The Stability of Chromium in CrAPO-5, CrAPO-11, and CrS-1 during Liquid Phase Oxidations

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Chromium substituted aluminophosphate-5 (CrAPO-5), aluminophosphate-11 (CrAPO-11), and silicalite-1 (CrS-1) were synthesized, characterized, and investigated with regard to their stability under the conditions of liquid phase oxidations with *tert*-butyl hydroperoxide (TBHP). Experimental evidence is presented that these reactions did not take place in the micropores or at the outer surface of these catalysts but were homogeneously catalyzed by small amounts of leached chromium. The amount of chromium leached is related to the crystal size of the catalyst. In the case of the large CrAPO-5 crystals only 0.3% of its chromium is leached during the reaction, which corresponds to a substrate/Cr ratio of 17.000. Nevertheless, this very small amount is responsible for the observed catalysis. The necessity for catalyst filtration at the reaction temperature in catalyst recycling experiments is emphasized. Moreover, previous results purported to be consisted with the notion that the reaction takes place in the micropores are reinterpreted in the light of the above results. © 1998 Academic Press

Key Words: **chromium molecular sieves; chromium leaching.**

INTRODUCTION

The first example of a redox molecular sieve was titanium silicalite-1 (TS-1) developed by Enichem workers (1–4), which proved to be an active catalyst for selective oxidations with 30% aqueous H_2O_2 in the liquid phase under mild conditions. Examples of oxidative transformations catalyzed by TS-1 include the hydroxylation of phenols and aromatics (5), the epoxidation of olefins (6), the ammoximation of ketones to oximes (7), and the selective oxidation of primary alcohols to aldehydes and secondary alcohols to ketones (8).

The success of TS-1 stimulated the investigation of a broad range of metal substituted molecular sieves as oxidation catalysts, e.g., ZrS-1 for the hydroxylation of benzene to phenol with H_2O_2 (9), cobalt substituted aluminophosphates (CoAPOs) as catalysts for the oxidation of cyclohexane with O_2 (10), vanadium substituted aluminophosphates (VAPOs) as olefin epoxidation catalysts (11, 12) and

chromium substituted silicalite-1 (CrS-1) and aluminophosphates (CrAPOs) for the oxidation of alkyl aromatics, alcohols and allylic oxidation of olefins (13–15). More recent developments include the incorporation of redox metals into the framework of mesoporous molecular sieves, such as MCM-41 (16), and the design of redox ship-in-a-bottle catalysts whereby a redox metal complex is encapsulated in a zeolite (17). One aspect which is generally overlooked in the euphoric rush to develop new catalytic systems is the stability and, hence, the true heterogeneity of these materials under oxidizing conditions. For example, VAPO-5 catalyzed liquid-phase olefin epoxidation and benzylic oxidation with TBHP were originally believed to occur solely inside the micropores (18). However, a recent more careful study of this material under liquid-phase oxidation conditions showed that vanadium is leached and that the observed catalysis is due to homogeneous vanadium (19, 20). We have previously reported (21) on the synthesis, characterization, and catalytic properties of chromium-substituted molecular sieves in oxidations with O_2 and RO_2H. We have now investigated in more detail the stability of chromium in CrS-1, chromium substituted aluminophosphate-5 (CrAPO-5) and chromium substituted aluminophosphate-11 (CrAPO-11) under the conditions of a catalytic oxidation with *tert*-butyl hydroperoxide (TBHP) as oxidant.

EXPERIMENTAL

Catalyst Preparation

CrAPO-5, CrAPO-11, and three different samples of CrS-1 were prepared as described previously (21). CrAPO-5 was hydrothermally synthesized using a gel composition of 0.026 Cr_2O_3 : 0.89 Al_2O_3 : P_2O_5 : Pr_3N : 50 H_2O, yielding crystalline CrAPO-5. CrAPO-11 was hydrothermally synthesized using a gel composition of 0.025 Cr_2O_3 : 0.96 Al_2O_3 : P_2O_5 : Pr_2NH : 50 H_2O, producing crystalline CrAPO-11. CrS-1A was synthesized in a fluoride-assisted synthesis from a gel composition of 0.014 Cr_2O_3 : SiO_2 : 0.126 TPABr : 0.024 NH_4F : 35 H_2O. CrS-1B and CrS-1C were synthesized in the same way, except for a different

chromium concentration in the synthesis gel. The CrS-1B material was synthesized with a gel composition of 0.007 Cr_2O_3 : SiO_2 : 0.10 TPABr : 1.5 NH_3 : 20 H_2O while CrS-1C was synthesized with a gel composition of 0.014 Cr_2O_3 : SiO_2 : 0.10 TPABr 3.0 NH_3 : 30 H_2O. Sodium ion exchange treatments, to remove loosely bound chromium were carried out by stirring 2 g of catalyst in 250 ml 1 M NaCl at 40°C for 1 h. This ion exchange treatment was repeated two times. Similar treatments of these catalysts were carried out with 1 M TBHP solutions.

