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# Cyclohexane Oxidation Catalyzed by Titanium Silicalite (TS-1): Overoxidation and Comparison with Other Oxidation Systems

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**At 100°C cyclohexanol and cyclohexanone, obtained in the TS-1 catalyzed oxidation of cyclohexane, are further oxidized in uncatalyzed and TS-1 catalyzed reactions. Cyclohexanol is very selectively oxidized to cyclohexanone inside the porous system of TS-1 and unselectively oxidized to several oxidation products on the external surface. This unselective oxidation can be suppressed by the addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT), which does not enter the molecular sieve pore system and which efficiently reduces uncatalyzed oxidation. Cyclohexanone oxidation is mostly uncatalyzed, forming predominantly dicarboxylic acids, and is not influenced by BHT. The products of the TS-1 catalyzed cyclohexanone oxidation are partially retained in the porous system, thus explaining the deactivation of the catalyst. Comparison with other systems shows that the turnover frequency of the TS-1 catalyzed cyclohexane oxidation is very similar to that of the radical-chain process, thus suggesting that the rate-determining step of the TS-1 catalyzed reaction is also the homolytic cleavage of a C–H bond.** © 1995 Academic Press, Inc.

## INTRODUCTION

Titanium silicalite (TS-1) catalyzes a variety of synthetically important oxidations with 30% aqueous hydrogen peroxide under mild conditions (1). Examples include olefin epoxidations, phenol hydroxylation, cyclohexanone ammoxidation with $NH_3/H_2O_2$, and alcohol oxidations (2). Alkane oxidations catalyzed by TS-1 have also been extensively studied showing that TS-1 can discriminate between linear and branched or cyclic alkanes (3). Although no extensive mechanistic study has been performed for alkane oxidations on TS-1, it has been postulated that the oxidation proceeds through a homolytic mechanism that gives rise to radical intermediates (4).

In a recent publication (5) we showed that TS-1 prepared as described by Enichem researchers (6) gives the most active catalyst for cyclohexane oxidation. Among the tested solvents, acetone gives the best results and temperatures as high as 150°C may be used in order to improve the activity, although $H_2O_2$ decomposition is also favored. The best turnover number obtained was not much higher than 100, possibly due to obstruction of the TS-1 channels by side-products. These side-products can be removed by calcination which allows recycling of TS-1 without loss of activity (5).

In order to understand which side-products are formed we compare in this work the TS-1 catalyzed oxidation of cyclohexane with those of cyclohexanol and cyclohexanone and have determined the initial oxidation rates. These results are compared with those of other cyclohexane oxidation systems, thus giving support for an oxidation mechanism involving the homolytic cleavage of a C–H bond.

## METHODS

### *Synthesis of TS-1*

TS-1 was synthesized hydrothermally using the procedure described by Clerici *et al.* (6). Tetraethylorthosilicate (Aldrich), tetraethylorthotitanate (Aldrich), tetrapropylammonium hydroxide solution (1 *M*, Aldrich), and distilled deionized water were mixed in a 1:0.03:0.45:35 molar ratio forming a clear solution, which was hydrolyzed for 3 h at 60°C. This sol was then crystallized in a Teflon-lined autoclave at 175°C for 1 day. Filtration of TS-1 was preceded by the addition of a 10% aqueous solution of ammonium acetate and followed by washing with large amounts of water. The product was initially heated to 550°C under argon for 2 h and then calcined in dry oxygen for 4 h at the same temperature. The TS-1 sample obtained was characterized by powder X-ray diffraction, infrared, and UV–Vis diffuse reflectance spectroscopies. The titanium content of the samples was determined by X-ray fluorescence. The crystal size was determined by scanning electron microscopy.

### *Catalytic Reactions*

The reactions were performed in a Teflon-lined 30 ml stainless-steel autoclave equipped with a magnetic stirrer.

