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Silica-Immobilized Chromium Colloids for Cyclohexane Autoxidation**

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The selective oxidation of cyclohexane (CyH) with molecular oxygen still constitutes a major challenge for chemists.[1] The synthesis of cyclohexanone (QO) is of special interest,[2] 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, with a limit of 5% on the conversion to prevent overoxidation of the desired products.[3–5] Currently, the industrial autoxidation of CyH is often carried out in the presence of small amounts of dissolved cobalt salts.[3,4] Cobalt ions are able to assist in the generation of new radicals from the primary chain-propagation product, cyclohexyl hydroperoxide (CyOOH), via a Haber–Weiss catalytic cycle [reactions (1) and (2)].[1,3–8] This catalytic decomposition is indeed much faster than thermal initiation through a bimolecular reaction of CyOOH with CyH or QO.[9]

$$\mathrm{CyOOH} + \mathrm{Co}^{2+} \rightarrow \mathrm{CyO}^{\cdot} + \mathrm{Co}^{3+}\mathrm{OH}^{-} \tag{1}$$

$$\mathrm{CyOOH} + \mathrm{Co}^{3+}\mathrm{OH}^{-} \rightarrow \mathrm{CyOO}^{\cdot} + \mathrm{H_2O} + \mathrm{Co}^{2+} \tag{2}$$

Chromium, however, is known to catalyze additionally the dehydration of CyOOH to QO, which results in a much more favorable product distribution.[3,4] Our recently developed insights into the mechanism of CyH autoxidation[10–12] prompted us to look at the opportunities for using Cr as a catalyst. The earlier mechanistic view,[3–5] which assumes that QO is responsible for the majority of by-products, is at odds with our results that stem from a combined experimental and theoretical approach to the subject.[10,11]

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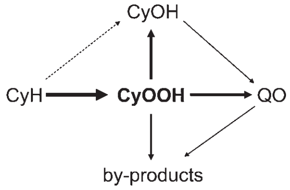
On the one hand, QO was found to be barely more reactive than CyH, which indicates that its overoxidation can only account for a small fraction of the by-products. On the other hand, CyOOH was identified as being very reactive towards the chain-carrying peroxyl radicals, on account of its weakly bonded α-H atom.[13] This hitherto overlooked, though very fast, α-H abstraction results in the formation of QO, cyclohexanol (CyOH), and the majority of the by-products (Scheme 1).[10,11] It can therefore be rationalized that the catalytic dehydration of CyOOH to QO can boost the selectivity of the reaction. Equally important is that the use of Cr could eliminate the need for a separate decomposition step of CyOOH. However, given its noxious nature, immobilization of Cr is an important prerequisite to its industrial breakthrough.



Scheme 1. Formation of QO, CyOH, and by-products via fast propagation reactions in the CyH autoxidation.[10,11]

Retention of (isomorphically) substituted Cr in Cr/$AlPO_4$-*n* under autoxidation conditions was difficult.[1,14] Despite several attempts, the heterogeneous nature of the active site in Cr/$AlPO_4$-*n* or Cr/silicalite-like materials could not always be established unambiguously. Indeed, rigorous testing for the heterogeneity of so-called heterogeneous Cr catalysts is crucial, as many of these materials slowly release Cr under oxidizing conditions.[14] For the conventional Cr/$AlPO_4$-5, experimental evidence was found that the Cr is not incorporated in the framework, but rather is present as octahedral Cr^{III} ions at the surface of the zeolite crystal.[15] However, it cannot be excluded that changing the synthesis conditions[16,17] might result in stable, supported, Cr-based autoxidation catalysts. The performance of recently discovered three-dimensional mesoporous chromium oxide in autoxidation reactions remains to be examined.[18] Alternatively, Cr immobilization is possible by covalent anchoring of its complexes to a solid support.[19] Although these materials are more resistant to leaching, labile C–H bonds in the organic spacer can be slowly oxidized under the severe autoxidation conditions.

Herein, a new approach to the immobilization of Cr is presented, aimed at the design of stable autoxidation catalysts. Use is made of a novel column precipitation chromatographic (CPC) technique, which was recently developed to quantify oxidic eigencolloids of Tc^{IV}.[20] Cr^{III} eigencolloids, generated in situ by reduction of dosed $K_2Cr_2O_7$ with hydrazine, were precipitated onto a silica support in a chromatography column. The deposition of colloids flowing over a support column is interpreted mechanistically as a combination of coagulation of the colloids and heterocoagulation and heteroadagulation onto the packed bed.[20] As it is known that polyvalent ions can induce flocculation and facilitated deposition in a colloidal system,[20] and that sulfate ions can influence the Cr^{III} hydrolysis,[21] $CaSO_4$ was premixed with the dry silica support. The synthesis was carried out in a CPC 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 was vacuum-dried to remove water and residual hydrazine.

