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# Catalytic activity and stability of a chromium containing silicate in liquid phase cyclohexane oxidation

Rosenira Serpa da Cruz<sup>a,b</sup>, Juliana Martins de Souza e Silva<sup>a</sup>, Ulrich Arnold<sup>a</sup>,  
Ulf Schuchardt<sup>a,\*</sup>

<sup>a</sup> *Instituto de Química, Universidade Estadual de Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil*

<sup>b</sup> *Departamento de Ciências Exatas e Tecnológicas, Universidade Estadual de Santa Cruz,  
Rodovia Jiheus-Itabuna-Km 16-45650-000 Ilhéus, BA, Brazil*

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## Abstract

A chromium containing silicate has been prepared by an acid-catalyzed sol–gel process. The material was characterized by FTIR, UV–VIS and EPR spectroscopy as well as TPR, XRD and XRF analyses. The silicate is an efficient catalyst for the oxidation of cyclohexane with *tert*-butyl hydroperoxide. Leaching studies showed that catalysis is at least in part due to traces of Cr leached into the homogeneous phase. Weakly bound Cr species can be removed by soxhlet extraction, yielding a catalyst which is remarkably leaching resistant. The catalyst can be used at least four times without detectable loss of metal. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Metallosilicates; Chromium; Cyclohexane oxidation; *Tert*-butyl hydroperoxide; Sol–gel process

## 1. Introduction

Functionalization of hydrocarbons by selective oxidation is a very useful reaction and has been studied comprehensively over the past years. Catalytic oxidation in the liquid phase is becoming more and more important, whereas traditional processes involving stoichiometric amounts of inorganic oxidants are under considerable pressure due to environmental and economic concerns [1,2]. Catalytic oxidation reactions generally involve the use of soluble salts or transition metal complexes in combination with oxidants like O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> or RO<sub>2</sub>H (R = alkyl, aryl). Despite of good activities and very often

excellent selectivities, there are several problems encountered with these catalysts, particularly catalyst separation, recovery and recycling after reaction.

The current tendency is to replace the homogeneous catalysts by their immobilized counterparts, e.g. by incorporation of transition metal ions or complexes into the framework or cavities of zeolites and related molecular sieves [3], pillared clays [4], xerogels [5] or aerogels [6], etc. However, the predominant problem associated with the use of these catalysts is metal leaching to the liquid phase [7]. A detailed leaching study on chromium containing aluminophosphate AIPO-5 was reported by Sheldon et al. [8] and showed that the catalytic activity was due to metal ions leached to the liquid phase. Extensive metal leaching was also observed using vanadium-containing VPI-5 [9], ZSM-12 [10] and MCM-41 [11] as oxidation catalysts. The future development of new heteroge-

\* Corresponding author. Tel.: +55-19-3788-3071;  
fax: +55-19-3788-3023.  
E-mail address: ulf@iqm.unicamp.br (U. Schuchardt).

neous oxidation catalysts with high stability has been discussed critically in a recent review [12].

The sol–gel technique is a suitable method for the incorporation of metal ions in silicates [13] and to attach organic functional groups [14]. This technique represents a highly controllable preparation route with inherent advantages, such as molecular-scale mixing of the components, controllable purity of the precursors, homogeneity of the sol–gel product and the use of different preparation tailoring tools [15,16].

Rogovin and Neumann [17] prepared cobalt containing xerogels by the sol–gel method and used them as heterogeneous catalysts for the side-chain oxidation of alkyl arenes with anhydrous *tert*-butyl hydroperoxide. Good yields and very high selectivities were obtained in the oxidation of secondary benzylic carbon atoms. No leaching of cobalt to the liquid phase was observed, provided that anhydrous *tert*-butyl hydroperoxide was used. Nevertheless, the use of aqueous solutions of H<sub>2</sub>O<sub>2</sub> (30%) or *tert*-butyl hydroperoxide (70%) resulted in considerable metal leaching.

Neumann and Levin-Elad [18] reported that vanadium containing xerogels are active catalysts for a variety of oxidation reactions with H<sub>2</sub>O<sub>2</sub> including epoxidation of alkenes, oxidation of secondary alcohols to ketones and the hydroxylation of phenol. Alcohols were the preferred solvents for the reactions and no leaching of vanadium to the liquid phase was observed. Klein et al. [5] reported that amorphous microporous homogeneously mixed V/Si-oxides prepared by an acid-catalyzed sol–gel process are truly heterogeneous epoxidation catalysts.

