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Citation for published version (APA):

DOI:
10.1016/0926-860X(93)80158-M

Document status and date:
Published: 01/01/1993

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Oxidation of linear alcohols with hydrogen peroxide over titanium silicalite 1

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(Received 19 April 1993, revised manuscript received 19 July 1993)

Abstract

In this paper different parameters affecting the oxidation of alcohols with hydrogen peroxide are described. The influence of the amount and of the crystallite size of the catalyst, as well as the concentrations of hydrogen peroxide and substrate have been studied. The influence of the reaction temperature, the chain length of the alcohol (C6, C7, C8 and C9) and the position of the alcohol group (α, β or γ) on the reaction rate has also been investigated. As a result of this study it can be reported that the reaction is first order with respect to the amount of catalyst and the hydrogen peroxide concentration, and zero order in alcohol concentration. The activation energy for the oxidation of 2-octanol is 71 kJ/mol. The particle size has a considerable effect on the reaction rate; larger particles result slower reaction. There is a remarkable effect of the chain length on the reaction rate (C6 < C7 < C8 > C9) and the position of the hydroxyl group has a strong effect on the activity of TS-1 (β > α > γ). The crystallite size effect can be explained by means of diffusion limitations, as could be illustrated by Weisz modulus calculations. The observed difference in activity between β and γ alcohols can not be related to differences in diffusion (single component diffusion of β and γ alcohols show little difference) and therefore transition state restrictions of the alcohols in the pores of the TS-1 may be a possible explanation for this effect.

Key words: alcohol oxidation; diffusion limitations; titanium silicalite 1; transition state selectivity; TS-1; zeolites

INTRODUCTION

Titanium silicalite-1 (TS-1) is known as a catalyst for oxidation of various organic substrates. A number of patents and papers about oxidation of aromatics [1–3], alkanes [4,5], alkenes [6–8] and alcohols [9,10] are known. Most of these oxidation reactions have already been studied extensively by a number of research groups. However, the oxidation of alcohols has attracted...
little attention until now. Although this reaction is commercially less im-
portant, it can probably give additional information about some mechanistic as-
pects of liquid-phase reactions in titanium silicalite-1.

Reports concerning the oxidation of simple linear alcohols are scarce. how-
ever, some information has been published on zirconium [11] and vanadium 
[12] as catalysts for alcohol oxidation. Literature about zirconium as an ox-
dizing centre indicates oxidation of primary alcohols and hardly any oxidation 
of secondary alcohols; while vanadium catalysts perform best in the oxidation 
of secondary alcohols. The exact reason for this behaviour was not mentioned 
in these papers. In general, primary alcohols show lower activity than second-
ary alcohols. Large differences between the oxidation of the $\beta$ and the $\gamma$ position 
are not expected. Any detailed studies on the oxidation of linear alcohols with 
zeolitic catalysts have not been reported previously.

To obtain mechanistic information about the oxidation of different alcohols 
in TS-1 with hydrogen peroxide we initiated a more detailed study. Special 
attention was paid to the effect of mass transfer and chemical reactivity by 
varying the chain length and the position of the hydroxyl group.

EXPERIMENTAL

The catalytic reaction

The standard reaction was performed in a 100 ml stirred batch reactor (stir-
ring rate > 800 rpm) using 10 ml acetone, 10 ml alcohol and 0.5 g of catalyst 
at 70°C. At the beginning of the reaction 3 ml of 35 wt.-% $\text{H}_2\text{O}_2$ was added 
instantaneously to the reaction mixture, and the reaction was monitored by 
taking small samples (0.2 ml) at different times. Due to the different molecular 
weights of the alcohols the maximum conversion varies from 45% for 2-hex-
anol to 60% for 2-nonanol. The samples were filtered and cooled before they 
were analyzed by gas chromatography (GC). For GC analysis a 6000 VEGA 
series 2 GC with autosampler from Carlo Erba, equipped with a capillary DB-
1 column from Chrompack was used. The detector temperature was 250°C and 
the injector temperature was 280°C. The column temperature was varied from 
100 to 150°C depending on the alcohol analyzed. The decrease in hydrogen 
peroxide concentration was measured by standard iodometric titration.

