Alumina-Catalyzed Epoxidation with Hydrogen Peroxide: Recycling Experiments and Activity of Sol-Gel Alumina

Renato G. Cesquini,[a] Juliana M. de S. e Silva,[a] Camile B. Woitiski,[b] Dalmo Mandelli,[a,b] Roberto Rinaldi,[a] Ulf Schuchardt[a,*]

[a] Instituto de Química, Universidade Estadual de Campinas, P.O. Box 6154, 13083-970 Campinas-SP, Brazil
  Fax: (+55)-19-37883023; e-mail: ulf@iqm.unicamp.br
[b] Instituto de Ciências Biológicas e Químicas, Pontifícia Universidade Católica de Campinas,
  P.O. Box 1111, 13020-904 Campinas-SP, Brazil

Dedicated Prof. Roger A. Sheldon on the occasion of his 60th birthday.

Abstract: Commercial alumina looses some activity after the first epoxidation reaction of (S)-limonene with hydrogen peroxide, but maintains a good activity and a very high selectivity in the subsequent three reactions. After this its activity is strongly reduced, probably due to structural modifications. Aluminas obtained by sol-gel methods are normally less active than the commercial alumina. However, the use of monomeric aluminum sec-butoxide and of oxalic acid to form stable alumina mesophases allows a very active alumina to be obtained, which catalyses the epoxidation of the less reactive cyclohexene with hydrogen peroxide in 98% yield. Close to 50% of the active oxygen is used up in the formation of molecular oxygen.

Keywords: catalyst recycling; catalytic epoxidation; cyclohexene oxide; green chemistry; (S)-limonene oxide; sol-gel-derived alumina

Introduction

In a joint project with Roger A. Sheldon's group we showed that only alumina effectively heterogenizes homogeneous rhenium epoxidation catalysts.[1] Under epoxidation conditions, however, alumina itself was already active for the epoxidation of cyclooctene and cyclohexene with anhydrous hydrogen peroxide in ethyl acetate.[1] In a subsequent investigation[2] we optimized the alumina system and showed that it is also useful for the epoxidation of terpenes and 1-olefins. We were able to achieve productivities of up to 4.3 g epoxides per g of alumina.[2] In a parallel paper,[3] we reported that the yields of epoxides were normally above 70% and very few by-products were formed. A small amount of water in the reaction medium was shown to be of crucial importance as it suppressed the decomposition of the epoxide. To our surprise, a variety of different aluminas showed a similar catalytic behavior.[3] In this paper we present our results on recycling experiments of a commercial alumina and the catalytic behavior of aluminas R1 – R4 obtained by sol-gel methods.

Results and Discussion

Recycling Experiments

The commercial alumina Rc and (S)-limonene (**1**) were used in the recycling experiment. The diasteriomeric monoepoxides **2a** and **2b** the external epoxide **3** and the diepoxide **4** are formed (Figure 1).

The products were analyzed in 8 consecutive reactions after 0.5, 2, and 5 h. The results are shown in Table 1.

With exception of the initial reaction, the selectivity for the epoxides **2a**, **2b**, **3** and **4** is always better than 97%. In the initial reaction the selectivity is also very high after 30 min, however, decreases due to secondary reactions of the epoxides. This is probably caused by strong acid sites of the alumina which are neutralized during the initial reaction. In the first recycle the catalyst
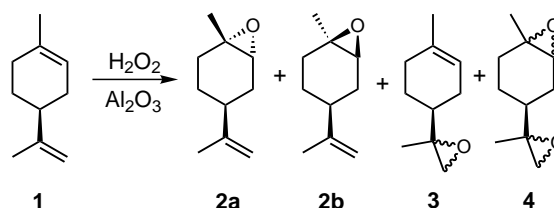

Figure 1. Epoxidation of (S)-limonene.

Table 1. Recycling of the commercial alumina Rc in the epoxidation of (*S*)-limonene.

Reaction	30 min			120 min			300 min		
	conv. [%]	select. [%]	epoxide distribution **2a**:**2b**:**3**:**4**	conv. [%]	select. [%]	epoxide distribution **2a**:**2b**:**3**:**4**	conv. [%]	select. [%]	epoxide distribution **2a**:**2b**:**3**:**4**
Initial	38	98	47:41:10:2	74	91	46:39:7:8	78	86	43:37:6:14
Rec.1	17	99	48:41:11:0	57	99	46:39:8:7	70	98	46:38:8:8
Rec.2	15	98	48:41:11:0	60	98	48:40:8:6	72	98	46:39:7:7
Rec.3	12	99	48:40:12:0	56	98	48:39:7:6	69	98	46:39:7:8
Rec.4	11	98	48:41:11:0	34	98	48:38:10:4	38	97	47:38:10:5
Rec.5[a]	12	99	48:40:12:0	35	97	46:39:11:4	40	97	47:40:10:3
Rec.6[a]	12	98	49:39:12:0	36	98	44:36:11:9	42	98	47:39:12:2
Rec.7[a]	9	98	47:39:13:0	37	98	45:39:11:5	43	98	45:39:12:4

[a] Calcined at 520 °C before the reaction.

is less active but reaches a similar high conversion after 300 min as it was in the initial reaction, with a selectivity as high as in the beginning of the reaction. In the following two recycles the activity and selectivity of the catalyst remain the same. From the forth recycle on the activity is strongly reduced and the good selectivity maintained. We tried to regain the activity observed for the first three recycles by calcining the catalyst at 520 °C, however, the process was not effective, showing that the deactivation must be due to structural changes and not to organic compounds deposited on the catalyst. The total amount of epoxides produced during the recycling experiments was higher than 13 g per g of alumina.