Catalyst Characterization

The catalysts were characterized by X-ray diffraction using a Philips PW 1877 automated powder diffractometer with CuKα radiation; scanning electron microscopy (SEM) using a Jeol JSM-35 scanning microscope; temperature programmed desorption (TPD) and temperature programmed reduction (TPR) using a micromeritics TPD/TPR 2900. H_2O TPD was carried out using He as carrier gas with a flow rate of 10 ml/min and a temperature program of 5°C/min. TPR was carried out using a Ar/H_2 mixture (95/5) with a flow rate of 10 ml/min and a temperature program of 5°C/min.

Filtration Experiments

The catalytic oxidations were carried out in a 25-ml round bottom flask equipped with a condenser and a magnetic stirrer. Typically, 2 mmol of substrate (alpha-pinene or ethylbenzene), 10 mmol of TBHP in chlorobenzene (25 wt%), 10 ml chlorobenzene (solvent), 100 mg nonane as internal standard and the catalyst (substrate/chromium = 50) were introduced and the mixture heated at 80°C. After 30 min the catalyst was filtered while maintaining the reaction mixture at 80°C. The filtrate was then stirred at 80°C for an additional 150 min. The conditions for the carveol oxidation were somewhat different: 10 mmol of carveol, 5 mmol TBHP, and a reaction temperature of 85°C. The conversion of carveol was based on the amount of TBHP charged. Quantitative analyses were carried out by GC with a semi-capillary column (CP SIL 5 CB, 50 m × 0.53 mm and on a CB wax 52 CB, 50 m × 0.53 mm).

Analysis of Leached Chromium (22)

100 mg catalyst was stirred in 10 ml chlorobenzene containing 10 mmol TBHP for 3 h at 80°C, after which the catalyst was filtered at the reaction temperature. After evaporation of solvent and TBHP under vacuum 15 ml of water, 4 drops concentrated H_2SO_4, and 4 drops 0.1 N KMnO$_4$ solution were added. The solution was heated without boiling for 15 min. If the colour disappeared during the heating more KMnO$_4$ solution was added dropwise. The solution was cooled to room temperature and excess KMnO$_4$ was reduced by adding a 2.5% solution of NaN$_3$

until the solution was decolourized. Addition of a large excess is avoided by adding the NaN$_3$ solution dropwise. 1 ml of diphenyl carbazide solution was added (0.2 g diphenyl carbazide in 100 ml acetone containing 1 ml H_2SO_4), diluted to an appropriate concentration with water and the absorbance was measured at 545 nm.

RESULTS

Catalyst Preparation and Characterization

Three different samples of CrS-1 were synthesized for testing in oxidation reactions. Sample CrS-1A was synthesized from a neutral fluoride-assisted medium producing large coffin-shape crystals (75 × 20 μm). CrS-1B and CrS-1C were synthesized from an alkaline medium differing only in chromium concentration. This method resulted in smaller coffin-shape crystals (14 × 3 μm). The three samples of calcined CrS-1 were ion exchanged with a 1 M NaCl solution. This treatment resulted in a chromium loss from 0.97 to 0.81 wt% for CrS-1A, 0.62 to 0.23 wt% for CrS-1B, and 0.90 to 0.43 wt% for CrS-1C (Table 1). Additional ion exchange treatments did not show any further loss of chromium, and therefore it was previously concluded that the remaining chromium was stable framework-bonded (14). CrAPO-5 and CrAPO-11 were obtained as sphere-like aggregates of 75 × 50 μm 6 × 4 μm, respectively.

The chromium substituted aluminophosphate and silicalite were characterized by XRD which showed highly crystalline materials. No extra phases related to AlPO$_4$ hydrates, quartz, chromium clusters, or chromium oxides were observed. SEM photographs of the CrS-1 samples showed elongated prismatic crystals while the chromium substituted aluminophosphates showed sphere-like morphology. TPD, TPR, and chromium weight percentage data of these materials are presented in Table 1.

