Cyclohexene and Cyclooctene Epoxidation with Aqueous Hydrogen Peroxide using Transition Metal-Free Sol-Gel Alumina as Catalyst

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Abstract: It is shown that sol-gel alumina calcined at 400 ^{0}C is a very efficient catalyst for the epoxidation of cyclohexene and cyclooctene with aqueous 70 wt % hydrogen peroxide. The overall yield per g of catalyst was 0.28 mol of cyclohexene oxide in 5 cycles of 450 min each and 0.43 mol of cyclooctene oxide in 4 cycles of 750 min each. The selectivity for the epoxides was always better than 99%. However, the catalyst deactives slowly, which we believe is caused by a non-radical decomposition of hydrogen peroxide.

Keywords: alumina; catalytic epoxidation; green chemistry; hydrogen peroxide; sol-gel

Introduction

A strong effort has been made for the development of new catalysts for the synthesis of epoxides in a more environmental friendly way.[1,2,3] We have shown that alumina is an efficient heterogeneous catalyst for the epoxidation of a variety of nucleophilic olefins using hydrogen peroxide in anhydrous conditions[4,5] and that is possible to improve considerably the catalytic activity of the alumina surface when sol-gel methods are used to prepare ultrapure alumina.[6] In the present work, we report that the sol-gel alumina is also very efficient with aqueous (70 wt %) hydrogen peroxide and that the alumina can be recycled for several times, allowing a good total yield of epoxide per gram of catalyst.

Results and Discussion

We calcined the sol-gel alumina precursor (aluminum hydroxide) at temperatures from 200 up to 1000 °C in order to find the calcination temperature that gives the best catalytic activity of the alumina for the epoxidation of cyclohexene. During the thermal dehydration of aluminum hydroxide, in the intermediate temperature range various so-called transition aluminas are formed, until the most stable and anhydrous phase is obtained (corundum, α-Al_2O_3).[7] Many factors such as precursor type, structural properties of the precursor (crystallinity, crystallite size and impurities), mode of heating and final temperature affect the structural properties of the transition aluminas and modify their reactivity in organic reactions.[8] The sol-gel alumina precursor has a boehmite structure up to 300 °C, which is gradually lost above 300 °C giving γ-alumina at 400 °C. Above 300 °C a progressive decrease of the surface area is observed as shown in Table 1. The materials show no structural pores; the determined pore volume and diameter are due to interparticle void spaces. The alumina calcined at 800 °C consists of a mixture of γ- and δ-alumina. At 1000 °C, the material is completely transformed into δ-Al_2O_3.

In all catalytic experiments ethyl acetate was used as solvent because other solvents, such as acetonitrile, methanol or *tert*-butanol, gave lower conversions and selectivity in the epoxidation of (*S*)-limonene.[9] In this work, the alumina/olefin ratio was decreased from 500 mg of alumina per 10 mmol of the olefin[4–6] to 100 mg of alumina per 20 mmol of olefin without a significant loss of catalytic activity, showing that alumina has a high catalytic activity for olefin epoxidation.

Table 1. Textural properties of the alumina calcined at different temperatures.

Calcination Temperature [°C]	A_{BET} [m^2/g]	Pore Volume [cm^3/g]	Average Porous Diameter [nm]
200	285	0.47	6.6
300	339	1.46	16.9
400	280	1.29	17.9
520	282	1.09	15.1
600	255	1.20	18.3
800	184	0.93	19.6
1000	128	0.76	23.7

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Figure 1 shows the yield of cyclohexene oxide obtained when using alumina calcined at different temperatures.

The yield of cyclohexene oxide shows a similar behavior for both aqueous and anhydrous hydrogen peroxide when using alumina calcined in the temperature range of 300 up to 800 °C. However, in the extremes of this temperature range the presence of water gives different results. At 200 °C, the yield of cyclohexene oxide is strongly reduced when water is present in the oxidant. After calcination at this temperature a large number of hydroxy groups is present on the alumina surface and, therefore, an additional amount of water increases the already existing dense hydrophilic layer on the surface, making the approach of the olefin to the active sites more difficult. At 300 °C, the alumina is already sufficiently dehydrated; the yield of cyclohexene is higher and small amounts of water in the oxidant are no longer harmful. The most active alumina for epoxidation of cyclohexene was obtained at 400 °C when the γ-alumina is already formed, but it is not yet well crystallized, having on its surface a large number of acid sites.[10] In all further experiments the alumina calcined at 400 °C was used. The aluminas calcined at 520, 600 and 800 °C show an intermediate activity, which is similar to that of the commercial alumina.[6] The alumina is still active even after calcination at 1000 °C, although its transformation to δ-alumina has been already completed. Aqueous 70 wt % hydrogen peroxide gives a slightly better result because this alumina has an extensively dehydrated surface and the presence of water in the reaction mixture helps to rehydrate the surface, increasing the number of catalytic sites (Al-OH).[4,11,12]

In Figure 2 the profile of the epoxidation of cyclohexene to cyclohexene oxide using the alumina calcined at 400 °C together with aqueous (30 and 70 wt %) and anhydrous (24 wt %) hydrogen peroxide is shown.

