A Molecular Approach to Well-defined Metal Sites Supported on Oxides with Oxidation State and Nuclearity Control

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Abstract: A molecular understanding of the catalytically active site is essential to rationally develop metal-containing heterogeneous catalysts. The controlled grafting of molecular precursors on pre-treated supports, often referred to as surface organometallic chemistry, is an approach to prepare well-defined heterogeneous catalysts with complex organic functionalities. However, many heterogeneous catalysts do not contain organic ligands coordinated to their active sites. To model such sites, the principles of surface organometallic chemistry therefore have to be adapted. Here, we describe a method, which provides access to molecularly-defined metal sites supported on oxides, which do not contain organic functionalities and are uniform in oxidation state and nuclearity. By consecutive grafting of suitable molecular precursors and controlled thermal treatment, we prepared and characterized well-defined dinuclear Cr(II) and Cr(III) species and mononuclear Cr(III) species supported on silica. We also investigated the polymerization activity of these materials in view of the well-known ethylene polymerization catalyst based on CrO_x/SiO_2, the so-called Phillips catalyst. This study led to new insights on the catalytically active sites in ethylene polymerization, which are based on Cr(III), not Cr(II).

Keywords: Chromium · Ethylene polymerization · Molecular approach · Oxide support · Surface organometallic chemistry

1. Introduction

Heterogeneous catalysts are central to chemical industry. Over 90% of industrial chemical processes use heterogeneous catalysts.[1] But the search for more efficient, more selective and more stable catalysts still remains a challenge. It is limited by the lack of understanding of the active site in heterogeneous catalysts, which leads to their development by mostly empirical approaches. Traditional synthetic methods to heterogeneous catalysts, such as impregnation and calcination (thermal treatment under air or O_2), are highly unselective and lead to a mixture of many different sites. The main challenge in determining the structure of the active site in a heterogeneous catalyst is hence the complex surface chemistry associated with the presence of various types of sites, of which only a small fraction is catalytically active. Spectroscopic information on these catalysts relates to an average of all different types of sites and therefore corresponds to mainly inactive sites.

Considerable efforts have been undertaken to shed light on active species in heterogeneous catalysts. In the last 30–40 years a molecular approach has emerged, referred to as surface organometallic chemistry (SOMC).[2] SOMC combines molecular tools and controlled surface functionalization to construct well-defined active sites on oxide supports. Usually, molecular precursors react with an oxide support to give organometallic surface species that have defined local environments. This approach enables the design of heterogeneous catalysts based on molecular insights, an approach commonly reserved for homogeneous catalyst development.

To limit the interaction between individual grafted metal sites on the surface, the reactivity of the supports has to be controlled. In case of silica, the surface consists of siloxane bridges and different kinds of silanol groups (isolated, vicinal and geminal) (Fig. 1a).[3] Their concentrations and types can be controlled by pre-treat-ing the material at elevated temperatures. When heated, silanols condense to give siloxane bridges and water, a process called dehydroxylation. A treatment at 700 °C leads to mainly isolated silanols with only *ca.* 0.8 OH groups per nm^2, which effectively leads to site-isolation. A transition-metal complex can then be reacted with the partially dehydroxylated surface to generate well-defined surface species, which can be characterized using spectroscopic techniques. Fully characterized surface complexes have been achieved for a wide range of transition-metal complexes.[2] For example, considerable effort is put in the study and characterization of supported alkylidene complexes, in view of their reactivity in olefin metathesis (Fig. 1b).[4] This has led to the development of catalysts with very high activity and stability, in some cases surpassing their homogeneous analogues.[5] SOMC is thus a powerful approach for molecularly-defined supported structures including complex molecular functionalities. Traditional SOMC cannot be used, though, to model the sites of many heterogeneous catalysts, which are based on supported metal sites that do not contain organic ligands (Fig. 1c). For example, industrial heterogeneous metathesis catalysts are actually Re_2O_7 supported on Al_2O_3,[6] or MoO_3 or WO_3 supported on SiO_2 or Al_2O_3.[7]