H_2O TPD of both CrAPO-5 and CrAPO-11 showed a strong desorption signal at 159°C. The CrS-1 samples showed a much smaller desorption signal at approximately 140–150°C. This difference in intensity between the

TABLE 1

TPD-, TPR Data and the Chromium Contents (Before and After Ion Exchange Treatment) of the CrAPO-5, CrAPO-11, and CrS-1 Materials

Catalyst	TPD (°C)	TPR (°C)	Cr (wt%) Before	Cr (wt%) After
CrAPO-5	159, 360	478, 538	0.88	
CrAPO-11	159	403	0.85	
CrS-1A	143	331	0.97	0.81
CrS-1B	147	359	0.62	0.23
CrS-1C	140	407	0.90	0.43

aluminophosphate and silicalite is caused by the difference in electronegativity between Al and P in the aluminophosphate, resulting in an increased polarity of the surface and, thus, a stronger H_2O interaction, compared to the silcalite lattice (23). A very weak desorption at a higher temperature was observed for the CrAPO-5 and was assigned to H_2O chemically bonded chromium. TPR of CrAPO-5 showed a reduction at 478°C with a weak shoulder at 538°C, indicating that two different coordination spheres around the chromium are present. The CrAPO-11 showed a reduction at 403°C, while CrS-1 was reduced in a temperature range of 331–407°C. These lower reduction temperatures suggest that the chromium in CrS-1 and CrAPO-11 does not consist of isolated chromium ions but of chromium aggregates, although no sign of these aggregates were found in the XRD.

Catalyst Filtration Experiments

As a test reaction for checking the stability of chromium in the lattice the allylic oxidation of alpha-pinene with TBHP, affording verbenone (Reaction [1]), was chosen (15). The catalyst was filtered after 30 min, which corresponded to approximately 25% conversion and the filtrate allowed to react further. Catalyst filtration was performed at the reaction temperature (80°C) in order to avoid readsorption of leached chromium on the catalyst surface during cooling of the reaction mixture.

$$\text{(structure)} + 2\,TBHP \xrightarrow{Cr} \text{(structure)} + 2\,TBOH + H_2O \quad [1]$$
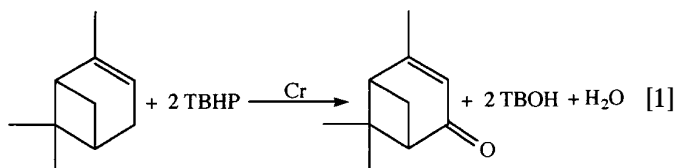
In Fig. 1 the results are presented on the CrS-1 filtration experiments in the allylic oxidation of alpha-pinene
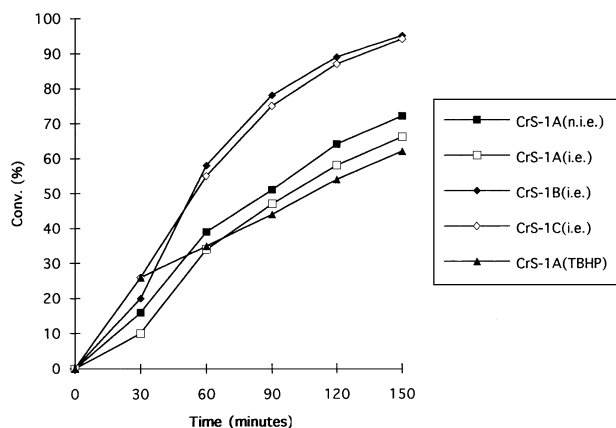

FIG. 1. Filtration experiments (after 30 min) of different CrS-1 samples. (n.i.e.) = not ion exchanged, (i.e.) = ion exchanged, (TBHP) = TBHP treatment.
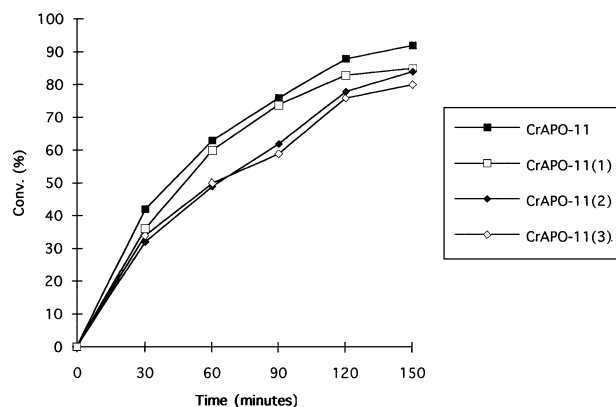