At the beginning of the reaction the yield of cyclohexene oxide is slightly lower when aqueous 70 wt % hydrogen peroxide is used, because the water makes the alumina surface more hydrophilic, which renders the approach of the olefin to the active sites more difficult. On the other hand, high amounts of water (using aqueous 30 wt % hydrogen peroxide) strongly reduce the rate of epoxidation reaction due to the formation of a dense water layer on the alumina surface. For longer reaction times aqueous 70 wt % hydrogen peroxide gives higher yields of cyclohexene oxide due to a slower deactivation of the alumina surface. In all reactions described in this paper, the selectivity for epoxide was always better than 99%, indicating that there are no strong acid sites on the alumina surface under reaction conditions. The presence of weak to moderate acid sites is not enough for catalyzing the opening of the oxirane ring under these reaction conditions. No allylic oxidation products were obtained since ultrapure aluminum *sec*-butoxide, which contained no measurable amounts of transition metals, was used in the alumina synthesis. Allylic oxidation products are an indication that radicals are formed during the process either by radical decomposition of hydrogen peroxide or by the formation of organic hydroperoxides, which may initiate a radical process.[13]

From the profile of the curves in Figure 2 it is clear that the catalyst is still active after 500 min. In order to determine the lifetime of the catalyst we performed

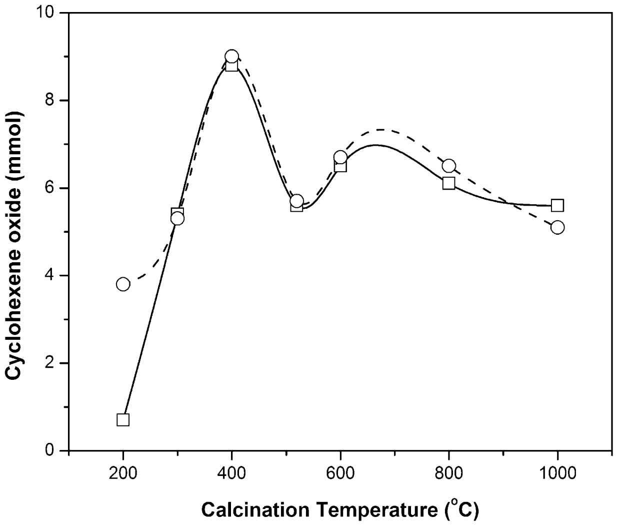

Figure 1. Yield of cyclohexene epoxide as a function of the calcination temperature of alumina using aqueous (□) and anhydrous (○) hydrogen peroxide (100 mg of alumina, 20 mmol of cyclohexene, 40 mmol of hydrogen peroxide, 400 min).

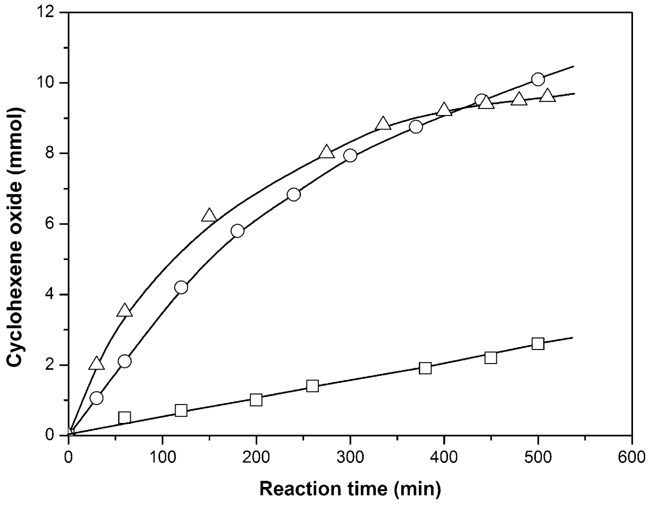

Figure 2. Alumina-catalyzed epoxidation of cyclohexene using aqueous 30 wt % (□), aqueous 70 wt % (○) and anhydrous 24 wt % (△), hydrogen peroxide. Reaction conditions: 100 mg of alumina (calcined at 400 °C), 20 mmol of cyclohexene and 40 mmol of hydrogen peroxide.

recycling experiments using aqueous 70 wt % (Figure 3) and anhydrous (Figure 4) hydrogen peroxide. After each run, the alumina was dried at 110 °C. It was not calcined in order to avoid structural and textural changes.

