Letter

Oxidation of hydrocarbons with peroxides catalyzed by chromium(III) and iron(III) incorporated in SAPO-37 framework

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Abstract

SAPO-37 containing structural chromium(III) and iron(III) ions were tested as catalysts in liquid phase oxidation of benzene and cyclohexane, using hydrogen peroxide and *tert*-butylhydroperoxide as oxidants. Only chromium(III) is active as oxidation catalyst. In spite of the SAPO-37 framework stability under the reaction conditions, leaching of small quantities of chromium occurs and the observed catalytic reaction is mainly due to the chromium ions in solution. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: SAPO-37; Chromium(III); Iron(III); Liquid phase oxidation; Benzene; Cyclohexane; Redox molecular sieves

1. Introduction

Since the discovery of titanosilicalite-1 (TS-1) by Enichem researchers in 1983 [1] a great deal of effort has been employed in the study of the synthesis and the catalytic properties of new redox molecular sieves. These materials exhibit interesting catalytic behavior in a variety of liquid phase oxidations using molecular oxygen, hydrogen peroxide, or organic peroxides as primary oxidants [2]. SAPO-37 has a FAU structure, like zeolites X and Y, and is synthesized using a mixture of tetrapropylammonium (TPAOH) and tetramethylammonium (TMAOH) hydroxides as templates. In the as-synthesized material, TMA^+ ions are located in the sodalite cages and TPA^+ ions in the supercages. When completely free of templates, the SAPO-37 lattice is not stable to humidity in an ambient atmosphere. However, the TPA^+ ions can be removed selectively from the supercages by ion exchange, while the TMA^+ ions remaining in the sodalite cages help to keep the structure stable [3–5].

In a previous work [6], we described the incorporation of new transition metals in SAPO-37 framework, namely chromium(III) and iron(III), by direct synthesis. It was found that iron replaces tetrahedrally coordinated aluminum in the structure, whereas chromium is preferentially coordinated to the oxygen atoms of the lattice, probably in structural defects. In these ma-

terials a large part of TPA$^+$ ions was exchanged by sodium ions in methanolic solution, while TMA$^+$ ions were maintained in the sodalite cages.

A prerequisite for an industrially useful redox molecular sieve catalyst is that the metal is not leached from the internal surface of the molecular sieve and that its framework is stable under reaction conditions [2]. In order to verify the activity of these new materials, they were tested as catalysts in benzene and cyclohexane oxidation using hydrogen peroxide (H$_2$O$_2$) and *tert*-butylhydroperoxide (TBHP) as oxidants. The stability of these catalysts structure was assured by maintaining the TMA$^+$ ions in the sodalite cages.

2. Experimental

2.1. Synthesis and characterization of chromium(III) and iron(III) SAPO-37

The synthesis and characterization are described elsewhere [6].

2.2. Catalytic reactions

The catalytic reactions at 80°C, using H$_2$O$_2$ as oxidant, were performed in a 10 ml round bottom flask using a magnetic stirrer. The solvent, the substrate, the oxidant and the catalyst were added to the flask in that order, which was connected to a condenser and immersed into a thermostated oil bath, where it was maintained for the indicated reaction time. After a given reaction time, the flask was cooled and the reaction mixture was filtered in order to separate it from the catalyst. For the reactions using *tert*-butyl hydroperoxide (TBHP) as oxidant, the catalyst was transferred to a Schlenk flask and dried under vacuum (1 mbar) at room temperature for 5 min and at 80°C for 5 min. Then, the cyclohexane and the TBHP were added under argon and the reaction performed as described before.

The catalytic reactions at 100°C were performed in a Teflon-lined, 30 ml, stainless steel autoclave equipped with a magnetic stirrer, as described before. The autoclave was maintained for the given reaction time plus 30 min, time considered necessary for the system to achieve the reaction temperature.

The leaching tests were performed at 80°C using a 10 ml two necked round bottom flask. The solvent, the substrate, the oxidant and the catalyst were added to the flask in that order, which was connected to a condenser and immersed in a thermostated oil bath. After 2 h, the reaction mixture was sampled using a syringe and filtered at reaction temperature, using a HPLC filter to separate the catalyst. The filtrate was transferred to a round bottom flask, which was coupled to a condenser, and maintained at 80°C for 22 h.

Blank experiments were made under the same conditions, without the addition of catalyst.

2.3. Analysis

The reaction samples from benzene oxidation were analyzed using an HP 5890 series II gas chromatograph, equipped with a 25 m × 0.22 mm × 0.33 μm CBP1 capillary column, coupled to a flame ionization detector. After 5 min at 70°C the temperature was programmed at 20°C min^{-1} from 70 to 250°C. Phenol was quantified using a calibration curve and toluene, added after the reaction, as internal standard. The reaction samples from cyclohexane oxidation were analyzed using a packed column (3 m × 3.2 mm) of Carbowax 20M on Chromosorb W-HP coupled to a flame ionization detector. The temperature was programmed at 10°C min^{-1} from 40 to 170°C, and that temperature maintained for 10 min. Cyclohexanone (one) and cyclohexanol (ol) were quantified using calibration curves and cyclooctane, added after the reaction, as internal standard. For reaction using TBHP as oxidant, the reaction mixtures were analyzed before and after addition of triphenylphosphine to investigate the formation of cyclohexylperoxides.

