	Experiment title: Synthesis and Performance of Silica Immobilized Chromium Colloids	Experiment number: 26-01/784	
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Introduction

The design of stable and active heterogeneous catalysts for liquid phase processes remains a challenging task. Especially for autoxidations it seems difficult to synthesize a selective catalyst which is not prone to leaching. A chemical process of significant interest is the the synthesis of cyclohexanone ($Q=O$) from cyclohexane as it is a key chemical for the production of polyamides such as nylon-6 and nylon-6,6. It is generally recognized that the thermal reaction of CyH with O_2 proceeds *via* a complex radical chain mechanism, limiting the conversion to about 5% to prevent overoxidation of the desired products. Currently, the industrial autoxidation of CyH is often carried out in the presence of small amounts of dissolved cobalt salts. Cobalt ions are able to assist in the generation of new radicals from the cyclohexyl hydroperoxide (CyOOH) product, *via* a Haber–Weiss catalytic cycle. Chromium, however, is known to additionally catalyze the dehydration of CyOOH to $Q=O$, which results in a much more favorable product distribution. The use of Cr could thus eliminate the need for a separate decomposition step of remaining CyOOH. However, given its noxious nature, immobilization of Cr is an important prerequisite to its industrial breakthrough.

Recently, we presented a new approach for the synthesis of heterogeneous chromium catalysts [1], based on the immobilisation of Cr colloids on silica gel. Strong evidence for the heterogeneous nature of these catalysts is supplied.[1] The active materials are demonstrated to increase the yield of cyclohexanone in the autoxidation of cyclohexane. The exact nature of the chromium nano-particles and their anchoring to the support is so far unknown. In order to gain mechanistic and structural insights in the synthesis and growth of the colloids, this XAFS study was initiated.

Experimental setup

Cr^{III} eigencolloids are generated *in situ* by reducing $K_2Cr_2O_7$, slowly dosed to a reactor containing hydrazine, a strong reductant. The size of the Cr(III) eigencolloids is a function of the $K_2Cr_2O_7$ dosing rate and concentration.[2] The colloids are subsequently precipitated onto a silica support in a chromatography column (Figure 1). As it is known that polyvalent ions can induce flocculation and facilitate deposition in a colloidal system and that sulphate ions can influence the Cr^{III} hydrolysis, $CaSO_4$ was premixed with the dry silica support.

The synthesis is carried out in a column precipitation chromatographic system, characterized by a high collector-particle radius and superficial velocity, in combination with a column flow reversal cycle, to achieve a homogeneous distribution of chromium. After chromium deposition, the column packing is vacuum-dried to remove water and residual hydrazine.

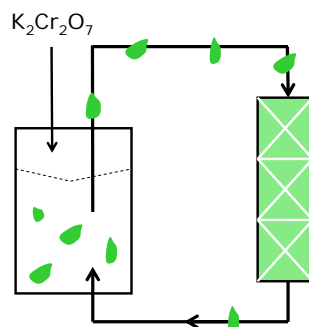


Figure 1. Immobilization of Cr(III) colloids on silica support via a column precipitation setup.

Results

➤ *Liquid samples*, withdrawn from the immobilization set-up, were measured in fluorescence mode (K-edge of Cr: XXX eV). Indeed, due to the low concentrations of Cr, and the high absorption coefficient of water at the Cr K-edge XAS measurements have to be performed in fluorescence mode. From the edge energy and the absence of a pre-edge, the oxidation state of the Cr could unambiguously be determined as being +III, consistent with previous UV-VIS and EPR measurements.[1]

Compound	formal oxidation state	K edge shift (eV)
Cr foil	0	0
Cr ₂ O ₃	III	10.5

In comparizon to purely dissolved Cr(III) ions, the spectra for the colloid solutions show additional features, most likely Cr-Cr scattering. This signal slightly increases with colloid size.

➤ *Solid samples* containing different amounts of different colloid sizes were also measured in fluorescence mode as also the silica support (SiO₂) strongly absorbs the X-rays at the Cr K-edge. An attempt to perform ‘in situ’ measurements was unsuccessful due to this strong absorption. Therefore the freshly prepared samples (at the beamline) were measured as a pellet, similar to the aged catalyst samples. The spectra obtained for all solid samples are similar to these for the colloid solutions, confirming the immobilization of colloids. Small variations could be observed between the samples, but in order to evaluate the significance and structural differences causing these changes, detailed data analysis will be necessary.

➤ *Visualisation of the catalytically active complex* was attempted by measuring catalyst pellets impregnated with hydrogen peroxide solutions. However, no changes in the catalyst spectra could be observed upon impregnation.

Preliminary results

➤ At present it can be concluded that although in situ measurements could not be realised, this XAS campaign was quite successful. Initial data analysis indicates that colloidal Cr(III) oxide could be identified both in the catalyst synthesis solutions and on the catalyst surface. Furthermore the Cr oxidation state was unambiguously confirmed and small changes between catalyst samples with different Cr loadings were observed.

References

- [1] E. Breynaert, I.Hermans, B. Lambie, G. Maes, J. Peeters, A. Maes, P. Jacobs, *Angew. Chem. Int. Ed.* **2006**, 45, 7684.
- [2] I. Hermans, E. Breynaert, H. Poelman, R. De Gryse, D. Liang, G. Van Tendeloo, A. Maes, J. Peeters, P. Jacobs, *Phys. Chem. Chem. Phys.* **2007**, 9, 5382.