In a preliminary paper [19], we described a chromium containing xerogel, which was shown to be an active catalyst for the oxidation of cyclohexane with *tert*-butyl hydroperoxide. Here we wish to give a full account of our work, including preparation and extensive characterization of the silicate as well as studies on its catalytic potential and stability with regard to metal leaching.

## 2. Experimental

### 2.1. Synthesis and characterization of Cr–SiO<sub>2</sub>

The catalyst was prepared by an acid-catalyzed sol–gel process [20], using tetraethoxysilane Si(OEt)<sub>4</sub>

(TEOS) and chromium(III) acetylacetonate [Cr(acac)<sub>3</sub>] as precursors. A solution of 49 mmol of TEOS (Aldrich, 98%) and 1 mmol of [Cr(acac)<sub>3</sub>] (Alfa Inorganics) in 150 mmol of ethanol was placed in a 100 ml polypropylene beaker equipped with a magnetic stirring bar and 18 mmol of aqueous HCl (8 mol l<sup>-1</sup>) were added dropwise to the well stirred solution. The reaction mixture was stirred for 5 min and then allowed to stand at room temperature to remove the volatiles by slow evaporation. Gelation was complete after 5 days and the material was heated to 323 K with a heating rate of 15 K min<sup>-1</sup>. The material was kept at this temperature for 24 h and subsequently heated to 423 K at a heating rate of 15 K min<sup>-1</sup>. After 12 h at 423 K the silicate was further heated to 523 K at the same heating rate and kept at this temperature for 12 h. After cooling to room temperature, the glass was crushed and sieved (100 mesh). A modified material was prepared by 18 h soxhlet extraction of the obtained Cr–SiO<sub>2</sub> with acetonitrile followed by 4 h drying at 393 K.

The catalyst was characterized by infrared spectroscopy (FTIR), UV–VIS spectroscopy, electron paramagnetic resonance (EPR), temperature-programmed reduction (TPR), X-ray diffraction (XRD) and X-ray fluorescence (XRF). IR spectra were obtained on a Perkin Elmer 1600 instrument from KBr pellets containing 1% of the catalyst. UV–VIS spectra were recorded on a Varian Cary 5 spectrometer, using the diffuse reflectance technique. Absorptions of the pure silicate without transition metal were subtracted. EPR spectra were measured at room temperature, using a Bruker 200 D spectrometer. TPR analysis was carried out in a homebuilt instrument, using a H<sub>2</sub>/N<sub>2</sub> mixture (3 vol.% H<sub>2</sub>) at a heating rate of 10 K min<sup>-1</sup>. Powder X-ray diffraction was performed on a Shimadzu XD-3A diffractometer. Metal contents were determined by XRF on a Spectrace TX-5000 instrument, using calibration curves prepared from mixtures of SiO<sub>2</sub> and chromium acetylacetonate.

### 2.2. Catalytic cyclohexane oxidation reactions

Cyclohexane oxidation was carried out in a three-necked flask, placed in a temperature equilibrated oil bath and fitted with a reflux condenser. Typically, a mixture of 95 mmol of cyclohexane,

9.5 mmol of *tert*-butyl hydroperoxide (TBHP, 82% in cyclohexane) and 100 mg ( $2.3 \times 10^{-5}$  mol Cr) of Cr–SiO<sub>2</sub> was magnetically stirred at 348 K for 24 h. Blank reactions under the same reaction conditions without catalyst were also performed. The reaction mixture was analyzed by gas chromatography (GC), taking aliquots at different reaction times. A Hewlett Packard HP 5890 gas chromatograph equipped with an Innowax 80/100 capillary column (25 m × 0.2 mm × 0.4 μm film thickness) and a flame ionization detector (FID) was used. Product quantification was carried out using calibration curves obtained with standard solutions of cyclohexane, cyclohexanone, cyclohexanol and 4-heptanone as internal standard. Since cyclohexyl hydroperoxide (CHHP) decomposes in part during chromatographic analysis, CHHP contents were determined by decomposition with PPh<sub>3</sub> [21] and quantification of the additionally formed cyclohexanol by GC. By-products were identified by GC coupled to a HP 5979 mass selective detector (MSD). The formation of acids was investigated by esterification of the reaction mixture with methanol and identification of the products by GC-MSD. Consumption of TBHP was determined after the reaction by iodometric titration [22].