The amount of peroxides remaining after the catalytic reaction was determined by iodometric titration [7].

3. Results and discussion

The chemical composition of the catalysts is given elsewhere [6]. For the as-synthesized catalysts, denominated MeAPSO-37 (Me = Cr or Fe), TPA$^+$ ions are present in the supercages and TMA$^+$ ions in the sodalite cages. For Na$^+$–MeAPSO-37, TPA$^+$ ions were exchanged by sodium ions in a methanolic so-

Table 1
Benzene oxidation (5 mmol of benzene, 5 mmol of H_2O_2 (30% in water), 3 ml of acetonitrile, 20 mg of catalyst, 24 h)

Catalyst	$T(°C)$	Conversion (%)	Phenol (mmol)	H_2O_2 consumed(%)
	100	1.0	0.05	5
Na^+–SAPO-37	100	1.2	0.06	15
Na^+–FeAPSO-37	100	2.0	0.10	97
Na^+–CrAPSO-37	100	5.6	0.28	70
Na^+–CrAPSO-37	80	4.8	0.24	40

lution of sodium acetate. Under these conditions the TMA^+ ions are not exchanged and were held in the sodalite cages [6]. The results obtained in the oxidation of benzene using H_2O_2 as oxidant are shown in Table 1. The principal product formed is phenol (almost 100% of selectivity) with a minor amount of benzoquinone. At 100°C, in the absence of catalyst, a benzene conversion of 1.0% and a 5% of H_2O_2 consumption are observed. Using Na^+–SAPO-37 as catalyst the results are similar to the blank experiment except for the H_2O_2 consumption which increases to 15%. In the presence of Na^+–FeAPSO-37 the conversion increases only slightly to 2%, but H_2O_2 is almost completely consumed. The Na^+–CrAPSO-37 is more active giving a conversion of 5.6% and a 70% of H_2O_2 consumption at 100°C, in spite of its low metal content (0.3% of framework T-positions) in relation to the iron catalyst (2.0%). At 80°C the conversion decreases to 4.8% and the H_2O_2 consumption to 40%. Interestingly, when the same reactions shown in Table 1 are performed in the presence of TBHP as oxidant we do not observe the formation of any product. The benzene oxidation catalyzed by Na^+–CrAPSO-37, using H_2O_2 as oxidant, was performed in the presence of different solvents. Among the solvents tested, the following activity was observed: acetonitrile > *tert*-butanol ∼ acetone > methanol. It has been shown [8] that these solvents act as trapping agents for hydroxyl radicals ($^•OH$), being effective in the following order: methanol > acetone ∼ *tert*-butanol > acetonitrile Thus, the catalytic activity decreases when the reactivity of solvent with hydroxyl radicals increases. This suggests that the hydroxyl radicals play an important role in the reactions and that the mechanism of oxidation is probably similar to the hydroxylation of benzene by Fenton reagent [8]. The lack of activity of TBHP in benzene oxidation could

be explained by the formation of *tert*-butoxy radicals, which are not sufficiently energetic to react with benzene [9].

Curiously, when as-synthesized CrAPSO-37, containing 1.4 TPA^+ ions per supercage [6], is used as catalyst in the benzene oxidation at 100°C in the presence of H_2O_2 as oxidant, the results are very similar to the ones obtained with Na^+–CrAPSO-37. This suggest that: (i) TPA^+ ions are removed during the reactions, or (ii) the reaction is occurring mainly on the external surface of the catalyst or the framework collapses during the reactions, or (iii) the transition metal is leaching to the solution and the reactions is mainly homogeneous. The thermogravimetric analyses of as-synthesized CrAPSO-37 used in benzene oxidation at different reaction times are shown in Fig. 1. For the as-synthesized CrAPSO-37 (Thermogram A), the weight loss occurs in three steps: the first between 25–200°C due to desorption of water, the second step, between 200–450°C, due to the thermal decomposition of TPA^+ ions occluded in the supercages and the third, between 450–650°C, corresponding to the decomposition of TMA^+ ions in the sodalite cages [6]. Thermogram B shows that after 1 h of reaction time the major part of TPA^+ ions was removed from supercages, suggesting that the reaction could be occurring inside the channels. However, the other hypotheses outlined above for the catalytic activity, can not be ruled out yet.
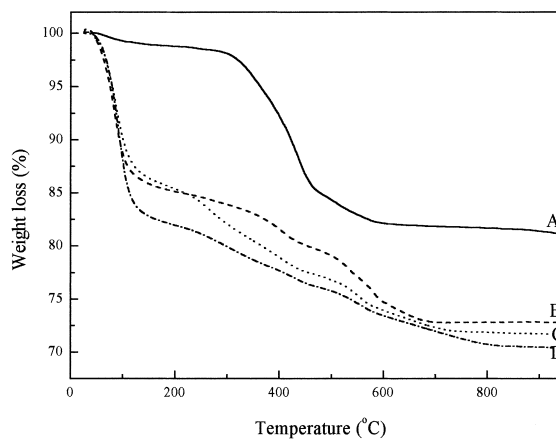

Fig. 1. Thermogravimetric analyses (A) as-synthesized CrAPSO-37; (B) A after 1 h; (C) A after 24 h of reaction time and (D) Na^+–CrAPSO-37.