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The ratio of acetone (Merck, p.a.)/substrate (Aldrich)/ $H_2O_2$ (30% in $H_2O$, Merck, p.a.) was 15/2/2 (v/v/v) giving a total of 19 ml; 0.10 g of TS-1 and, in some reactions, 0.25 g of 2,6-di-*tert*-butyl-4-methylphenol (BHT, Shell Ionol CP) were added. The autoclave was closed and submerged in a thermostated oil bath at 100°C, where it was maintained for the indicated reaction time plus 30 min, time considered necessary for the system to achieve reaction temperature. Blank experiments were performed under the same conditions without addition of TS-1. In some experiments the substrate was a mixture of cyclohexane plus ca. 20 mol% of cyclohexanol or cyclohexanone. After the reactions, the oxygen formed was vented-off, the autoclave was opened, and the reaction mixture filtered.

### *Analysis*

Approximately 80 mg of cyclooctane (internal standard, weighed with precision of 0.1 mg) was added to the reaction mixture, which was then analyzed with a CG 37 gas chromatograph, equipped with a 4 m × 3.2 mm o.d. packed column of Carbowax 20M on Chromosorb W-HP, coupled to a flame ionization detector. The temperature was programmed at 10°C $min^{-1}$ from 70 to 170°C at which it was maintained for 10 min. Cyclohexane (ane), cyclohexanone (one) and cyclohexanol (ol) were quantified using calibration curves obtained under the same chromatographic conditions.

The overoxidation products were identified by GC-MS analysis after esterification of the free acids with ethanol/ sulfuric acid. The ethyl ether extract was injected into a HP 5980 gas chromatograph equipped with a 12.5 m × 0.33 $\mu$m HP-1 column, coupled to a HP 5970B mass detector. After 10 min at 40°C the temperature was programmed at 10°C $min^{-1}$ from 40 to 250°C. The overoxidation products were semiquantified by comparison of their peak areas with those of cyclohexanone and cyclohexanol which had been quantified before by gas chromatography.

The amount of $H_2O_2$ consumed ($H_2O_2$ cons.) was determined by iodometric titration of the unreacted portion. The efficiencies with respect to $H_2O_2$ ($H_2O_2$ eff.) were calculated taking into account that 1 mol of $H_2O_2$ is needed to produce 0.5 mol of cyclohexanone or 1 mol of cyclohexanol, respectively. The amount of oxidized products given in the Tables have been corrected for blanks. The turnover numbers (TN) are given as mmol of substrate oxidized per mmol of titanium present in the catalyst. The initial rates of oxidation were estimated from plots showing the amount of oxidized products as a function of time.

## RESULTS AND DISCUSSION

The $SiO_2/TiO_2$ ratio in the TS-1 sample obtained is 44 (2.93 wt% $TiO_2$) which is very close to the value of 46 (2.8 wt% $TiO_2$) reported by Clerici *et al.* (6). The powder X-ray diffractogram shows a typical pattern for a highly crystalline zeolite having MFI structure (7). Analysis of the IR bands at 450 and 550 $cm^{-1}$ confirms these results; the spectrum shows the characteristic band of —(Si—O—Ti)— groups at 978 $cm^{-1}$ (8). The UV–Vis diffuse reflectance spectrum shows no band between 300 and 350 nm, demonstrating that anatase is not present (9). The scanning electron micrograph shows that the particles have a uniform size of approximately 0.4 $\mu$m with a prismatic shape.

The blank experiments of cyclohexane oxidation at 100°C show that after 24 h only 10% of $H_2O_2$ is decomposed and that only very small amounts of cyclohexanone (0.05 mmol) and cyclohexanol (0.04 mmol) are formed (Table 1). Since at higher temperatures decomposition was more pronounced, all the experiments were performed at 100°C. On the other hand, approximately 0.5 mmol of cyclohexylacetone is formed, probably by the abstraction of hydrogen atoms by OH radicals produced in the thermal decomposition of $H_2O_2$ (10). Addition of BHT totally suppresses the formation of cyclohexylacetone.

The results obtained in the oxidation of cyclohexane are shown in Table 1 as a function of the reaction time. After 4 h almost half of the $H_2O_2$ has been consumed and 39% of the oxidation products (one + ol) are already formed. $H_2O_2$ consumption and formation of oxidation products increase almost linearly between 4 and 24 h, when 98% of the $H_2O_2$ has been consumed. The turnover number after 24 h is 76 while the efficiency with respect to $H_2O_2$ is only 22%. The mass balance closes at 98% showing that, besides the cyclohexylacetone already observed in the blank experiments, no major amounts of side-products or overoxidation products have been formed.