### 2.3. Leaching and recycling tests

In leaching tests, the catalyst was separated from the reaction mixture after 4 h by filtration at reaction temperature [7]. Another portion of 9.5 mmol of oxidant was added and the reaction mixture was immediately allowed to react further in the absence of the catalyst. The reaction mixture was analyzed by GC immediately after removal of the catalyst and after the total reaction time of 24 h. Furthermore, the Cr content of the catalyst was determined by XRF before the reaction and after removal of the catalyst from the reaction mixture.

Recycling tests with repeated use of Cr–SiO<sub>2</sub> in five consecutive reactions were carried out. The catalyst was removed from the reaction mixture after 24 h by filtration, washed with acetone, dried at 393 K for 6 h and subjected to the next catalytic run, using the same molar ratio substrate:oxidant:catalyst. The Cr content of the catalyst was monitored by XRF.

## 3. Results and discussion

### 3.1. Catalyst characterization

Cr–SiO<sub>2</sub> was characterized by FTIR, UV–VIS and EPR spectroscopy and by TPR, XRD and XRF analyses. Since it is known that weakly bound metal species can easily be removed from the materials by extraction with polar, coordinating solvents, Cr–SiO<sub>2</sub> was pretreated by soxhlet extraction with acetonitrile. The spectroscopic data of the thus obtained material, named as Cr–SiO<sub>2</sub><sup>ex</sup> were compared to those of the untreated catalyst.

The FTIR spectra of SiO<sub>2</sub>, Cr–SiO<sub>2</sub> and Cr–SiO<sub>2</sub><sup>ex</sup> (Fig. 1) show the typical silicate absorptions at about 1080, 790, 550 and 450 cm<sup>-1</sup>, which can be attributed to Si–O–Si bending and stretching vibrations. The absorption at 955 cm<sup>-1</sup> can be attributed to surface Si–OH vibrations and possibly superposes absorptions of Si–O–Cr bonds [23]. The intensity of this band was taken as indication of the heterogeneity in mixed oxides [24]. However, since the metal content in Cr–SiO<sub>2</sub> is low, this method is not applicable. Nevertheless, the shift of this band from 946 cm<sup>-1</sup> in the pure silicate to 955 cm<sup>-1</sup> in Cr–SiO<sub>2</sub> and Cr–SiO<sub>2</sub><sup>ex</sup> suggests that there is a contribution of Si–O–Cr bonds. Furthermore, a very weak band at 700 cm<sup>-1</sup>, observed for Cr–SO<sub>2</sub> and not for the pure silicate, can be attributed to the symmetric Si–O–Cr

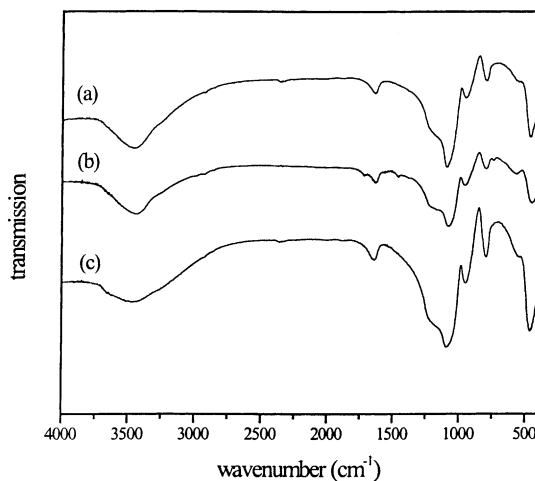


Fig. 1. IR spectra of (a) SiO<sub>2</sub>; (b) Cr–SiO<sub>2</sub>; and (c) Cr–SiO<sub>2</sub><sup>ex</sup>.