The percentage of the epoxides **2a** and **2b** in the products is always 80% or higher. The diastereoselectivity observed is very low. The percentage of the external epoxide **3** is at least 10% at the beginning of the reactions, however, is reduced during the reaction course in the first four reactions, as the diepoxide **4** is mainly formed by further oxidation of **3**. The percentage of **4** depends strongly on the activity of the catalyst. The yield of **4**, formed in the initial reaction (14%), is reduced to 8% in the next three cycles and further reduced in the subsequent cycles.

Activity of Sol-Gel Alumina

The activities of the sol-gel aluminas R1 – R4 were first compared with that of the commercial alumina Rc in the epoxidation of cyclohexene. Figure 2 shows the conversion of cyclohexene as a function of time for the five types of alumina tested.

The aluminas R1 and R2 are less active than the commercial alumina Rc, showing that the sol-gel preparation did not form an appropriate catalyst for this kind of reaction. The alumina R3 was as active as the commercial alumina Rc. This can be explained by the rapid formation of alumina mesophases[4] by coordination of the oxalic acid to the aluminum avoiding the
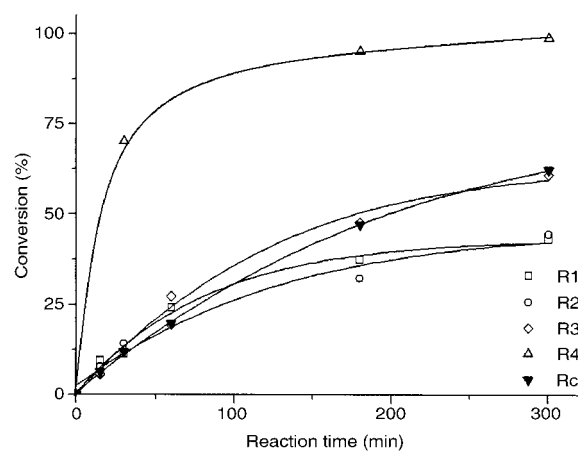

Figure 2. Conversion of cyclohexene to cyclohexene oxide catalyzed by different aluminas.

formation of a bayerite phase, which seems to form a less active alumina on calcination. The alumina R4 shows a much higher activity than the commercial alumina Rc, which is probably due to a beneficial effect of the oxalate in combination with the use of aluminum *sec*-butoxide which being a liquid allows a rapid coordination of the oxalic acid to the aluminum monomer. The surface areas of the aluminas are similar with exception of alumina R1 and the pore diameter of the aluminas is apparently not important for their activity as only aluminas Rc and R2 have a porous system.

We also tested the catalytic activity of the sol-gel alumina R1-R4 in comparison with the commercial alumina Rc in the epoxidation of (*S*)-limonene. The conversion of the limonene as function of time is shown in Figure 3.

The aluminas R1, R2 and R3 are less active than the commercial alumina Rc. The sol-gel alumina R4 again shows a higher activity than Rc, although the difference is not as striking as that observed in the epoxidation of cyclohexene. This can be explained by the higher reactivity of the limonene in comparison of with
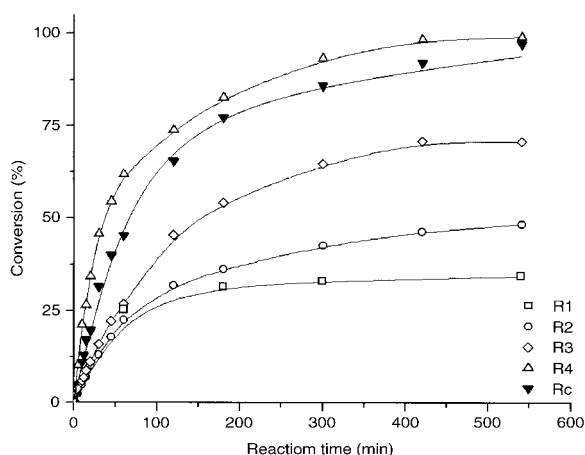
Figure 3. Conversion of (*S*)-limonene catalyzed by different aluminas.

cyclohexene, since the commercial alumina already allows conversions above 90%. The higher activity of R4 in the epoxidation of limonene is probably due to the same reasons already explained for the epoxidation of cyclohexene.