FIG. 2. Filtration experiments (after 30 min) of different CrAPO-11 samples. CrAPO-11(1), CrAPO-11(2), CrAPO-11(3) are treated once, twice, and three times with TBHP, respectively.

to verbenone. As expected for a non-ion exchanged CrS-1 sample (CrS-1A (n.i.e.)), which contains loosely bound chromium, the reaction continues and is catalyzed by leached chromium. However, in the case of ion exchanged CrS-1A (i.e.) catalyst the reaction also continues after filtration and in the case of CrS-1B (i.e.) and CrS-1C (i.e.) the reaction even goes toward completion (210 min; not shown). The same applies to a CrS-1A catalyst which had been pretreated with TBHP to remove loosely bound chromium. The observed differences indicate that the small crystallites CrS-1B and CrS-1C are less stable than the larger CrS-1A crystallites which was also observed in the case of VS-1 samples (24).

All these CrS-1 catalysts were recalcined after the ion-exchange or TBHP treatment. In order to investigate if this recalcination step is responsible for the leaching behaviour of these catalysts, by creating loosely bound chromium, experiments were performed with an untreated CrAPO-11, and samples of CrAPO-11 which were pretreated once, twice, and three times with TBHP, respectively. The TBHP treatments were carried out by stirring CrAPO-11 in a 1 *M* TBHP solution at 40°C for 1 h. These TBHP treated catalysts were not recalcined before use. Figure 2 shows the results of these four catalysts. It is very clear that even after the catalyst had received three TBHP treatments it still leaches enough chromium to give a continuation of the reaction after filtration. Hence, we conclude that reaction of the catalyst with TBHP, not recalcination, is responsible for the observed leaching.

Similar results were obtained with the CrAPO-5 catalysts (Fig. 3). Although the results were not as dramatic as in the case of CrAPO-11 and CrS-1, it is clear from these data that ion exchange and TBHP treatments without recalcination (samples B and D) give similar results to those observed when these treatments are followed by recalcination (samples C and E), namely a continuation of reaction after filtration of the CrAPO-5 catalyst.
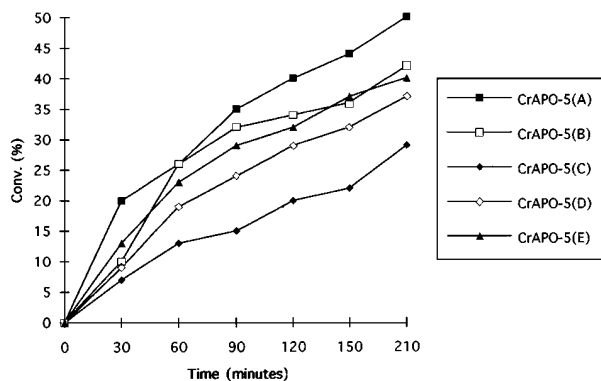
FIG. 3. Filtration experiments (after 30 min) of different CrAPO-5 samples. CrAPO-5(A) = not treated; CrAPO-5(B) = ion exchanged, not recalcined; CrAPO-5(C) = ion exchanged recalcined; CrAPO-5(D) = treated with TBHP, not recalcined; CrAPO-5(E) = treated with TBHP, recalcined.

Comparing the results of CrAPO-11 and CrAPO-5 there is, as with the CrS-1 samples, a relation between crystal size and stability of chromium (CrAPO-11: sphere-like aggregates 6×4 μm, CrAPO-5: sphere-like aggregates 75×50 μm). The larger the crystal-size the more stable the catalyst is towards leaching.

Oxidations with a Bulky Substrate/Hydroperoxide

Further proof (Fig. 4) that TBHP is responsible for the leaching of chromium from the pores was obtained in an experiment performed with a bulky substrate (valencene) which is too large to enter the CrAPO-5 pores.