The catalysts were also tested in the cyclohexane oxidation using TBHP as oxidant. In the absence of a catalyst a conversion of 0.9% was observed and cyclohexylperoxide (CHP) is the principal product formed which is not decomposed under the reaction conditions [10]. The results obtained in the presence of FeAPSO-37 and Na$^+$–FeAPSO-37 are very similar to the blank experiment revealing that iron(III) is not active in the formation nor in the decomposition of CHP. As already observed in benzene oxidation with H$_2$O$_2$, the results obtained for as-synthesized CrAPSO-37 and Na$^+$–CrAPSO-37 in cyclohexane oxidation are very similar. After 24 h at 100°C, a conversion of 1.4% and an one/ol ratio of 8 were obtained in the analyses performed in the absence and in the presence of triphenylphosphine [10]. This indicates that chromium acts in the formation and decomposition of CHP, as described by others authors [11]. On the other hand, the thermogravimetric analysis of as-synthesized CrAPSO-37, after 24 h at 100°C, shows that the major part of TPA$^+$ ions remains in the supercages, contrary to the observed when H$_2$O$_2$ is used as oxidant. These facts could suggest that the reactions are occurring on the external surface of the crystallites. This is unlikely because the crystallite dimensions are very large (20–30 μm) and the quantity of chromium is small [6]. Another possibility is that the catalyst framework collapses during the reactions. The X-ray diffractogram analyses show that there is a crystallinity decrease but the structure is maintained in the presence of H$_2$O$_2$ and TBHP as oxidant. Thus, leaching of metal to the solution and, consequently, the occurrence of catalysis in homogeneous phase is the most probable hypothesis.

The leaching tests were made according to the procedure described by Sheldon and Lempers [12] which suggest that the definitive test for heterogeneity is to filter the catalyst during the course of the reaction at reaction temperature and allow the filtrate to react further. A conversion of benzene of 1.8% was obtained after 2 h in the presence of Na$^+$–CrAPSO-37 as catalyst and H$_2$O$_2$ as oxidant. After this period, the catalyst was separated from the solution at 80°C and the filtrate was maintained at this temperature for another 22 h. The quantity of phenol obtained in the filtrate was very similar to that obtained in the presence of the catalyst, showing that the reaction occurs in the homogeneous phase catalyzed by chromium leached from

Table 2
Recycling of Na$^+$–CrAPSO-37 (5 mmol benzene, 5 mmol H$_2$O$_2$ (30% in water), 3 ml acetonitrile, 20 mg catalyst, 100°C, 24 h each cycle)

Cycle	Cr (%)	Conversion (%)	Phenol (mmol)	H$_2$O$_2$ consumed (%)	Crystallinity (%)
1	0.30	6.0	0.30	78	100
2	0.18[a]	5.2	0.26	60	50
3	n.d.[b]	4.6	0.23	50	n.d.[b]
4	0.05[a]	4.0	0.20	36	50

[a] % of chromium after first and fourth 4 cycles.
[b] not determined.

the catalyst. The leaching of transition metal from molecular sieves is probably a result of solvolysis of metal–oxygen bonds by polar molecules such as water or peroxides [2,13,14]. The leaching of chromium was also observed for cyclohexane oxidation with TBHP using Na$^+$–CrAPSO-37.

The recycling experiments were performed using Na$^+$–CrAPSO-37 as catalyst in benzene oxidation with H$_2$O$_2$ as oxidant (Table 2). The conversion decreases with each cycle and is 67% of the original value after four cycles. The quantity of H$_2$O$_2$ consumed also decreases with each cycle and is ca. 50% of the original in the fourth cycle. After the fourth cycle the quantity of chromium present in the catalyst is only 17% of the original, while the quantities of silicon, aluminum and phosphorus are essentially the same. The crystallinity decreases to 50% after the first cycle and does not change until the fourth cycle. These results show that small quantities of chromium(III) are leached from the catalyst during the reactions, even though the MeAPSO-37 framework is stable under reaction conditions. As also observed by Sheldon and Lempers [12], small quantities of chromium, added in form of a salt to the solution, are sufficient to explain the catalytic results.

4. Conclusions

The as-synthesized CrAPSO-37 as well as the exchanged Na$^+$–CrAPSO-37 are active in the liquid phase oxidation of benzene and cyclohexane. In the as-synthesized catalyst the TPA$^+$ ions are removed from the supercages during the reactions in the presence of H$_2$O$_2$ as oxidant, which was not observed

when TBHP was used. The presence of TMA$^+$ ions in the sodalite cages maintains the framework stable under reaction conditions, but leaching of small quantities of chromium occurs. The leached chromium is responsible for the catalytic activity observed.

Acknowledgements

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