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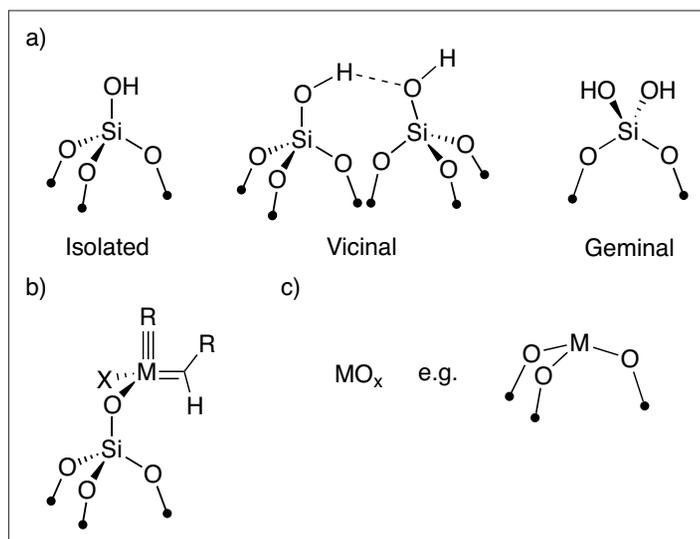Tel.: +41 44 633 4319
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Fig. 1. a) Types of silanols on the surface of silica: isolated, vicinal and geminal. b) Supported alkylidene complex. c) Supported metal sites without organic ligands.

A method that can generate oxide materials with no organic ligands has been developed by Tilley and coworkers and is referred to as the 'thermolytic molecular precursor' (TMP) approach.[8] Oxygen-rich metal complexes, such as $L_nM[OSi(O^tBu)_3]_m$[9] or $L_nM[O_2P(O^tBu)_2]_m$[10] (L_n = *e.g.* alkoxide, amide or alkyl), are converted at T < 473 K in O_2 to 3D networks of oxide materials *via* release of isobutene and water. The obtained metal-silicates do not contain organic ligands, but high-valent metal centers since the final step corresponds to a calcination.

In many large-scale industrial applications low-valent metal sites are operative, though. CrO_3 supported on SiO_2, for example, the so-called Phillips – ethylene polymerization – catalyst is responsible for *ca.* 50% of the world production of high-density polyethylene and is based on catalytically active Cr sites that are in a reduced state.[11] Cr(II) is usually proposed to polymerize ethylene, but this has remained highly controversial. To gain a molecular understanding of the active sites of catalysts such as the Phillips catalyst, a method is needed for the preparation of low-valent metal sites supported on oxides without coordination of organic ligands. Here, we show that the concepts of the TMP approach and SOMC can be combined and adapted to prepare low-valent Cr/silica materials in defined (low) oxidation state and nuclearity.[12]

2. Results and Discussion

We synthesized a dinuclear Cr(II) siloxide complex, $[Cr(OSi(O^tBu)_3)_2]_2$ (**1**), which was characterized using standard molecular spectroscopic techniques (NMR, X-ray crystallography) and X-ray absorption spectroscopy (XAS).[12a] **1** reacts with partially dehydroxylated silica, $SiO_{2-(700)}$, in benzene to give a supported Cr

material. Elemental analysis (0.31 mmol Cr g⁻¹; 18 C per Cr) combined with the stoichiometry of the reaction (formation of 0.16 mmol SiOH g⁻¹) indicates that the Cr surface species, $[(\equiv SiO)Cr_2(OSi(O^tBu)_3)_3]$, retains the dinuclear structure upon grafting. Further treatment at 400 °C under high-vacuum (10⁻⁵ mbar) leads to a full removal of the organic ligands and formation of the dinuclear Cr(II) silicate material, **2** (Scheme 1). To elucidate the structure of $[(\equiv SiO)Cr_2(OSi(O^tBu)_3)_3]$ and **2** on a molecular level, these hetereogeneous materials were characterized using a combination of various spectroscopic techniques and the resulting spectra were compared to the spectroscopic signatures of the molecular model **1**. Infrared spectroscopy confirms the presence of siloxide ligands on the grafted complex $[(\equiv SiO)Cr_2(OSi(O^tBu)_3)_3]$ as evidenced by the presence of C–H vibrational bands (Fig. 2a). In the IR spectrum of **2** no remaining C–H bands are