CrAPO-5 catalyzed the allylic oxidation of valencene to nootkatone, with TBHP as the oxidant, which would not be possible if the reaction took place inside the micropores. In contrast, when a bulky hydroperoxide (triphenylmethylhydroperoxide) was used with alpha-pinene as substrate no
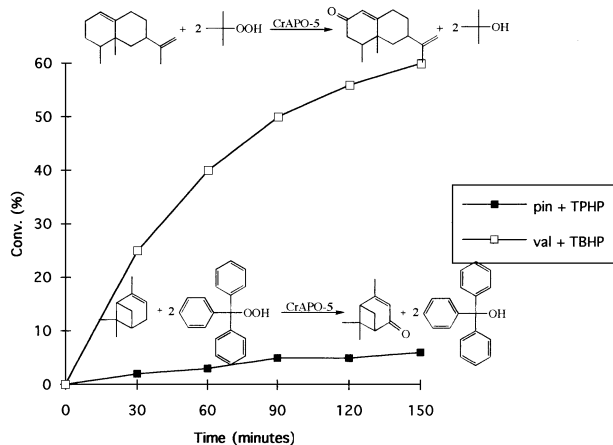

FIG. 4. Oxidation of a bulky substrate (valencene) with a small hydroperoxide and oxidation of a small substrate (alpha-pinene) with a bulky hydroperoxide (triphenylmethyl hydroperoxide).
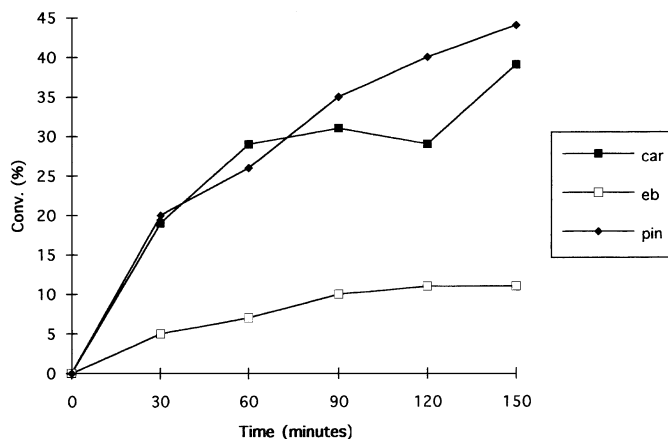

FIG. 5. Filtration experiments (after 30 min) with alpha-pinene (pin), carveol (car), and ethylbenzene (eb) as substrate.

reaction was observed, consistent with the bulky hydroperoxide not being able to enter the pores and, hence, not being able to leach chromium from the internal surface. This was confirmed by an experiment in which TBHP was stirred with CrAPO-5. After filtration of the catalyst substrate was added whereupon the reaction started. The reverse experiment, in which CrAPO-5 was first stirred with the substrate, filtered, and then hydroperoxide added, did not show any reaction.

Carveol and Ethylbenzene Oxidation

In addition to allylic oxidations we also studied the oxidation of an alcohol (carveol) and an alkylbenzene (ethylbenzene) with TBHP in the presence of CrAPO-5. The results are presented in Fig. 5.

Chromium is well known to catalyze the oxidation of alcohols to ketones (25). We chose the oxidation of carveol to carvone (Reaction [2]) because we previously observed (26) that one of the two isomers of carveol (cis/trans) appeared to react much faster than the other, which we attributed to, the CrAPO-5 catalyst exhibiting some (shape) selectivity.
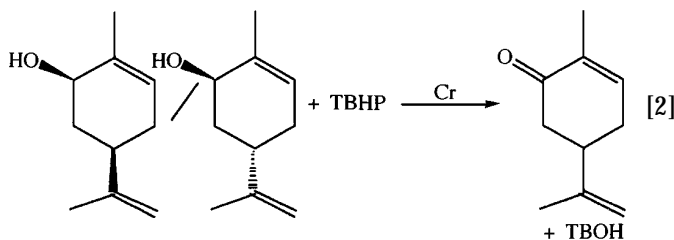
After filtration of the catalyst the reaction continues (see Fig. 5) consistent with the chromium being leached. Indeed, the cis isomer reacted much faster, but we subsequently found that this was also the case when a homogeneous chromium catalyst (Cr(acac)3) was used and is,

hence, not due to a shape selectivity effect of the micropores of CrAPO-5. It is presumably due to the greater steric relief when the cis alcohol is oxidized compared to the trans isomer (27).

Similarly, in the benzylic oxidation of ethylbenzene to acetophenone, after filtration of the catalyst at the reaction temperature the reaction continued consistent with catalysis being due to leached chromium.