The blank reactions

Blank reactions were performed in the same way as the catalytic reactions 
with the exception that no catalyst was added. These experiments were per-
formed to verify whether homogeneous reactions, or even oxidations in the 
injector of the GC took place.
The preparation of the TS-1 samples

The TS-1 materials were prepared according to a slightly modified procedure as described in the original patent of Enichem [13] and has already been described in detail elsewhere [14]. The products obtained were washed, dried and finally calcined at 550 °C in laboratory air for three hours prior to their use as catalysts.

The characterization of the TS-1 samples

The crystallization products were characterized by a number of different techniques. To the catalyst used we applied: X-ray powder diffraction (XRD) to check the crystallinity, infrared (IR) spectroscopy to quantify the characteristic peak at 960 cm\(^{-1}\), \(^{29}\)Si magic angle spinning nuclear magnetic resonance (MAS NMR) to check if a shoulder was present on the high field site of the Q4 signal, diffuse reflectance electron absorption spectroscopy (DREAS) to check whether or not TiO\(_2\) was present, atomic absorption spectroscopy (AAS) to determine the titanium content, and scanning electron microscopy (SEM) to determine particle sizes and morphology of the different samples. The description of the equipment used and the results of these different characterization techniques have been presented elsewhere [15]. All these techniques together with a catalytic test (an activity test in the hydroxylation of phenol) made it clear that the TS-1 samples were of high quality (at least comparable to the EUROTS-1 [16]).

RESULTS AND DISCUSSION

The blank reactions

The results of blank reactions in which 1-octanol, 2-octanol, 3-octanol, 2-heptanol and 2-hexanol were used as substrate are shown in Fig. 1. The alcohols were oxidized to the corresponding aldehydes and ketones, without subsequent formation of carboxylic acids. Fig. 1 suggests that in all cases an instantaneous reaction took place by which a certain amount of the starting alcohol was oxidized, and that this reaction stopped immediately thereafter. This behaviour is even more peculiar if the hydrogen peroxide consumption is measured separately by titration; while GC analysis showed that products were formed, iodometric titration showed no hydrogen peroxide consumption. The explanation for the initial formation of oxidation products, and no further reaction in spite of the presence of hydrogen peroxide, is the same as we gave for the formation of paraquinone from hydroquinone in ref. 17. It is expected that the ketones and aldehydes are formed in the injector of the GC at the high temperatures used. This explanation is supported by the results of the direct
Fig. 1. Blank reactions of different alcohols. (□) 2-Hexanol, (+) 2-heptanol, (◇) 1-octanol, (△) 2-octanol, (×) 3-octanol.

GC analysis of mixtures of 10 ml acetone and 10 ml 2-octanol to which different amounts of hydrogen peroxide were added (see Fig. 2). It is clear from this figure that the amount of products formed is directly related to the amount of hydrogen peroxide added. Even if the injection temperature is reduced to 150°C, a certain amount of alcohol is still oxidized.

In the subsequent experiments the conversion in the blank reaction, which is related to the amount of hydrogen peroxide present in the system, was subtracted from the measured data. In this way only effects which are related to the catalyst were considered. By subtracting this blank reaction, the amount of products which were already present in the starting material, as impurity, were also eliminated.