observed, consistent with the formation of Cr sites without additional organic ligands. UV-Vis spectroscopy of **1**, $[(\equiv SiO)Cr_2(OSi(O^tBu)_3)_3]$ and **2** is consistent with the conservation of the Cr(II) oxidation state throughout the two synthetic steps. The Cr K-edge XANES (X-ray absorption near edge spectroscopy) signatures of **1**, $[(\equiv SiO)Cr_2(OSi(O^tBu)_3)_3]$ and **2** display nearly identical edge energy, consistent with the retention of the +2 oxidation state (Fig. 2b). The analysis of the scattering paths accounting for the EXAFS (extended X-ray absorption fine structure) features is consistent with the presence of isolated dinuclear Cr species throughout the process. These spectroscopic results taken together show that **2** can be described as dinuclear Cr(II) silicates coordinating no organic ligands. Note however that EPR indicates the presence of a small amount of Cr(III) species.

Compound **1** was selectively oxidized using N_2O to a dimeric Cr(III) complex (**3**), which could be crystallized. Similarly, exposure of silica-supported dinuclear Cr(II) to N_2O yielded well-defined dinuclear Cr(III) species (**4**) as evidenced by detailed spectroscopy on molecular models and surface species (IR, UV-Vis, XANES, EXAFS and EPR) (Scheme 1 and Fig. 2b).

