce, not the least because well-defined homogeneous models for the self-activating chromate sites have yet to be discovered. The fraction of active sites in the heterogeneous catalyst is low, typically ca. 1 %, making the interpretation of spectroscopic studies challenging. We aim to understand the activation of the Phillips catalyst by synthesizing well-defined chromate sites on silica, in order to correlate their structures with their reactivity.

## Materials and Methods

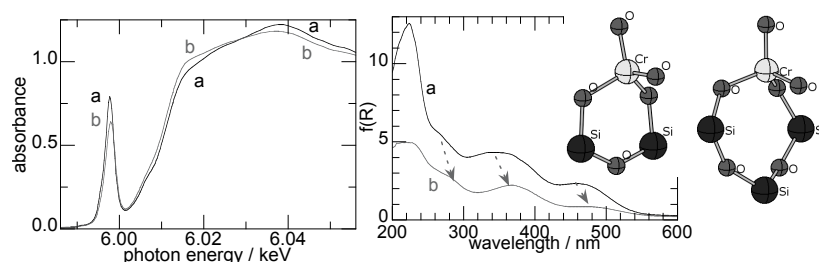
CrO<sub>2</sub>Cl<sub>2</sub>-modified silicas were prepared by grafting CrO<sub>2</sub>Cl<sub>2</sub> vapor under reduced pressure at room temperature onto dehydrated and partially dehydroxylated Sylopol 952 to yield an orange powder [2]. After evacuation of volatiles, the modified silicas were heated at 200 °C under dynamic vacuum for a minimum of two hours, to effect the quantitative transformation of grafted  $\equiv\text{SiOCrO}_2\text{Cl}$  sites to  $(\equiv\text{SiO})_2\text{CrO}_2$ . A standard Phillips catalyst was prepared by stirring aqueous CrO<sub>3</sub> with Sylopol 952 until the water evaporated, giving an orange powder. This material was heated slowly to 800 °C, then calcined at 800 °C in O<sub>2</sub> for 4 hours. All spectra were recorded until strictly anaerobic conditions. Ethylene polymerization was tested in an isothermal batch reactor, without addition of any activator or cocatalyst.

Geometry optimizations, reaction enthalpies and frequency calculations for model clusters were performed using the DFT implementation within Gaussian03 and the hybrid exchange functional B3LYP. The basis set LANL2DZ was used for Cr, while the basis set 6-311+G(2d,p) was used for all other elements. Low-lying excited states and UV-vis spectra were calculated with time-dependent density functional theory (TD-DFT). To simulate the XANES of model clusters, *ab initio* real-space, full multiple-scattering calculations were performed using FEFF 8.20.

## Results and Discussion

The reaction of chromyl chloride with dehydrated silica results in the formation of grafted  $\equiv\text{SiOCrO}_2\text{Cl}$  sites and the liberation of HCl [2]. Transformation of the  $\equiv\text{SiOCrO}_2\text{Cl}$  sites to chromates,  $(\equiv\text{SiO})_2\text{CrO}_2$ , takes place upon mild heating (200 °C). The loss of chloride

from the coordination sphere of Cr was verified by elemental analysis, the disappearance of a prominent peak due to chloride in the Cr K-edge XANES, and modification of the EXAFS. The chromate formed on silica pretreated at 200 °C was unable to initiate ethylene polymerization, while the chromate formed on silica pretreated at 800 °C showed the ethylene uptake profile (induction period followed by accelerating activation) typical of the Phillips catalyst [3]. Small differences in the IR, XANES and DRUV-vis spectra, Figure 1, are consistent with chromates embedded in siloxane rings of different sizes, based on a comparison of calculated spectra for simple chromasiloxane ring models. We conclude that when the support is pretreated at 200 °C, predominantly low-strain 8-membered chromasiloxane rings are formed, while high-strain 6-membered chromasiloxane rings are present when the support is pretreated at 800 °C. The role of ring strain in lowering the barrier for insertion of ethylene in the active site has been discussed. [4]



**Figure 1.** Comparison of Cr K-edge XANES (left), and DRUV-vis (right), for chromates on silica pretreated at (a) 200 °C; and (b) 800 °C. DFT models for 6- and 8-membered chromasiloxane rings used to simulate the spectra are shown.

## Significance

The need for high temperature activation of the Phillips' catalyst is usually attributed to a poisoning effect of surface hydroxyls. However, model molecular chromate compounds (e.g., with silsesquioxane ligands) are unable to initiate polymerization of ethylene, despite the absence of silanols. The recognition that isolated sites on supported metal oxides are metallasiloxanes suggests that ring size differences may influence reactivity and contribute to heterogeneity. Our non-aqueous grafting approach allows us to prepare supported chromates with high site uniformity, facilitating a detailed correlation of spectroscopic properties and computational analysis of structures.

## References

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