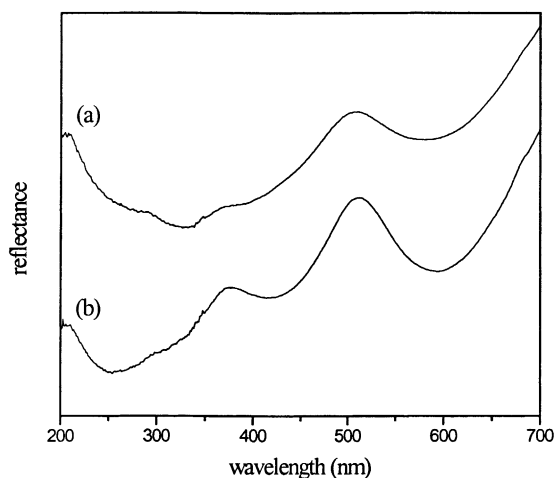


Fig. 2. UV-VIS spectra of (a) Cr-SiO<sub>2</sub>; and (b) Cr-SiO<sub>2</sub><sup>ex</sup>.

stretching vibration [25]. This band does not appear in the spectrum of Cr-SiO<sub>2</sub><sup>ex</sup>, which indicates removal of Cr species by extraction. The IR spectrum shows that the acetylacetonate ligand has been completely removed.

In the UV-VIS spectra (Fig. 2) two absorptions at about 420 and 600 nm are observed, for both, Cr-SiO<sub>2</sub> and Cr-SiO<sub>2</sub><sup>ex</sup>. These bands can be attributed to the <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub>(F) and <sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>2</sub> transitions of Cr(III) in octahedral coordination [25]. The reduced number of absorptions of Cr-SiO<sub>2</sub><sup>ex</sup> compared to Cr-SiO<sub>2</sub> at smaller wavelengths indicates removal of Cr species by extraction.

The EPR spectra of Cr-SiO<sub>2</sub> and Cr-SiO<sub>2</sub><sup>ex</sup> are compared in Fig. 3. The spectrum of Cr-SiO<sub>2</sub> with signals at *g* = 4.45, 2.07, and 1.98 shows unambiguous presence of different Cr species. However, only the signal at 1.98 is observed for Cr-SiO<sub>2</sub><sup>ex</sup> indicating the presence of only one EPR visible Cr species. Signals at *g* ≈ 2 can be assigned to Cr(III) in octahedral coordination [26,27].

TPR experiments showed no reduction peaks up to 1023 K and after calcination at 923 K under a flow of air, no X-ray diffraction pattern was observed. These results exclude the formation of a separate chromium oxide phase and suggest the formation of stable Si-O-Cr bonds and a high dispersion of Cr in the silicate matrix.

XRF analyses of the silicate before and after acetonitrile extraction showed a considerable loss of Cr

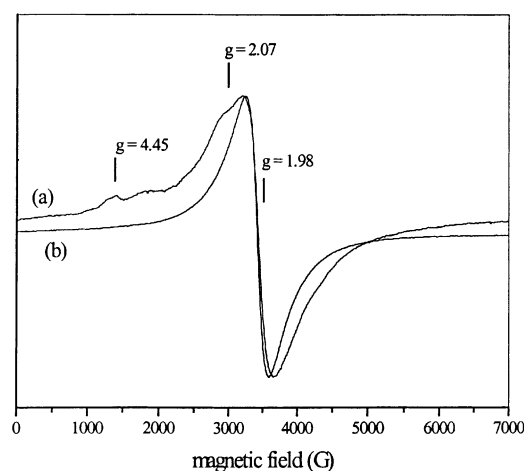


Fig. 3. EPR spectra of (a) Cr-SiO<sub>2</sub>; and (b) Cr-SiO<sub>2</sub><sup>ex</sup>.

during the extraction step. The Cr content decreases from 1.21 wt.% in the beginning to 0.75 wt.% after extraction.

### 3.2. Catalytic cyclohexane oxidation

The time dependent product distribution of the Cr-SiO<sub>2</sub>-catalyzed cyclohexane oxidation is given in Fig. 4. Blank experiments without catalyst gave only