**The influence of crystallite size**

To study the possibility of mass transport problems during the reaction, five batches of TS-1 with different crystallite sizes (see Table 1) were tested in the oxidation of 2-octanol at 70°C. The results of these tests are shown in Fig. 3. The crystallite size has a considerable effect on the activity of the catalyst. Two reasons can be given to explain the influence of the crystallite size. First, the reaction can take place mainly at the outer surface of the crystallites, and
because smaller crystallites have a larger specific surface area this will result in a higher activity. The second reason could be that the reaction is restricted by pore diffusion limitations. A low activity of non-calcined samples, a strong decrease of activity after preadsorption of a strongly adsorbed organic substrate, a very low reaction rate in reactions involving large substrates, and no activity with oxidants larger than hydrogen peroxide, suggest that diffusion limitations occur [15]. To verify if pore diffusion limitation is responsible for the observed differences in activity as function of the crystallite size, the Weisz theory [18–20] can be applied to the system under consideration. We have already reported the application of this method in a previous paper [15] and so here we will present only a short description of the method. From the results presented in Fig. 3, it is possible to obtain the initial reaction rate ($r_0$) on the five catalysts, while information about crystallite size ($d$) and diffusion path length ($p$) [21] can be obtained by SEM. It is then possible to calculate the relative Weisz modulus ($\phi'$) and a relative catalyst efficiency ($\eta'$), which can be plotted as presented in Fig. 4. In this figure the theoretical relation between the Weisz modulus and catalyst efficiency is also indicated. The fact that the line connecting the calculated points is almost parallel to the theoretical curve indicates the validity of this method and makes it also possible to estimate the real values of the Weisz modulus ($\phi$) and catalyst efficiency ($\eta$) by a transla-

Fig. 2. Blank reaction as function of hydrogen peroxide concentration. Injector temperature (□) 280°C, (+) 150°C.
Fig. 3. Influence of crystallite size on the reaction rate of 2-octanol oxidation. (□) Sample 1, (+) sample 2, (◊) sample 3, (△) sample 4, (×) sample 5.

ation of the relative curve to the theoretical curve. The result of these operations are listed in Table 1. From the obtained real values of the Weisz modulus it is possible to calculate the effective diffusion coefficient of 2-octanol under the conditions applied during the reaction. This results in a value of $3 \cdot 10^{-17}$ m$^2$/s (at 70°C). Although this value will not be very accurate, it is in the same order of magnitude as the diffusion coefficients that are reported in the literature for comparable molecules like n-octanol and n-heptanol in H-ZSM-5 [22]. Appropriate methods for determining $D_{eff}$ during catalytic experiments are not available until now. Therefore it is not possible to check these data with literature values.

To eliminate influences of diffusion limitation, sample no. 1 was used as catalyst for all other experiments.

**Influence of the amount of catalyst**

The oxidation of 2-octanol was studied under standard conditions with the exception that the amount of catalyst was changed from 0.5 to 0.25 and 0.10 g per reaction. The results of these experiments (Fig. 5a) show that the initial reaction rate increases almost linearly with increasing amount of catalyst, suggesting a first order dependency with respect to the amount of catalyst. This
Fig. 4. Catalyst efficiency versus Weisz modulus. (●) Theoretical curve, (+) relative value, (◇) real value.

TABLE 1

Crystallite size and average diffusion path length \( (p) \) as deduced from SEM pictures \([21]\), as well as the (relative) Weisz modulus \( (\phi' \text{ and } \phi) \) and the (relative) catalyst efficiency \( (\eta' \text{ and } \eta) \) of five TS-1 samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Initial reaction rate ( r_0 ) (mol/m(^3) min)</th>
<th>Average crystallite size (( \mu )m)</th>
<th>Diffusion path length ( (p) ) (( \mu )m)</th>
<th>( \phi' )</th>
<th>( \eta' )</th>
<th>( \phi )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.7</td>
<td>0.2</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>0.27</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>18.4</td>
<td>2.5</td>
<td>0.25</td>
<td>4.3</td>
<td>0.68</td>
<td>1.16</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>5.28</td>
<td>4</td>
<td>1.0</td>
<td>13.4</td>
<td>0.20</td>
<td>5.3</td>
<td>0.17</td>
</tr>
<tr>
<td>4</td>
<td>6.36</td>
<td>5</td>
<td>0.75</td>
<td>19.7</td>
<td>0.24</td>
<td>3.6</td>
<td>0.21</td>
</tr>
<tr>
<td>5</td>
<td>1.67</td>
<td>10</td>
<td>3.5</td>
<td>76</td>
<td>0.063</td>
<td>20.7</td>
<td>0.056</td>
</tr>
</tbody>
</table>