Dynamic light scattering (DLS) analysis of a liquid sample from the recirculation reactor reveals the presence of 6-nm particles that are reasonably stable in time (Figure 1). These nanosized Cr colloids are fixed on the silica gel by the CPC technique, and they remain invisible by SEM. It should be emphasized that our synthesis procedure yields nanoparticles that are much smaller than those commonly reported.[21,22]

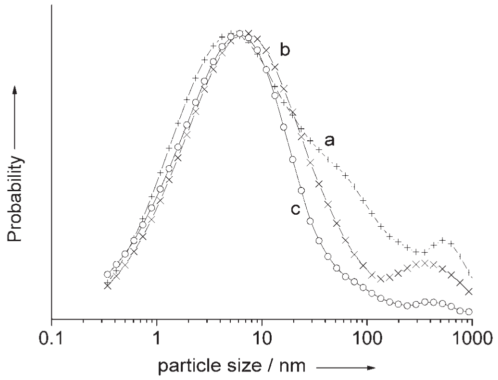


Figure 1. Particle size distribution as determined by DLS. Liquid sample withdrawn from the recirculation reactor without passing over the CPC column, measured after a) 4, b) 8, and c) 12 days (initially filtered over a 0.22-μm filter to remove dust particles).

The UV/Vis spectra of the green aqueous phase (Figure 2) are characteristic of octahedral Cr^{3+} ions.[23] The Cr speciation in solution does not change significantly over the range of free chromium concentrations used (10–40 mM).[24] The average extinction coefficients of (23 ± 5) and $(17 \pm 5)\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ at 422

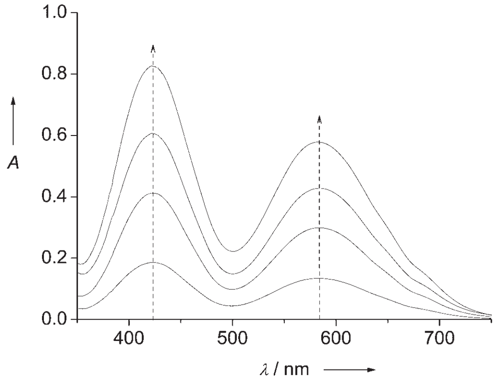


Figure 2. UV/Vis spectra of the solution phase depending on the amount of $K_2Cr_2O_7$ added to the CPC system (0.25, 0.50, 0.75, 1.5 mmol).

and 582 nm, respectively,[24] are in good agreement with reported values for (oligomeric) chromium species.[25]

Column precipitation[20] is the dominant immobilization mechanism, as the achieved loadings of up to 13 mg g^{-1} are higher than the maximal loading one could possibly obtain with ion exchange.[24,26] The diffuse reflectance spectra (DRS) of the dry chromium-loaded solids[24] are very similar to the liquid-phase UV/Vis spectra and also reveal the presence of octahedral Cr^{3+} species.[23]

The X-band EPR spectra of Cr-loaded silica gel and a liquid aliquot from the recirculation reactor are analogous (Figure 3 a and b). The intense and broad β signal around $g = 2$ is characteristic for Cr^{3+} ions surrounded by six oxygen ligands in an octahedral coordination.[23,28] This finding, in combination with the UV/Vis and DRS information, indicates that the chromium nanoparticles identified in solution are immobilized on the silica support. No change in the surface area upon Cr loading was observed with N_2 adsorption.[29] X-ray diffraction showed no sign of a crystalline chromium oxide phase, and small-angle X-ray scattering (SAXS) was unable to characterize nanoparticles because of the structure of the silica support (broad peak below $2\theta = 8°$).[24]

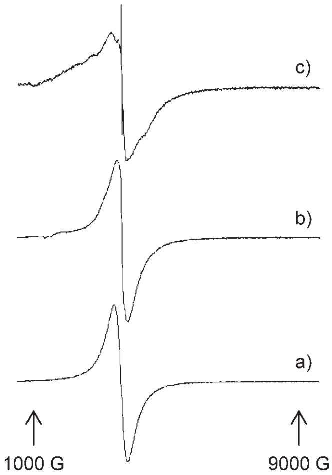


Figure 3. EPR spectra of a) a liquid sample withdrawn from the CPC reactor, b) Cr-loaded silica gel (1.60 mg Cr per g gel), and c) sample (b) after an autoxidation reaction at 403 K. All spectra were recorded at 110 K (9.588 GHz).