Oxidations with Homogeneous Chromium Catalysts and the Analysis of Leached Chromium

The filtration experiments described so far were conducted at the reaction temperature. Initially, we conducted filtration experiments by first cooling the reaction mixture to room temperature (after 30 min reaction) filtering the catalyst and continuing the reaction by heating it to the reaction temperature. In these experiments only a slight increase in conversion was observed after filtration, which led us to conclude that the CrAPO-5 was stable and that the catalysis was heterogeneous (Fig. 6). However, when filtration of the catalyst was performed at the reaction temperature a much higher increase in conversion after filtration (Fig. 7) was observed.

In order to further understand this dramatic effect of filtration temperature on the activity of the filtrate we studied analogous oxidations with homogeneous chromium catalysts at substrate/chromium ratios ranging from 1 to 10,000 (see Table 2).

Experiments were carried out using either a chromium (III) source (Cr(acac)3) or a chromium(VI) source ((pyr)$_2$Cr$_2$O$_7$). In the experiments where chromium was added in its hexavalent state the reaction always started instantaneously. This was also the case when chromium(III) was used at low substrate/chromium ratios (1 or 10). Increasing the substrate/chromium ratio to 100 resulted in an induction period of 5 min. A further increase in substrate/chromium ratio to 1000 and 10,000 resulted in in-
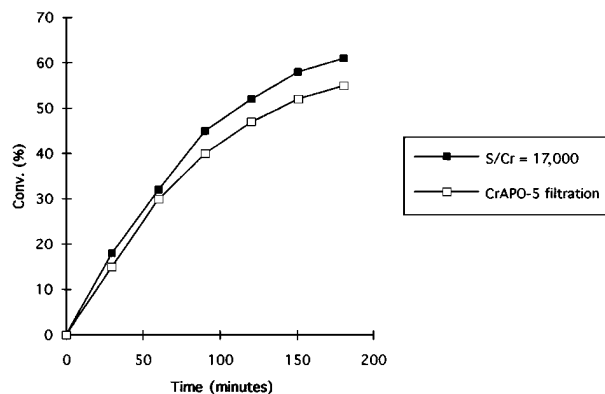

FIG. 7. Comparison of a homogeneous chromium source with leached chromium from CrAPO-5 (both substrate/Cr = 17000).

duction periods of 90 and 300 min, respectively. Hence, low concentrations of chromium(III) lead to long induction periods.

The amount of chromium leached from catalysts under the reaction conditions was determined spectrophotometrically (see experimental part). The catalyst, e.g., CrAPO-5, was allowed to react with a 0.9 M solution of TBHP in chlorobenzene at 80°C for 3 h, followed by filtration at the reaction temperature and evaporation of the filtrate in vacuo. Since the spectrophotometric method analyzes only for chromium(VI) the residue was treated with aqueous KMnO$_4$ to be sure that all the chromium was present in the hexavalent state. The excess of KMnO$_4$ was reduced with NaN$_3$. In the case of CrAPO-5 0.3% of the total amount of chromium present in the catalyst was leached (Table 3). When the experiment was repeated with exclusion of the KMnO$_4$ treatment no chromium was detected. Hence we conclude that upon cooling and evaporation of solvent and TBHP the chromium(VI) in the filtrate is reduced to chromium(III).

Combination of this result with the observation that chromium(III) at low concentrations results in long induction periods (see above) provides an explanation for the observed difference in the hot and cold filtration

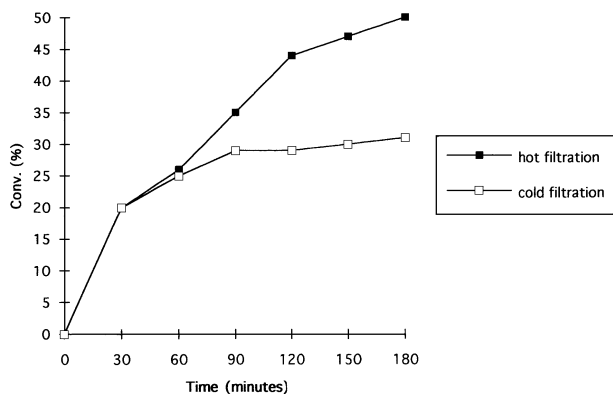FIG. 6. Reaction temperature and room temperature filtration of CrAPO-5 in the allylic oxidation of alpha-pinene.