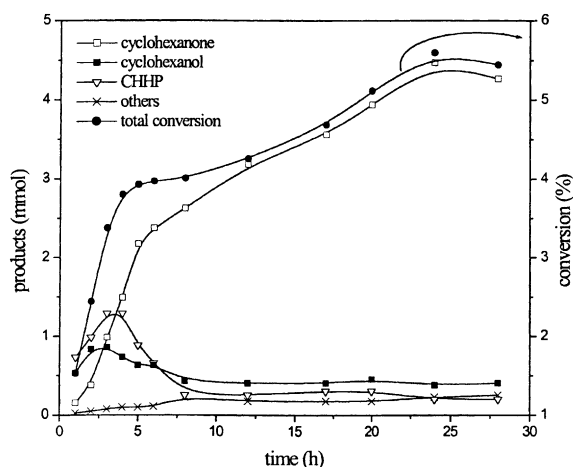


Fig. 4. Time dependence of product distribution in the Cr-SiO<sub>2</sub>-catalyzed oxidation of cyclohexane. Reaction conditions: 95 mmol cyclohexane, 9.5 mmol TBHP (82% in cyclohexane) and 100 mg of Cr-SiO<sub>2</sub> ( $2.3 \times 10^{-5}$  mol Cr); 348 K.

Table 1  
Leaching tests in the Cr–SiO<sub>2</sub>-catalyzed oxidation of cyclohexane<sup>a</sup>

| Experiment no. | Catalyst                          | Cyclohexanone (mmol) |      | Initial Cr content (%) | Final Cr content (%) |
|----------------|-----------------------------------|----------------------|------|------------------------|----------------------|
|                |                                   | 4 h                  | 24 h |                        |                      |
| 1              | Cr–SiO <sub>2</sub>               | 1.96                 | 5.10 | 1.21 ± 0.02            | 0.74 ± 0.02          |
| 2              | Cr–SiO <sub>2</sub> <sup>b</sup>  | 0.80                 | 2.40 | 0.75 ± 0.02            | 0.75 ± 0.02          |
| 3              | Cr–SiO <sub>2</sub> <sup>ca</sup> | 0.45                 | 1.19 | 0.88 ± 0.01            | 0.74 ± 0.01          |

<sup>a</sup> Filtration after 4 h, addition of 9.5 mmol of TBHP to the filtrate and continuation of the reaction for 20 h.

<sup>b</sup> Soxhlet extraction with acetonitrile for 18 h followed by drying at 393 K for 4 h.

<sup>c</sup> Calcination under a flow of air (40 ml min<sup>-1</sup>) at 723 K for 2 h followed by soxhlet extraction with acetonitrile.

negligible amounts of products. It can be seen that the formation of cyclohexyl hydroperoxide (CHHP) and cyclohexanol is favored in the beginning of the reaction. These products are subsequently converted to cyclohexanone, which is obtained with high selectivity after reaction times of 12 h or more. Experiments where 2 mmol of cyclohexanol were added to the reaction mixture in the beginning of the reaction showed that 1.9 mmol were consumed, indicating that cyclohexanol is more easily converted than cyclohexane. Oxidation of cyclohexanol in the presence of Cr–SiO<sub>2</sub> gave 60% conversion with 97% selectivity to cyclohexanone, thus confirming facile oxidation of cyclohexanol. On the other hand, addition of 2 mmol of cyclohexanone to the reaction mixture slightly reduced the activity of the catalyst.

To evaluate whether the reactions are catalyzed in the heterogeneous or in the homogeneous phase, the catalyst was removed after 4 h and the reaction mixture was allowed to react further in the absence of the catalyst. The Cr content in Cr–SiO<sub>2</sub> decreased from 1.21 to 0.74% (Table 1, experiment 1). The same Cr content was found after acetonitrile extraction of Cr–SiO<sub>2</sub>. Using Cr–SiO<sub>2</sub><sup>ex</sup>, no loss of metal could be detected (Table 1, experiment 2) and the Cr content remained at 0.75%. As leaching proof materials can be obtained by calcination at elevated temperatures, Cr–SiO<sub>2</sub> was pre-treated at 723 K. However, subsequent soxhlet extraction yielded a silicate with a reduced Cr content of 0.88%, which lost further metal down to 0.74% Cr during the leaching test (Table 1, experiment 3). It can be seen from Table 1 that the untreated catalyst shows the highest activity, which should be attributed mainly to leached Cr species.