Dependency is more clear (see Fig. 5b) if the experiments are repeated under more dilute conditions (30 ml acetone instead of 10 ml).
Fig. 5. (a) Influence of the amount of catalyst on the oxidation of 2-octanol (measured under standard reaction conditions). (Δ) 0.5 g, (X) 0.25 g, (▽) 0.10 g. (b) Influence of the amount of catalyst on the oxidation of 2-octanol (measured in a more diluted system). (Δ) 0.5 g, (X) 0.25 g, (▽) 0.10 g.
Influence of hydrogen peroxide concentration

The experiments were performed as described in the experimental section. Only the amount of hydrogen peroxide was changed between the different experiments. The amounts of hydrogen peroxide added were 1.5, 3.0 and 4.5 ml, respectively. Fig. 6, where the conversion of 2-octanol versus time is displayed for the three different hydrogen peroxide concentrations, shows a linear increase in the initial reaction rate with increasing hydrogen peroxide content, which means that the alcohol oxidation is first order in oxidant concentration. The maximum conversion was proportional to the hydrogen peroxide concentration. The conversion was ca. 27, 54 and 80% in the three different tests. This shows that the hydrogen peroxide selectivity in all cases was above 95%. Only 2-octanone was formed, no consecutive oxidation took place.

Influence of alcohol concentration

In Fig. 7, four experiments with 2-octanol concentrations of 0.75, 1.5, 3.0 and 4.5 mol/l are plotted. The identical initial reaction rate of experiments
with different alcohol concentration is a strong indication for a zero order dependency in the alcohol concentration.

From the reported influences on the measured reaction rates of the amount of catalyst and the hydrogen peroxide and alcohol concentration, it can be concluded that the overall reaction rate for the oxidation of 2-octanol can be described by the following equation:

\[ r = k' \cdot [\text{cat}]^1 \cdot [\text{H}_2\text{O}_2]^1 \cdot [\text{alc}]^0 \]  

(1)

which, for a constant amount of catalyst, can be simplified to the following first order rate equation:

\[ r = k' \cdot [\text{H}_2\text{O}_2]^1 \]  

(2)

According to this the following relation between the relative conversion \( X \) and the reaction time \( t \) can be derived:

\[ \ln(1 - X) = -k' \cdot t \]  

(3)

The validity of this relation can be checked, by plotting \( \ln(1 - X) \) versus time for an arbitrary experiment (see Fig. 8). From the slope of this curve the value
Fig. 8. First order relation between relative conversion $X$ and reaction time.

Fig. 9. Influence of reaction temperature on the conversion of 2-octanol. (□) 70°C, (+) 60°C, (◇) 50°C, (△) 40°C, (×) 30°C.
of the first order rate constant \( k' \) can be obtained, which can be used to characterize the catalyst activity.

**Influence of reaction temperature**

The influence of reaction temperature on the oxidation of 2-octanol is shown in Fig. 9. In this figure the percentage of the maximum product concentration (which can be formed if all hydrogen peroxide is used for product formation) versus time is plotted for reactions conducted at 30, 40, 50, 60 and 70°C. From these measurements it can be concluded that temperature only influences activity and not selectivity. A high ketone selectivity (\( >95\% \) at total hydrogen peroxide conversion) is obtained at all reaction temperatures used. An Arrhenius plot of the first order reaction rate constants obtained from these conversion curves is shown in Fig. 10, and from this graph an activation energy of 71 kJ/mol can be derived for the oxidation of 2-octanol.