In our previous publications[2,3] we already mentioned that some molecular oxygen is formed during the catalytic reactions. Small amounts of water retard the decomposition of hydrogen peroxide,[3] however, the epoxidation requires an excess of hydrogen peroxide. In order to understand when and how much molecular oxygen is formed, we monitored its formation during the epoxidation of limonene in the presence of commercial alumina Rc. The profile of the molecular oxygen formation is the same as the profile of the conversion of limonene. Molecular oxygen is produced constantly during the reaction, reaching a maximum of 4.2 mmol after 300 min. This means that 42% of the active oxygen is consumed in the production of molecular oxygen, while the rest is used for the epoxidation of the limonene. It should be mentioned that in this reaction approximately 14% of diepoxide **4** is formed, explaining why more than 50% of the active oxygen are incorporated in the epoxidation products.

Conclusion

Alumina can be conveniently recycled for three times in the epoxidation of alkenes with hydrogen peroxide/ethyl acetate, however, it strongly looses its activity after the fourth reaction. The reason for this deactivation is not yet understood. The sol-gel alumina synthesized in this work by using oxalic acid and aluminum *sec*-butoxide in the synthesis gel is more active than the commercial alumina. The surface area and the non-porosity of this alumina were not different from the other aluminas tested. We, therefore, believe that the

higher activity is due to the amount and/or acidity of surface hydroxy groups which we are presently investigating.

Experimental Section

Synthesis of the Catalysts

The commercial alumina Rc was purchased from Fluka (type 507C, neutral, 100 – 125 mesh). The surface area, obtained by BET (Micrometrics ASAP 2010 with nitrogen as probe molecule), was 195 m^2/g, and the average pore diameter was 5.1 nm. Sol-gel alumina R1 was prepared by mixing of aluminum isopropoxide (9.39 g, 46 mmol) with nitric acid (8 mol L^{-1}, 2.2 mL, 17.6 mmol) and water (3.2 mL, 0.18 mol) at 75 °C for 30 min. No homogeneous solution was obtained. The sol was dried for 3 days at open air. The gel was treated under a flow of synthetic air at 100 °C, 200 °C, and 400 °C for 24 h each. The alumina obtained was non-porous with a surface area of 180 m^2/g. Sol-gel alumina R2 was prepared as reported by Buelna and Lin,[5] by dissolving aluminum isopropoxide (9.12 g, 45 mmol) in water (22.3 mL, 1.23 mol) at 85 °C for 1 h. Nitric acid (8 mol L^{-1}, 0.39 mL, 3.1 mmol) was added and the sol refluxed for 12 h. After distilling off the water, it was dried at 35 °C for 48 h. The gel was calcined as described before. The alumina obtained was porous (pore diameter of 3.4 nm) with a surface area of 293 m^2/g. Sol-gel alumina R3 was obtained using a recipe of Wang et al.[6] by dissolving aluminum isopropoxide (10.2 g, 50 mmol) in 2-propanol (15 mL, 0.2 mol). A solution of oxalic acid (0.7 g, 5.6 mmol) in water (7.5 mL, 0.41 mol) was added and the mixture refluxed for 3 h. The sol was dried at 70 °C and then calcined as described before. The alumina obtained was non-porous with a surface area of 290 m^2/g. Sol-gel alumina R4 was prepared using the same procedure of alumina R3, but substituting aluminum isopropoxide by aluminum *sec*-butoxide (10.0 g, 40.6 mmol). The sol obtained was dried and calcined as described for R3. The alumina obtained was non-porous with a surface area of 287 m^2/g.

Catalytic Reactions

Solutions of anhydrous hydrogen peroxide in ethyl acetate were prepared by the Dean–Stark method as described before[2,3] and contained approximately 7 mmol of hydrogen peroxide per gram of ethyl acetate. The other reagents were used without pre-treatment.

A mixture of the alkene (10 mmol, Fluka), hydrogen peroxide (20 mmol), di-*n*-butyl ether (5 mmol, internal standard) 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 (0.50 g). Aliquots of the reaction mixture were taken after the indicated reaction times for a total of 9 h. The samples were 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). Products were quantified using calibration curves obtained with standard solutions. Selectivities are

always given with respect to the converted alkene. In the recycling experiments the reaction mixture was centrifuged and the decanted catalyst dried in an oven at 110 °C or calcined at 520 °C for 4 h. In some reactions the production of molecular oxygen was monitored using a burette.

Acknowledgements

References

[1] D. Mandelli, M. C. A. van Vliet, U. Arnold, R. A. Sheldon, U. Schuchardt, *J. Mol. Catal. A: Chemical* **2001**, *168*, 165 – 167.

[2] D. Mandelli, M. C. A. van Vliet, R. A. Sheldon, U. Schuchardt, *Appl. Catal. A: General* **2001**, *219*, 209 – 213.

[3] M. C. A. van Vliet, D. Mandelli, I. W. C. E. Arends, U. Schuchardt, R. A. Sheldon, *Green Chem.* **2001**, *3*, 243 – 246.

[4] F. Vaudry, S. Khodabandeh, M. E. Davis, *Chem. Mater.* **1996**, *8*, 1451 – 1464.

[5] G. Buelna, Y. S. Lin, *Micropor. Mesopor. Mater.* **1999**, *30*, 359 – 369.

[6] J. A. Wang, X. Bokhimi, A. Morales, O. Novaro, T. López, R. Gómez, *J. Phys. Chem. B* **1999**, *103*, 299 – 303.