Using aqueous 70 wt % hydrogen peroxide the catalyst could be used in 5 reactions giving a total amount of 0.28 mol of cyclohexene epoxide per g of alumina, while when using anhydrous 24 wt % hydrogen peroxide only three reactions were possible and only 0.17 mol of cyclohexene epoxide per g of alumina were obtained. The amount of molecular oxygen formed in the reaction with anhydrous hydrogen peroxide, which is *ca.* 50%,[6] is reduced to *ca.* 30% when using aqueous 70 wt % hydrogen peroxide. Thus, alumina in combination with aqueous 70 wt % hydrogen peroxide is more efficient, as less hydrogen peroxide is lost by decomposition and higher epoxide yields are obtained. The deactivation of alumina observed after several cycles seems to be correlated to the decomposition of the hydrogen peroxide. Work is in progress to clarify what changes occur on the alumina surface during the reactions.

We repeated the recycling experiments with cyclooctene. Since the epoxidation of cyclohexene was not finished after 450 min, we extended the reaction time to 750 min. The results are shown in Figure 5 for aqueous 70 wt % hydrogen peroxide and in Figure 6 for anhydrous 24 wt % hydrogen peroxide.

Using aqueous 70 wt % hydrogen peroxide the reaction is not finished even after 750 min, however, the yields of cyclooctene oxide are higher due to the longer reaction time. We recycled the catalyst four times and were able to obtain 0.43 mol of cyclooctene oxide per g of alumina. Using anhydrous 24 wt % hydrogen peroxide the reaction is less efficient and only three runs were possible, giving a total of 0.20 mol of cyclooctene oxide per g of alumina.

The much better results obtained in the cyclohexene and cyclooctene epoxidation with aqueous 70 wt % hydrogen peroxide are due to a smaller extent of hydrogen peroxide decomposition and a slower deactivation of the alumina surface. We believe that hydrogen peroxide reacts with the weak acidic sites of the alumina surface to form hydroperoxo groups, which are respon-

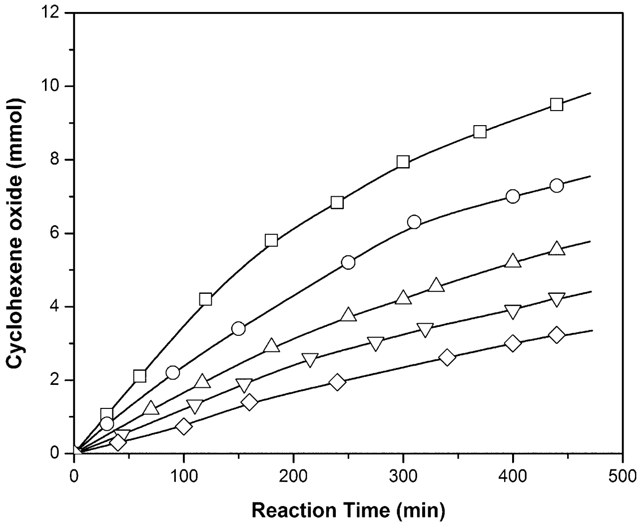

Figure 3. Recycling of alumina using aqueous 70 wt % hydrogen peroxide: first run (□), second run (○), third run (△), fourth run (▽) and fifth run (◇). Reaction conditions: 100 mg of alumina (calcined at 400 °C), 20 mmol of cyclohexene, 40 mmol of hydrogen peroxide.