The catalytic performance of the new Cr-on-silica catalyst was evaluated in the autoxidation of CyH with 30 ppm of Cr, at a temperature of 403 K where thermal autoxidation is very slow. It was found that the new material (13.0 mg Cr g^{-1}) is slightly more active than homogeneous [Cr(acac)$_3$] (acac = acetylacetonate; $\Delta p(O_2)$ after 300 min equals 1.6 and 1.4 MPa, respectively), which should be ascribed to an ideal dispersion of Cr colloids with a high surface area. The turnover frequency (TOF) of the immobilized Cr species was fairly independent of their loading. The CyOOH concentration remained very low throughout the reaction,[24] compared to that in the pure autoxidation reaction at the same temperature (Table 1).[11,24] This low concentration is the result of the catalytic dissociation and catalytic dehydration of CyOOH,[30] also explaining the rather remarkable linear O_2 consumption (Figure 5 a). Normally the CyOOH concentration initially increases almost exponentially,[9,10] thus causing a large increase in the rate of initiation, which results in an exponential increase in the O_2 consumption. The high QO yield relative to that of by-products compensates the slightly higher by-product yield that results from overoxidation of QO.

Table 1: Product yield at 3 % conversion during the autoxidation of CyH at 403 K.

Experiment	QO	CyOH	CyOOH	By-products
pure[a]	23.5	31.0	40.0	5.5
new Cr catalyst[b]	60.0	24.3	1.2	14.5
Co catalyst[c]	37.5	50.5	1.5	10.5

[a] Pure CyH autoxidation, reaction time = 1150 min. [b] Cr-catalyzed autoxidation (30 ppm Cr as 13.0 mg Cr per g silica gel), reaction time = 150 min. [c] Co-catalyzed autoxidation (homogeneous reaction with 5 ppm Co^{II} octoate (2-ethylhexanoate), ICN Pharmaceuticals), reaction time = 150 min.

Immediately after a catalytic run, an EPR analysis of the catalyst with 1.60 mg Cr g^{-1} reveals the presence of an additional sharp γ signal (Figure 3 c), often assigned to a single Cr^V species.[23,28] However, other studies attribute this signal to a mixed-valence trinuclear cluster of the type $Cr^{VI}OCr^{III}OCr^{VI}$ (pseudo Cr^{5+}).[31] Such in situ generated Cr^{VI} species could be the actual active sites of the catalyst. Indeed, a study of the CyOOH dehydration activity of chromium demonstrated the formation of an intermediate cyclohexyl peroxychromate ester between CyOOH and Cr^{VI}, which is able to decompose to QO.[30] When the used catalyst is stored for a few days in a desiccator, the sharp γ signal disappears, which suggests that it corresponds to a very reactive Cr species.

To evaluate the stability of the catalyst, the solid was separated at 353 K from the liquid phase after approximately 5 % conversion (reaction at 403 K), to avoid re-adsorption of potentially leached Cr species. The liquid phase was checked for Cr by electrothermal vaporization (ETV) atomic absorption spectroscopy (AAS) and the concentration was below 5 ppb for all tested samples. Important is the fact that the same amount of Cr was measured when the catalysts were stirred for the same time at the same temperature in CyH, without O_2. Meanwhile, DLS analysis of this CyH liquid revealed particles of several hundred nanometers, probably caused by abrasion and attrition of the silica powder in the batch reactor.

This finding presents strong evidence that the new Cr catalyst is chemically stable under the current process conditions, and that the very small amount of Cr detected in the liquid phase is a result of physical impact of the stirrer on the material. It is expected that these effects will be absent if the reaction is carried out in a tubular reactor. Anyway, the (remaining) activity of the supernatant at 403 K can be safely attributed to the oxidation-enhancing nature of the products. Indeed, Figure 4 illustrates that an artificial autoxidation mixture, devoid of any chromium and mimicking the supernatant composition, exhibits the same activity, thus pointing to the heterogeneous nature of the new colloid-based system.

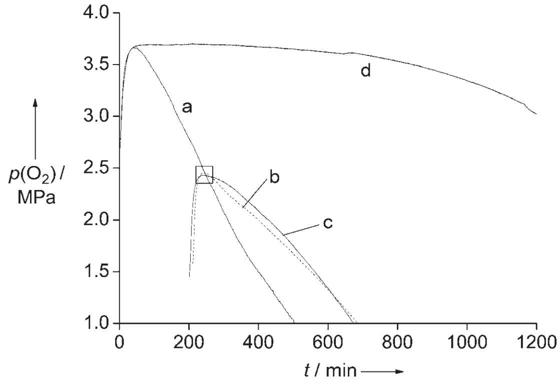


Figure 4. The activity at 403 K of a) fresh Cr catalyst (5.5 mg Cr g^{-1}), b) the hot-filtered supernatants (separated after 210 min), c) an artificial mixture containing the same amount of CyOOH (ca. 1 mM), CyOH (34 mM), QO (99 mM), and adipic acid (ca. 1 mM), and d) pure CyH autoxidation.