The observation that Cr is easily removed from Cr–SiO<sub>2</sub> indicates the presence of weakly bound Cr

species besides a stable phase containing 0.75% Cr. These results are in agreement with the above mentioned spectroscopic data obtained from Cr–SiO<sub>2</sub> and Cr–SiO<sub>2</sub><sup>ex</sup>, which suggest the presence of different Cr species in Cr–SiO<sub>2</sub> but only one species in Cr–SiO<sub>2</sub><sup>ex</sup>. However, even in the experiment with Cr–SiO<sub>2</sub><sup>ex</sup>, where no loss of Cr could be detected by XRF (Table 1, experiment 2), further production of cyclohexanone after removal of the catalyst was observed (Fig. 5), suggesting that traces of metal, leached to the liquid phase, catalyze the oxidation of cyclohexane. Although the cyclohexanone yield is remarkably reduced, the catalytic reaction continues after removal of the catalyst, thus confirming catalysis in the homogeneous phase. Lempers and Sheldon [28] have shown

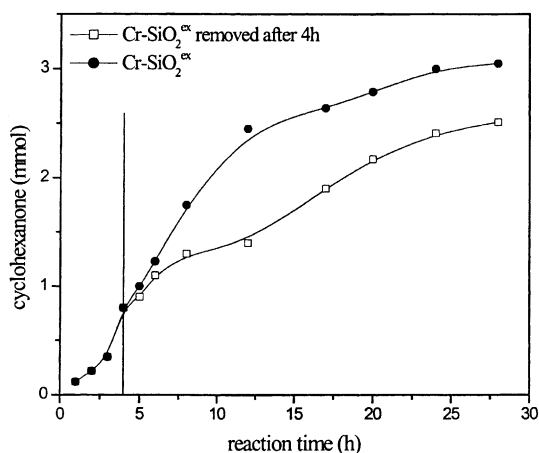


Fig. 5. Time dependence of cyclohexanone formation in the Cr–SiO<sub>2</sub><sup>ex</sup>-catalyzed oxidation of cyclohexane without and with removal of the catalyst after 4 h reaction time. Reaction conditions: 95 mmol cyclohexane, 9.5 mmol TBHP (82% in cyclohexane) and 100 mg of Cr–SiO<sub>2</sub><sup>ex</sup> ( $1.4 \times 10^{-5}$  mol Cr); 348 K.

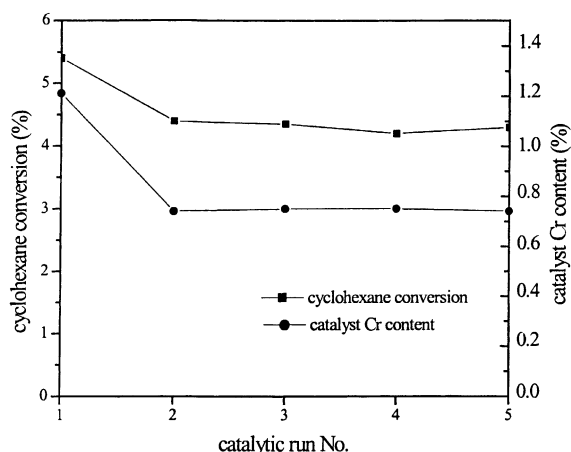


Fig. 6. Catalyst recycling test. Cyclohexane conversions in five consecutive reactions with reuse of Cr-SiO<sub>2</sub>. Reaction conditions: 95 mmol cyclohexane, 9.5 mmol TBHP (82% in cyclohexane) and 100 mg of Cr-SiO<sub>2</sub> ( $2.3 \times 10^{-5}$  mol Cr); 348 K.

that traces of Cr, leached from redox molecular sieves like Cr-APO-5, Cr-APO-11 or Cr-S-1, are remarkably active in liquid phase oxidations with TBHP.

Catalyst recycling experiments were carried out with repeated use of Cr-SiO<sub>2</sub>. The results of five consecutive catalytic reactions using the same catalyst are given in Fig. 6. It can be seen that cyclohexane conversion decreases significantly from the first (5.4%) to the second catalytic run (4.4%) and remains constant within the experimental error after the second run. After a decrease from 1.21 to 0.74% after the first reaction, no further loss of Cr could be detected in the following four reactions, thus confirming that, after initial removal of weakly bound Cr species, a stable catalyst can be obtained. However, as shown in the leaching tests, this catalyst loses traces of Cr, which catalyze at least part of the reaction in homogeneous phase.