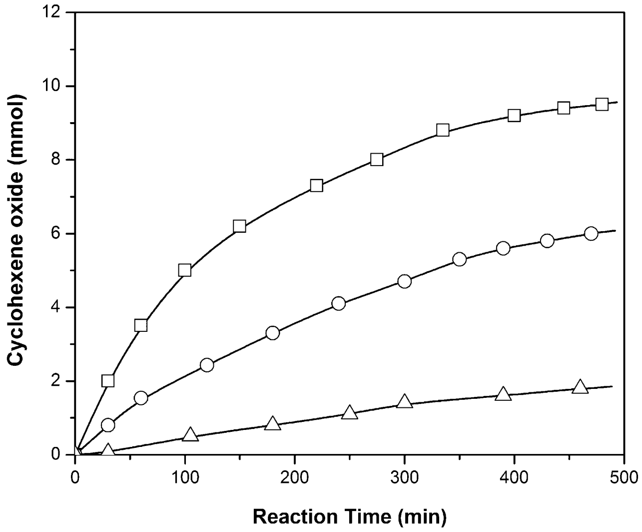

Figure 4. Recycling of alumina using anhydrous 24 wt % hydrogen peroxide: first run (□), second run (○) and third run (△). Reaction conditions: 100 mg of alumina (calcined at 400 °C), 20 mmol of cyclohexene, 40 mmol of hydrogen peroxide.

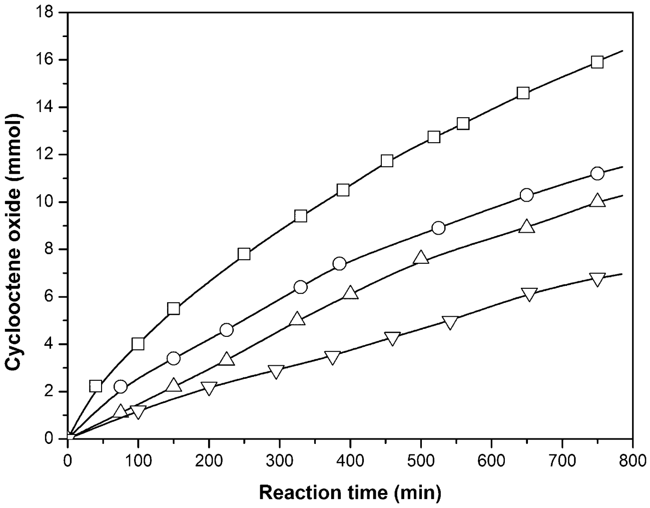

Figure 5. Recycling of alumina using aqueous 70 wt % hydrogen peroxide: first run (□), second run (○), third run (△) and fourth run (▽). Reaction conditions: 100 mg of alumina (calcined at 400 °C), 20 mmol of cyclooctene, 40 mmol of hydrogen peroxide.

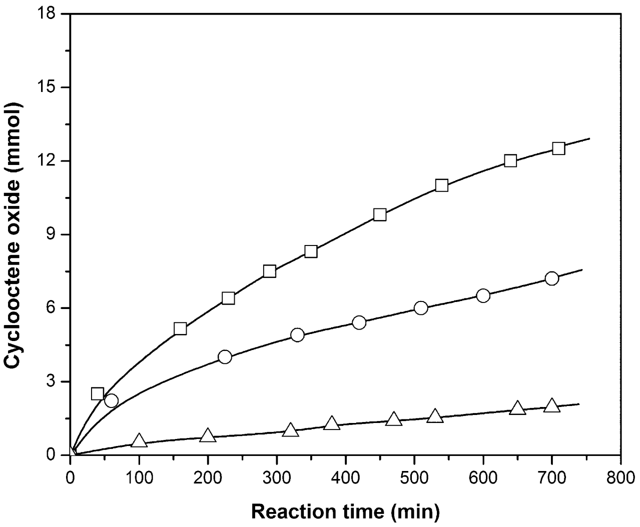

Figure 6. Recycling of alumina using anhydrous 24 wt % hydrogen peroxide: first run (□), second run (○) and third run (△). Reaction conditions: 100 mg of alumina (calcined at 400 °C), 20 mmol of cyclooctene, 40 mmol of hydrogen peroxide.

sible for the transfer of oxygen to the olefin. However, these hydroperoxo groups may also suffer a redox reaction with vicinal hydroxy groups to form molecular oxygen and water as shown in Figure 7. The Lewis acid sites formed in the redox reaction normally react with water to reestablish the original alumina surface. However, this rehydration step may stress the alumina surface and/or structure, causing the deactivation of the catalyst after several cycles. More studies have to be done for a better understanding of the relationship between the decomposition of hydrogen peroxide and the deactivation of the surface.

The kinetics of the alumina-catalyzed hydrogen peroxide decomposition depend on the amount of water in the reaction mixture as this can coordinate to the active sites, protecting them from the redox reaction with a vicinal hydroperoxo group. Using aqueous 70 wt % hydrogen peroxide, the amount of molecular oxygen formed is, therefore, reduced and the amount of epoxide increased. We would like to point out that in all these reactions the only products observed are the epoxides and, therefore, we are certain that the decomposition of hydrogen peroxide follows a non-radical pathway as proposed in the mechanism in Figure 7. Blank experiments without catalyst also produce only epoxides, however, the amount is much smaller (1 to 2 mmol after 750 min).