TABLE 2

Induction Period Using Cr(VI) and Cr(III) as Catalyst

	Induction period (min)	
S/Cr	Cr(VI)[a]	Cr(III)[b]
1	0	0
10	0	0
100	0	5
1000	0	90
10,000	0	300

[a] Cr(VI) = (pyr)$_2$Cr$_2$O$_7$.
[b] Cr(III) = Cr(acac)$_3$.

TABLE 3

Spectrophotometric Determination of Leached Chromium

Catalyst	Amount of leaching (%)[a]	Substrate/chromium[b]
CrAPO-5	0.3	17000
CrAPO-11	2.1	2400
CrS-1(A)	0.3	17000
CrS-1(B)	19.9	250
CrS-1(C)	34.0	150

[a] Determined by the spectrophotometric method described in the experimental section.

[b] The substrate/chromium ratio in reaction, calculated from the spectrophotometric determination of chromium leaching.

experiments. Upon cooling the reaction mixture the chromium(VI) oxidizes substrate but is not reoxidized by the TBHP and after filtration of the catalyst only chromium(III) is present at a very low concentration (0.3% of chromium leaching = S/Cr of 17,000). This results in a very long induction period, so that hardly any catalysis is observed, leading to the erroneous conclusion that no leaching occurred. We subsequently investigated if this low amount of leached chromium could be responsible for the observed catalysis, by comparing the activity of a filtrate obtained from TBHP treatment of CrAPO-5 followed by hot filtration (3 h) with that of a solution containing an amount of homogeneous Cr(VI), added as pyridinium dichromate ((pyr)$_2$Cr$_2$O$_7$), corresponding with the amount of leached chromium, i.e. a substrate/chromium ratio of 17,000. These experiments (Fig. 7) exhibit a very similar reaction profile which leads us to conclude that all of the observed catalytic activity can be attributed to homogeneous chromium(VI) leached from the CrAPO-5 by reaction with TBHP.

The amount of chromium leaching from the other chromium-substituted molecular sieves was also determined with this spectrophotometric method (Table 3). The results are in agreement with the observed results from the filtration experiments. The small crystallites of CrAPO-11, CrS-1B, and CrS-1C lose large amounts of chromium. In the case of CrS-1C up to 34% of the chromium is leached from the catalyst. The large crystallites of CrS-1A are much more stable and lose only 0.3% of chromium, i.e. approximately 100 times less than CrS-1C. However, the difference in the reaction curves between CrS-1A and CrS1-C does not reflect this large difference in stability (Fig. 1). Assuming a linear relationship between the rate of oxidation and the chromium concentration one would expect CrS-1C to be about 100 times as active as CrS-1A. That this was not so, suggested to us that the relationship between the reaction rate and chromium concentration may not be linear. Hence, we carried out the oxidation of alpha-pinene with TBHP at different substrate/chromium ratios and determined the turnover number (TON) at 30% conversion (Table 4).

The results showed that there is a nonlinear relationship between the alpha-pinene/chromium(VI) ratio and the reaction rate. This increase in relative activity of chromium at lower concentrations suggests that dimers and or oligomers are formed at higher concentrations of chromium leading to catalyst deactivation (28). This nonlinear relationship between rate of oxidation and catalyst concentration is one of the reasons that amounts below analytical detection limits can be responsible for the observed results.

DISCUSSION

The CrAPO-5, CrAPO-11, and CrS-1 catalysts have been found to leach chromium during the oxidation of alpha-pinene, ethylbenzene, and carveol using TBHP as oxidant. Bulky molecules, which are not able to enter the micopores are oxidized with TBHP. On the other hand, small substrates are not oxidized when a bulky hydroperoxide is used. This strongly suggests that leaching from the catalyst is caused by an interaction of the hydroperoxide with chromium. The bulky hydroperoxide is not able to enter the pores and, hence, is not able to leach chromium from the internal surface while TBHP can enter the pores in order to leach chromium and consequently to give the observed catalysis. Further proof that leaching of chromium was caused by TBHP was provided by the experiment in which the CrAPO-5 was stirred in a TBHP-containing solution. After filtration of the catalyst and addition of substrate catalytic activity was observed. In contrast, when the catalyst was stirred with a substrate-containing solution, no catalytic activity was observed in the filtrate. Since the catalysis is homogeneous one would not expect to observe any shape selectivity. The earlier reported faster oxidation of cis- compared to transcarveol, which we attributed to shape selectivity, was also observed with homogeneous chromium(VI) and is presumably due to the steric relief in the case of cis-carveol.