#### 4. Conclusions

Chromium containing silicates can be prepared by a simple acid-catalyzed sol-gel process. EPR data show the presence of at least three different Cr species. After removal of weakly bound Cr species by extraction with acetonitrile, a material with only one EPR visible

Cr species is obtained. Cr-SiO<sub>2</sub> is active in the oxidation of cyclohexane to cyclohexanone. The extracted catalyst can be used repeatedly for at least four times without measurable loss of metal. However, traces of Cr leached into the liquid phase which are not detectable by XRF analysis of the solid catalyst, catalyze at least part of the oxidation.

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#### References

- [1] R.A. Sheldon, *Chemtech* (1991) 566.
- [2] R.A. Sheldon, *J. Mol. Catal. A* 107 (1996) 75.
- [3] E.V. Spinaceé, U. Schuchardt, D. Cardoso, *Appl. Catal. A* 185 (1999) 193.
- [4] T.J. Pinnaiva, M.S. Tzou, S.D. Landau, *J. Am. Chem. Soc.* 107 (1985) 4783.
- [5] S. Klein, J.A. Martens, R. Parton, K. Verduyze, P.A. Jacobs, W.F. Maier, *Catal. Lett.* 38 (1996) 209.
- [6] R. Hutter, T. Mallat, A. Baiker, *J. Catal.* 153 (1995) 177.
- [7] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, *Acc. Chem. Res.* 31 (1998) 485.
- [8] H.E.B. Lempers, R.A. Sheldon, *Stud. Surf. Sci. Catal.* 105 (1997) 1061.
- [9] F.J. Luna, S.E. Ukawa, M. Wallau, U. Schuchardt, *J. Mol. Catal. A* 117 (1997) 405.
- [10] M.L.S. Corrêa, M. Wallau, U. Schuchardt, *Stud. Surf. Sci. Catal.* 105 (1997) 277.
- [11] W.A. Carvalho, P.B. Varaldo, M. Wallau, U. Schuchardt, *Zeolites* 18 (1997) 408.
- [12] R.A. Sheldon, I.W.C.E. Arends, H.E.B. Lempers, *Collect. Czech. Chem. Commun.* 63 (1998) 1724.
- [13] A. Baiker, *Stud. Surf. Sci. Catal.* 101 (1996) 51.
- [14] U. Schubert, *J. Chem. Soc., Dalton Trans.* (1996) 3343.
- [15] R. Gomez, R.D. Gonzalez, T. Lopez, *Catal. Today* 35 (1997) 293.
- [16] J.M. Rodríguez-Isquierdo, M.A. Cauqui, *J. Non-Cryst. Solids* 147 (1992) 724.

- [17] M. Rogovin, R. Neumann, *J. Mol. Catal. A* 138 (1999) 315.
- [18] R. Neumann, M. Levin-Elad, *Appl. Catal. A* 122 (1995) 85.
- [19] R.S. da Cruz, M.M. Dauch, U. Schuchardt, R. Kumar, *Stud. Surf. Sci. Catal.* 130 (2000) 1037.
- [20] S. Klein, S. Thorimbert, W.F. Maier, *J. Catal.* 163 (1996) 476.
- [21] P.A. Jacobs, P.O. Rouxhet, M.I. Genet, D.E. de Vos, D.L. Vannopen, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 560.
- [22] N. Baccan, J.C. de Andrade, O.E.S. Godinho, J.S. Barone, *Química Analítica Quantitativa Elementar*, 2nd Edition, Edgard Blücher Ltda, São Paulo, 1985, p. 201.
- [23] R. Neumann, M. Levin-Elad, *J. Catal.* 166 (1997) 206.
- [24] S.C. Miller, M. Fujino, E.I. Ko, *J. Catal.* 148 (1994) 673.
- [25] J.S.T. Mambrim, H.O. Pastore, C.U. Davanzo, E.J.S. Vichi, O. Nakamura, H. Vargas, *Chem. Mater.* 5 (1 993) 993) 166.
- [26] B.M. Weckhuysen, L.M. de Ridder, P.J. Grobet, R.A. Schoonheydt, *J. Phys. Chem.* 99 (1995) 320.
- [27] B.M. Weckhuysen, R.A. Schoonheydt, F.A. Mabbs, D. Collison, *J. Chem. Soc., Faraday Trans.* 92 (1996) 2431.
- [28] H.E.B. Lempers, R.A. Sheldon, *J. Catal.* 175 (1998) 62.