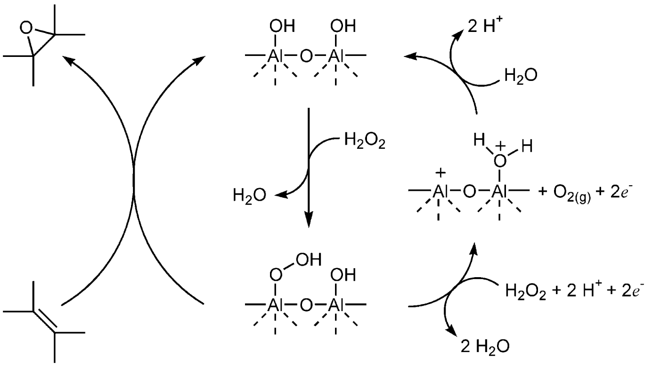

Figure 7. Proposed mechanism of the epoxidation and formation of molecular oxygen.

Conclusion

Sol-gel alumina is a very efficient catalyst for the epoxidation of olefins with aqueous 70 wt % hydrogen peroxide, allowing good yields with a reduced formation of molecular oxygen. Furthermore, the catalyst stays active for several cycles without a strong loss of activity. We are presently studying the reason for the deactivation of the catalyst in order to prepare an improved alumina, which can be used in a larger number of cycles.

Experimental Section

Synthesis of Sol-Gel Alumina

The alumina was prepared by acid hydrolysis of aluminum *sec*-butoxide (10.0 g, 40.6 mmol, Merck) in 15 mL of *sec*-butanol (Acros), adding dropwise an aqueous solution of oxalic acid (7.5 mL, 0.74 mol/L, 5.6 mmol) under vigorous agitation. The gel formed was aged during 3 h at 70 °C under stirring and kept for 3 days in the open air. After this, the material was dried at 70 °C for 24 h. The xerogel was treated under a flow (60 mL min^{-1}) of synthetic air at 100, 200, 300, 400, 520, 600, 800 or 1000 °C for 24 h each. The surface areas and pores volume of the alumina were determined by nitrogen adsorption at 77 K using a Micrometrics ASAP 2010 instrument and the BET method. The structures of the alumina were determined by powder X-ray diffraction on a Shimadzu XD-3A diffractometer, using CuK$_\alpha$ radiation and $2\theta = 10-90°$, a step size of the 0.02° and a counting time of 3 s per step.

Catalytic Reactions

The solution of anhydrous hydrogen peroxide (24 wt %) in ethyl acetate was prepared by azeotropic distillation (*caution*!).[4] The aqueous solution of hydrogen peroxide (70 wt %) was supplied by Peróxidos do Brasil S. A. and was used without pretreatment, as well as the other reagents. The aqueous solution of 30 wt % hydrogen peroxide was obtained from Merck.

A mixture of cyclohexene or cyclooctene (20 mmol, Acros), hydrogen peroxide (40 mmol), di-*n*-butyl ether (5 mmol, internal standard, Fluka) and ethyl acetate (10 mL) was heated under reflux with magnetic stirring for 1 h. A sample was taken for GC analysis (blank) and the reaction started by addition of the alumina (100.0 mg). The samples were taken at the indicated reaction times and treated with few milligrams of manganese dioxide for the decomposition of peroxides, and with anhydrous sodium sulfate to remove residual water. They were then analyzed, using a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with an HP 5 capillary column (25 m × 0.2 mm × 0.33 μm film thickness) and a flame ionization detector (FID). For chromatographic separation the following temperature program was used: 9 min at 55 °C; 30 °C/min up to 90 °C; 3 min at 90 °C; 30 °C/min up to 150 °C; 2 min at 150 °C; 30 °C/min up to 250 °C; 1 min at 250 °C. The order of elution was: internal standard, olefin and epoxide (i.e., $t_{R(n\text{-butyl ether})} = 6.5$ min, $t_{R(\text{cyclooctene})} = 7.2$ min and $t_{R(\text{cyclooctene oxide})} = 14.4$ min). Products were quantified using calibration curves obtained with standard solutions. Selectivity is always given with respect to the converted cyclohexene or cyclooctene. In the recycling experiments the reaction mixture was filtered off and the alumina washed with 3 × 10 mL of ethyl acetate and dried in an oven at 110 °C for 24 h.

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