We suspected that the increase of the one/ol ratio, observed during cyclohexane oxidation (Table 1), is due to further oxidation of cyclohexanol under reaction conditions. Blank experiments show that after 24 h 2.29 mmol of cyclohexanol are oxidized in an uncatalyzed reaction giving, 1.70 nmol of cyclohexanone (Table 2). This reaction can be efficiently suppressed by the addition of BHT as only 0.40 mmol of cyclohexanol are oxidized, giving 0.19

**TABLE 1**

**Time Dependence of Cyclohexane Oxidation**

| System | *t* (h) | one (mmol) | ol (mmol) | one/ol ratio | TN | $H_2O_2$ cons. (%) | $H_2O_2$ eff. (%) |
|---|---|---|---|---|---|---|---|
| Blank | 24 | 0.05 | 0.04 | 1.25 | — | 10 | 1 |
| Blank/BHT | 24 | 0.05 | 0.04 | 1.25 | — | 10 | 1 |
| TS-1 | 4 | 0.46 | 0.64 | 0.72 | 30 | 48 | 8 |
| TS-1 | 8 | 0.73 | 0.93 | 0.78 | 45 | 64 | 12 |
| TS-1 | 16 | 1.01 | 1.19 | 0.85 | 59 | 79 | 16 |
| TS-1 | 24 | 1.61 | 1.22 | 1.32 | 76 | 98 | 22 |
| TS-1/BHT | 24 | 0.99 | 1.81 | 0.55 | 76 | 99 | 19 |

*Note.* Reaction conditions: 0.10 g TS-1, 0.25 g BHT, 18.5 mmol cyclohexane, 20 mmol $H_2O_2$ (30% in $H_2O$), 15 ml acetone, and 100°C.

TABLE 2

Time Dependence of Cyclohexanol Oxidation

| System | *t* (h) | ol cons. (mmol) | one formed (mmol) | TN | $H_2O_2$ cons. (%) | $H_2O_2$ eff. (%) |
|---|---|---|---|---|---|---|
| Blank | 24 | 2.29 | 1.70 | — | 12 | 11 |
| Blank/BHT | 24 | 0.40 | 0.19 | — | 10 | 2 |
| TS-1 | 4 | 3.58 | 2.98 | 97 | 36 | 18 |
| TS-1 | 8 | 5.64 | 4.33 | 152 | 58 | 28 |
| TS-1 | 16 | 6.90 | 5.52 | 186 | 70 | 35 |
| TS-1 | 24 | 8.10 | 6.57 | 219 | 99 | 41 |
| TS-1/BHT | 24 | 4.70 | 4.70 | 127 | 98 | 24 |

*Note.* Reaction conditions: 0.10 g TS-1, 0.25 g BHT, 18.5 mmol cyclohexanol, 20 mmol $H_2O_2$ (30% in $H_2O$), 15 ml acetone, and 100°C.

TABLE 3

Time Dependence of Cyclohexanone Oxidation

| System | *t* (h) | one cons. (mmol) | TN | $H_2O_2$ cons. (%) | $H_2O_2$ eff. (%) |
|---|---|---|---|---|---|
| Blank | 24 | 2.76 | — | 15 | 14 |
| Blank/BHT | 24 | 2.58 | — | 15 | 13 |
| TS-1 | 4 | 0.57 | 15 | 42 | 3 |
| TS-1 | 8 | 0.89 | 24 | 65 | 5 |
| TS-1 | 16 | 1.25 | 34 | 82 | 6 |
| TS-1 | 24 | 1.95 | 53 | 100 | 10 |
| TS-1/BHT | 24 | 2.13 | 58 | 98 | 11 |

*Note.* Reaction conditions: 0.10 g TS-1, 0.25 g BHT, 18.5 mmol cyclohexanone, 20 mmol $H_2O_2$ (30% in $H_2O$), 15 ml acetone, and 100°C.

mmol of cyclohexanone, under the same conditions. The results of the TS-1 catalyzed cyclohexanol oxidation as a function of reaction time are shown in Table 2 and have already been corrected for the uncatalyzed reaction. Cyclohexanone formation is 45% after 4 h and then increases almost linearly, reaching a maximum of 6.57 mmol after 24 h, when 99% of the $H_2O_2$ is consumed. The turnover number, based on the amount of cyclohexanol oxidized, is above 200, showing that cyclohexanol oxidation is much faster than cyclohexane oxidation. The efficiency with respect to $H_2O_2$ reaches 41% for the catalyzed reaction and is 52% for the overall reaction, when the uncatalyzed reaction is taken into account.