**The influence of the chain length**

To study the influence of the chain length on the activity, the following four \( \beta \) alcohols were tested: 2-hexanol, 2-heptanol, 2-octanol and 2-nonanol. All
Fig. 11. (a) Influence of the chain length on the reactivity of $\beta$ alcohol. (□) 2-Hexanol, (+) 2-heptanol, (◇) 2-octanol, (△) 2-nonanol. (b) Influence of the chain length on the reactivity of $\alpha$ alcohol. (□) 1-Hexanol, (+) 1-heptanol, (◇) 1-octanol, (△) 1-nonanol.
catalytic tests were done with the same batch of TS-1 (sample 1 of Table 1) at 70°C. The results of these experiments are shown in Fig. 11a. As can be seen, the order of reactivity is 2-octanol > 2-heptanol > 2-hexanol > 2-nonanol. By applying a first order rate equation (vide supra) the first order rate constant of these reactions can be obtained (see Fig. 12), which shows quantitatively the influence of the chain length on activity. If the same experiments are repeated for the α alcohols the same order of reactivity is found (see Fig. 11b and 12); however with one important difference, the reactivity of the α alcohols is much lower than the reactivity of the β alcohols. The observed large differences between α and β alcohols can be explained by the much higher chemical reactivity in general of the secondary alcohols with respect to the primary alcohols. For the same reason, an increase in reactivity for increasing chain length can be expected. However, the fact that for both series the reactivity strongly decreases above C8 cannot be explained in this way. As preliminary measurements of diffusion coefficient [23] do not show significant differences, the explanation must probably be sought in a shape selectivity effect of the TS-1 catalyst.
Fig. 13. (a) Influence of the position of the hydroxyl group on the reaction of 1, 2 and 3-hexanol. (□) 1-hexanol, (+) 2-hexanol, (◇) 3-hexanol. (b) Influence of the position of the hydroxyl group on the reaction of 1, 2 and 3-octanol. (□) 1-octanol, (+) 2-octanol, (◇) 3-octanol.
The effect of the position of the hydroxyl group

To investigate the influence of the position of the hydroxyl group on the reactivity, two series of alcohols have been tested: \( \alpha, \beta \) and \( \gamma \) hexanols and \( \alpha, \beta \) and \( \gamma \) octanols. The results are shown in Fig. 13a and in Fig. 13b, respectively. It can be clearly seen from these figures that the position of the hydroxyl group has an important effect on the reactivity. For both series the following order of reactivity is found \( \beta \gg \alpha > \gamma \). As mentioned above the lower reactivity of \( \alpha \) alcohols with respect to \( \beta \) alcohols is caused by the lower chemical reactivity. However, the very low reactivity of the \( \gamma \) alcohols cannot be explained in this way. Since the chemical reactivity of \( \gamma \) alcohols is only slightly different from that of \( \beta \) alcohols (both are secondary alcohols), similar reactivities would be expected on that ground. Since diffusion measurements \[23\] show only small differences between the diffusivities of the corresponding \( \beta \) and \( \gamma \) alcohols, this also cannot be the explanation. There remains a possible shape selectivity effect of the TS-1 catalyst. As suggested earlier, the bulkier transition state in the oxidation of the \( \gamma \) alcohol (compared to the \( \beta \) alcohol) may lead to a faster oxidation of the \( \beta \) alcohol with respect to the \( \gamma \) alcohol \[24-26\].

CONCLUSIONS

— Aliphatic alcohols can be selectively oxidized in the liquid phase by hydrogen peroxide to ketones or aldehydes by application of a titanium silicalite-1 catalyst.

— Due to pore diffusion limitations, the catalyst particle size should be smaller than about 0.2 \( \mu \)m to obtain optimum catalyst efficiency.

— The oxidation of 2-octanol is shown to be first order in the amount of catalyst and hydrogen peroxide concentration and zero order in alcohol concentration, while from the temperature dependence of the reaction rate between 30 and 70\(^\circ\)C, an activation energy of 71 \( \text{kJ/mol} \) could be calculated.

— For the reactivity of different alcohols, the following relation could be obtained:

\[
\beta\text{-alcohols} \gg \alpha\text{-alcohols} > \gamma\text{-alcohols}
\]

\( C_6 < C_7 < C_8 \gg C_9 \)

— The low reactivity of the \( \alpha \) and \( \beta \) nonanols is probably due to reactant shape selectivity, while the low reactivity of the \( \gamma \) alcohols is probably caused by transition state selectivity effects.
REFERENCES