An important factor in chromium leaching is the crystalsize of the catalyst. The large CrAPO-5 (75×50 μm) and CrS-1A (75×20 μm) both lose less than 0.5% of their chromium after 3 h of reaction. The much smaller CrAPO-11 (6×4 μm) loses, under the same conditions, more than

TABLE 4

Turnover Numbers of Homogeneous Chromium(VI)[a]

S/Cr	TON[b] (h^{-1})
10^2	700
2×10^3	900
10^4	1500
10^5	7500

[a] Calculated from alpha-pinene oxidation.

[b] Determined at 30% conversion.

2% of its chromium, while CrS-1B and CrS-1C (both 14×3 μm) are very unstable and lose 20% and 34%, respectively. Another factor which might be important for the stability of these chromium molecular sieves was indicated by the TPR results, which suggest that CrAPO-5 consists of isolated chromium ions, while CrS-1 and CrAPO-11 show more the character of chromium aggregates. The effect of recalcination steps, NaCl or TBHP ion exchange steps, was found to be very minor, because as soon as the catalyst is in contact with TBHP it leaches chromium.

The different behaviour observed between hot and cold filtration can be explained on the basis of the observation that Cr(III) gives long induction periods at low concentrations and that upon cooling of the reaction solution no Cr(VI) could be detected. Upon cooling Cr(VI) oxidizes substrate but is not reoxidized by the TBHP. After cooling and filtration of the catalyst only Cr(III) is present at a very low concentration (0.3% of chromium leaching = S/Cr of 17,000). By comparison, when the reaction solution contained a substrate to chromium(III) ratio of 10,000 an induction period of 300 min was observed. Hence, this leached amount of 0.3% does not exhibit any catalytic activity for a long time after filtration. Hot filtration, on the other hand, will keep the chromium in the hexavalent state and leads to instant catalysis.

Furthermore, determination of the turnover number at different chromium ratios revealed a considerable increase of the turnover number at lower chromium concentrations. This is probably caused by association of chromium into di- and oligomeric species at higher chromium concentrations which is generally known to lead to catalyst deactivation in homogeneous systems.

CONCLUSIONS

In short, this study has taught us that one has to exercise caution in the interpretation of catalyst recycling experiments with heterogeneous catalysts in liquid phase oxidations. In the case of CrAPO-5 the catalyst could have been recycled 10 or even 100 times without any apparent loss of activity. Hence, claims for heterogeneity based on no significant loss of activity observed with recycled catalysts are questionable to say the least. As we have clearly shown the crucial test for heterogeneity involves filtration of the catalyst at the reaction temperature and examination of the filtrate for catalytic activity. In the case of chromium-catalyzed oxidations amounts of chromium below the detection level of ICP analysis were shown to account for the observed catalysis.

In this context we note that the 0.3% of available chromium which was leached from CrAPO-5 and CrS-1 corresponds to 1–2 ppm chromium in the reaction solution. In a recent report (29) of CrS-1 catalyzed oxidation of toluene and alkanes with TBHP the authors concluded

that the "minor" amount of Cr (± 2 ppm) leached from the CrS-1 may not be able to catalyze the reaction. Moreover, the usual practice of comparison with results observed with homogeneous catalysts at relatively high concentrations can lead to erroneous conclusions due to a nonlinear relationship between catalyst concentration and catalyst activity. We conclude, therefore, that much of the work reported in the literature on the use of redox molecular sieves or other materials as heterogeneous catalysts for liquid phase oxidations needs to be repeated and subjected to rigorous proof of heterogeneity.

Finally, we note that even if the chromium (or vanadium, or cobalt, etc.) would remain attached to the framework of these aluminophosphate systems it would probably not give good catalysis because, in general, in oxidation reactions a relatively apolar substrate, e.g. a hydrocarbon, is converted to a relatively polar product, e.g. an alcohol, or ketone and water. The TPD of the aluminophosphate materials showed a very hydrophilic character of the pores which, during an oxidation reaction, will mainly be filled with the polar products while the apolar substrates will be largely excluded. The same is true for the "ship-in-a bottle" catalysts which use the even more hydrophilic zeolite Y.

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