The cyclohexanol oxidation reaction produces, besides cyclohexanone (81% selectivity), 2-hydroxycyclohexanone (1%), 4-hydroxycyclohexanone (3%), 1,2-cyclohexanedione (2%), ε-caprolactone (1%), and adipic acid (6%), giving a total of 94% of the cyclohexanol consumed. If catalytic cyclohexanol oxidation is performed in the presence of BHT, only 4.70 mmol of cyclohexanol is consumed giving cyclohexanone with 100% of selectivity. This indicates that TS-1 probably has two types of active centers for cyclohexanol oxidation: one which is very selective and inside the porous system and another on the external surface which is very unselective and can be blocked by BHT.

Cyclohexanone is also easily oxidized in an uncatalyzed reaction at 100°C. Starting from 18.5 mmol, 2.76 mmol of cyclohexanone has been consumed after 24 h in the absence and 2.58 mmol in the presence of BHT (Table 3), which demonstrates that BHT has nearly no influence on the uncatalyzed cyclohexanone oxidation. The amount of cyclohexanone oxidized by TS-1 is lower and is shown in Table 3 as a function of time. After 24 h, when all $H_2O_2$ is consumed, a total of 4.71 mmol of cyclohexanone has been oxidized, of which 2.76 mmol is due to the uncatalyzed reaction and only 1.95 mmol to the reaction catalyzed by TS-1. As this oxidation is not influenced by BHT (Table 3), we can not decide if the active centers of TS-1 are on the external surface or in the porous system. The oxidation products of cyclohexanone are adipic acid (38%), glutaric acid (4%), succinic acid (2%), caproic acid (3%), ε-caprolactone (9%), 2-hydroxycyclohexanone (5%), and 4-hydroxycyclohexanone (3%), giving a total of 64%. These products are mostly formed by the uncatalyzed reaction as the product compositions of the uncatalyzed and the catalyzed reactions are very similar.

We conclude that cyclohexane is oxidized by TS-1 to a mixture of cyclohexanone and cyclohexanol. Cyclohexanol is further oxidized rapidly to cyclohexanone and overoxidation products while cyclohexanone is slowly overoxidized, mostly to organic acids, which are in part retained in the porous system, deactivating the catalyst. As the uncatalyzed cyclohexanol oxidation can be suppressed by BHT, we performed the catalyzed cyclohexane oxidation in the presence of BHT and found that cyclohexanone and cyclohexanol are obtained with the same turnover number of 76, as described in Table 1, but with an one/ol ratio of 0.55. Since even in the presence of BHT some of the cyclohexanol is oxidized to cyclohexanone, we tried to estimate the initial one/ol ratio. Considering an average of 0.9 mmol of cyclohexanol present in the reaction mixture and that, in agreement with Table 2, 25% of the cyclohexanol has been further oxidized to cyclohexanone, we estimate that 0.23 mmol of the cyclohexanone comes from cyclohexanol oxidation. This would give an initial one/ol

TABLE 4

Cyclohexane Oxidation Behavior in the Presence of Cyclohexanol and Cyclohexanone

| ol added (mmol) | one added (mmol) | one (mmol) | ol (mmol) | TN | $H_2O_2$ eff. (%) |
|---|---|---|---|---|---|
| 3.38 | — | 3.55 | 2.66 | 172 | 32 |
| — | 3.57 | 5.19 | 1.23 | 77 | 22 |

*Note.* Reaction conditions: 0.10 g TS-1, 18.5 mmol cyclohexane, 20 mmol $H_2O_2$ (30% in $H_2O$), 15 ml acetone, 100°C, and 24 h.