Probably, the stability can be attributed to the amorphous nature of the oxyhydroxide Cr colloids, which allows the accommodation of different coordination modes of Cr during a redox cycle.

As can be seen in Figure 5, the activity of the recycled catalyst is slightly lower than that of the fresh catalyst, although the oxidation remains much faster than a pure CyH autoxidation. After this initial decrease in performance, the activity is maintained during several recycles. The initial loss in activity before reaching a steady conversion points to the existence of a short transient period, the details of which are not well understood at this moment.

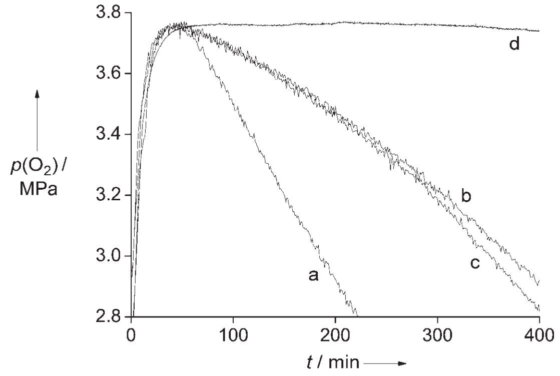


Figure 5. Comparison of the activity at 403 K of a) fresh CPC-synthesized catalyst (2.5 mg Cr g^{-1}), b) after one catalytic run, c) after four recycles, and d) the pure CyH autoxidation.

In conclusion, we have presented a new approach to the synthesis of heterogeneous chromium catalysts, based on the immobilization of Cr colloids generated in situ. The active materials are demonstrated to increase the yield of cyclohexanone in the autoxidation of cyclohexane. Strong evidence for the heterogeneous nature of the catalysis is supplied. More work is in progress to assess the nature of the support for heterogeneous chromium colloids in autoxidation catalysis, as well as that of colloids in other (liquid phase) reactions.

Experimental Section

In the CPC system, the content of a 100-mL stirred reactor was recirculated over a 25-mm-diameter column packed with silica powder (20 g) containing $CaSO_4 \cdot 2H_2O$ (10 wt %, dry premixed), at a flow rate of 20 mL min^{-1}. Silica 60 from Fluka with a particle size of 40–63 μm and a BET specific surface of 440 $m^2 g^{-1}$ was used as inert support material. A flow reversal was automatically initiated every 10 min to target a homogeneous Cr distribution over the column. After an initial equilibration of the column with the reactor volume (pH set at 4.0 ± 0.1 with HCl), the formation of chromium(III) colloid was achieved in situ by dosing the desired amount of $K_2Cr_2O_7$ at a rate of 3 μmol min^{-1} to the reducing stirred tank, which contained excess hydrazine (ratio $N_2H_2/Cr^{VI} \geq 1.3{:}1$). A synthesis pH of 4 was chosen, as PHREEQC modeling of the solution speciation indicates a mainly oligomeric nature of oversaturated Cr^{III} solutions, which favors the formation of Cr colloids.[32] The Cr content was measured by flame AAS after microwave digestion of the solid material.[33]

The autoxidation of CyH (50 mL, HPLC grade) was studied in a 100-mL stainless-steel Parr reactor, stirred at 500 rpm. The headspace was filled with O_2 at an initial room-temperature pressure of 2.75 MPa. The pressure was monitored continuously during the experiment. Products and by-products were collected in excess acetone and analyzed by GC (CP-Sil5 column, Chrompack), after silylation with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA).[24] 1-Heptanol was used as external standard to correct for sensitivity differences in the flame ionization detector.

UV/Vis, diffuse reflectance, and X-band EPR spectra were recorded on a Perkin–Elmer Lambda 12 spectrometer, a Cary 5 UV/Vis/NIR spectrophotometer, and a Bruker ESP 300E instrument with a rectangular TE104 cavity, respectively.

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[26] For example, at pH 4.68 the ion-exchange capacity (determined with $CrCl_3$) was found to be 0.024 meq g^{-1}, in good agreement with those determined for Pb^{II}, Cu^{II}, and Ni^{II} at the same pH value.[27] The pH value of 4.68 is above that of our synthesis (4.0), and more than twice that of the point of zero charge (PZC), determined to be 2.12 by potentiometric titration.

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[32] The Cr speciation in solution was modeled using PHREEQC, in combination with the Lawrence Livermore National Library (LLNL 85 2005-02-02) database; precipitation was disabled during the modeling because of the slow kinetics. http://www.geo.vu.nl/users/posv/phreeqc/index.html (PHREEQC for Windows, version 2.12.04 built using PREEQC 2.12.1-669).

[33] Powder (ca. 200 mg) was dissolved in concentrated perchloric acid (1 mL), HNO_3 (2 mL), and HCl (1 mL).