This approach, providing low-valent Cr silicate materials with no organic ligands, can also be employed for the preparation of mononuclear Cr(III) materials using $Cr(OSi(O^tBu)_3)_3(THF)_2$ (**5**) as the starting molecular precursor (Scheme 2).[12b] Using the same spectroscopic tools (elemental analysis, IR, UV-Vis, XANES, EXAFS and EPR), we showed that mononuclear Cr(III) silicates were obtained. The adsorption of CO, a typical probe molecule used to structurally characterize heterogeneous
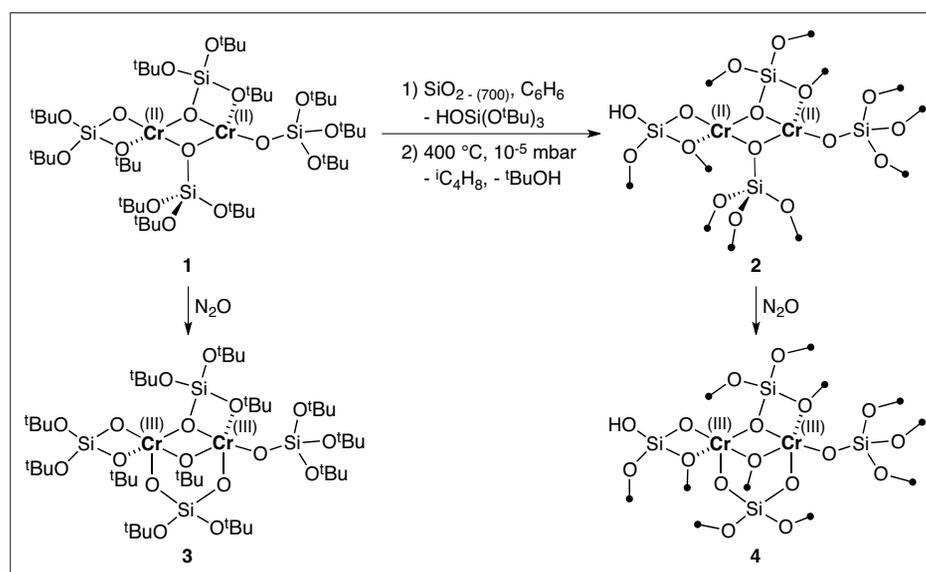
Scheme 1. $[Cr(OSi(O^tBu)_3)_2]_2$ (**1**) is reacted with $SiO_{2-(700)}$ and then thermally treated to give a dinuclear Cr(II) species supported on silica (**2**). **1** is oxidized with N_2O to a dinuclear Cr(III) siloxide complex (**3**) in analogy to their heterogeneous counterparts **2** and **4**.
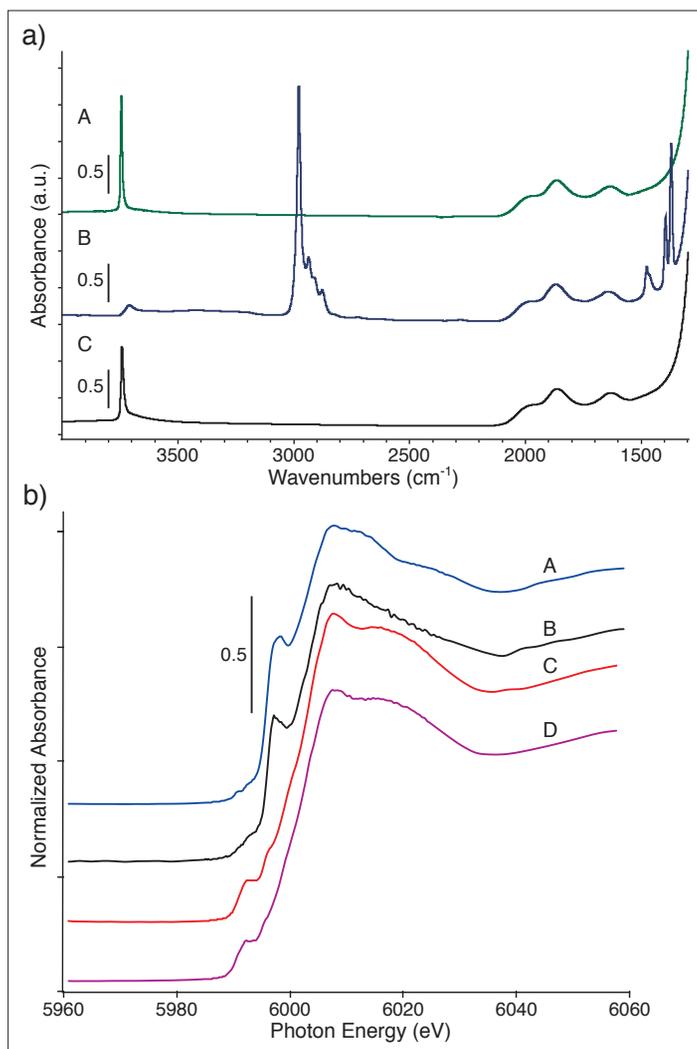
Fig. 2. a) Infrared spectra of SiO$_{2-(700)}$ (A), the grafted species [(≡SiO)Cr$_2$(OSi(O^{t}Bu)$_3$)$_3$] (B) and the thermally treated material **2** (C). b) Cr K-edge XANES spectra of molecular and supported dinuclear Cr(II): **1** (A) and **2** (B) and molecular and supported dinuclear Cr(III): **3** (C) and **4** (D).

Cr(III) on silica displays similar high activity in ethylene polymerization as the silica-supported dinuclear Cr(III) material **4**. Poisoning studies with 4-methylpyridine showed that only 60% of the Cr sites in **6** are active, which is in agreement with the presence of two different types of Cr(III) sites. DFT computation suggests that only the tricoordinated Cr(III) sites (**6a**) are active in ethylene polymerization, while Cr sites that coordinate an additional siloxane bridge (**6b**) are inactive.

3. Conclusion

We prepared well-defined dinuclear Cr(II) and Cr(III) supported on silica and well-defined mononuclear Cr(III) on silica using a molecular approach, which includes the grafting of molecular precursors and a controlled thermal treatment. A combination of advanced spectroscopic techniques (elemental analysis, IR, UV-Vis, XANES, EXAFS, EPR and the adsorption of probe molecules) and DFT computation allowed the characterization of the Cr oxidation state and local environment on a molecular level. In view of the industrial ethylene polymerization catalyst (Phillips), we investigated the ethylene polymerization activity of these well-defined Cr(II) and Cr(III) silicates. While Cr(III) polymerizes ethylene with a high activity, Cr(II) does not, in contrast to what is often proposed for the active site of the Phillips catalyst.