TABLE 5

**Initial Rates and Turnover Frequencies of Different Oxidation Systems**

| System/substrate | $T$ (°C) | Catalyst | one/ol ratio | Catalyst conc. (mmol liter$^{-1}$) | Initial rate (mmol liter$^{-1}$ h$^{-1}$) | TF (h$^{-1}$) |
|---|---|---|---|---|---|---|
| TS-1/ane | 100 | TS-1 | 1.32 | 1.9 | 16 | 8.4 |
| TS-1/ol | 100 | TS-1 | — | 1.9 | 52 | 27.4 |
| TS-1/one | 100 | TS-1 | — | 1.9 | 8 | 4.2 |
| Radical chain/ane[a] | 130 | Cobalt(II) stearate | 0.86 | 5.6 | 480 | 85.7 |
| Gif$^{IV}$/ane[b] | 20 | $[Fe(bipy)_3]Cl_2$ | 8.60 | 0.24 | 29 | 120.8 |
| GoAgg$^{II}$/ane[c] | 20 | $FeCl_3$ | 15.60 | 28.0 | 15 | 0.5 |
| GoAgg$^{III}$/ane[d] | 20 | $FeCl_3$/picolinic acid | 6.60 | 28.0 | 303 | 10.8 |

[a] Calculated from data of Ref. (11).
[b] Calculated from data of Ref. (12).
[c] Calculated from data of Ref. (13).
[d] Calculated from data of Ref. (14).

ratio of 0.37 which is in the same range as observed for industrial cyclohexane oxidation by the radical-chain mechanism, initially 0.35 and increasing during the reaction (11).

In order to understand cyclohexane oxidation in the presence of cyclohexanol and cyclohexanone, we performed two reactions and the results are shown in Table 4. In the presence of cyclohexanol the total amount of oxidized products corresponds to the amount of products obtained in the cyclohexane oxidation plus the amount of cyclohexanol added. This means that cyclohexane oxidation is not influenced by cyclohexanol oxidation. On the other hand, the amount of cyclohexanol observed in the reaction mixture is smaller than that initially added which shows that cyclohexanol rapidly undergoes further oxidation. Cyclohexane oxidation in the presence of cyclohexanone forms the same amount of cyclohexanone and cyclohexanol reported in Table 1, plus the cyclohexanone initially added, which shows that overoxidation of cyclohexanone is much slower.

To confirm these observations we estimated the initial rates of cyclohexane, cyclohexanol, and cyclohexanone oxidation using plots obtained from the data of Tables 1–3. These initial rates are shown in Table 5, along with the initial rates obtained from data of radical-chain (11) and Gif-type (12–14) cyclohexane oxidations. The initial rates confirm that cyclohexanol is much more rapidly oxidized than cyclohexane and that overoxidation of cyclohexanone is rather slow. In order to compare initial rates of cyclohexane oxidation by TS-1 with other systems, the initial rates were divided by the concentration of the catalysts, thus giving the turnover frequency (TF) of the reactions. These turnover frequencies show that the Gif$^{IV}$ system is already very rapid at 20°C, while the GoAgg$^{II}$ system is slow but can be accelerated by the addition of picolinic acid (GoAgg$^{III}$ system) giving a good turnover frequency of 11 h$^{-1}$. TS-1 and radical chain oxidations of cyclohexane are only possible at higher temperatures. Assuming an activation energy of approximately 100 kJ mol$^{-1}$ (15), the initial rate of cyclohexane oxidation by the radical chain process would be almost 10 times smaller at 100°C than at 130°C, thus giving a turnover frequency similar to that observed in the TS-1 catalyzed oxidation. These similar turnover frequencies at the same temperature indicate that the rate determining step of the radical chain oxidation and the TS-1 oxidation might be the same. Furthermore, the one/ol ratio of the TS-1 catalyzed reaction is similar to that of the radical-chain process and much smaller than that observed in the Gif-type oxidations. Since the radical-chain oxidation is initiated by the homolytic cleavage of a C–H bond (15), we believe, in agreement with the observations of other authors (3, 4, 16), that this is also the rate-determining step of the TS-1 oxidation. On the other hand, the Gif systems appear to form cyclohexyl-iron(V) complexes which interact with molecular oxygen to form the products (17, 18).

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