Our approach can thus be used for the preparation of well-defined supported metal sites in uniform local environment,

materials,[13] showed the presence of two blue shifted CO bands in the corresponding IR spectrum at 2202 and 2188 cm^{-1}. We confirmed by labeling studies that these two bands correspond to CO adsorbed on two different Cr sites (and not to symmetric and antisymmetric vibrational contributions). Combined with a computational approach (DFT), it was possible to assign these two sites to a mixture of tricoordinated Cr(III) sites (**6a**) and Cr(III) sites that coordinate an additional siloxane bridge (**6b**).

The role of chromium on silica as the Phillips catalyst in industrial ethylene polymerization, prompted us to investigate the ethylene polymerization activity of our well-defined Cr silicates. Cr(II) supported on silica (**2**) was barely active in ethylene polymerization when contacted with ethylene. This was unexpected in view of literature precedents on the Phillips catalyst, which often refer to Cr(II) as the active sites in ethylene polymerization.[11d,e] It has been reported, though, that the polymerization activity of the Phillips catalyst can be increased by pretreating the material with N$_2$O.[14] Consistent with these reports, **4** turned out to be a highly active ethylene polymerization catalyst. This

suggests that Cr(III) polymerizes ethylene, while Cr(II) is inactive. Mononuclear
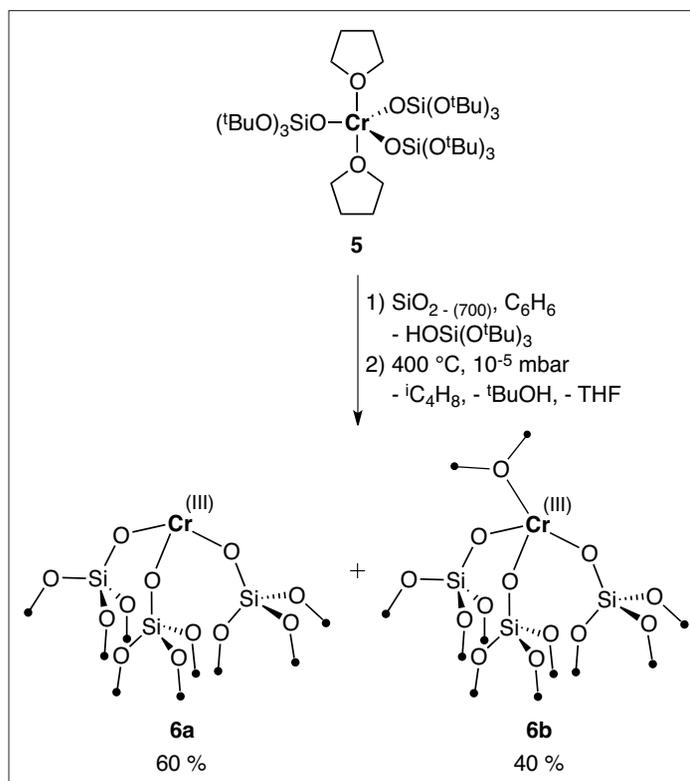
Scheme 2. Cr(OSi(O^{t}Bu)$_3$)$_3$(THF)$_2$ (**5**) is consecutively reacted with SiO$_{2-(700)}$ and thermally treated, which leads to mononuclear Cr(III) silicates, present as tricoordinated sites (**6a**) (active in ethylene polymerization) and sites that additionally coordinate a siloxane bridge (**6b**) (catalytically inactive).

nuclearity and (low) oxidation state with no organic functionalities coordinating to the metal. The uniformity and well-defined nature of these materials can enable molecular insights into heterogeneous catalysts, which are essential to further progress in their understanding and the rational design of new catalysts.

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