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Factors responsible for the activity of alumina surfaces in the catalytic epoxidation of *cis*-cyclooctene with aqueous H_2O_2

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Abstract

The structural, textural, and chemical properties as well as the hydrophilicity of four different sol–gel aluminas were determined by different methods and compared with their activity in the catalytic epoxidation of *cis*-cyclooctene with aqueous H_2O_2. It was found that the hydrophilicity of the γ-alumina surface is the principal factor responsible for the difference in catalytic activity. The hydrophilicity of γ-alumina should be sufficient to guarantee a fast reaction with hydrogen peroxide on the surface but should not to be too high in order to allow the approach of olefin to the active sites.

Keywords: Sol–gel alumina; Textural properties; Chemical properties; Surface hydrophilicity; Catalytic epoxidation; Hydrogen peroxide

1. Introduction

The term alumina embraces a large number of different products having a wide variety of properties and applications [1]. In catalysis, alumina is typically used as a support or as a catalyst for a variety of different reactions [1,2]. However, as the term alumina does not refer to only one compound but to a series of aluminum oxides and hydroxides, factors such as stoichiometry, crystallographic phase, and crystallinity must be considered in order to achieve suitable catalyst properties. Usually, for catalytic applications, it is necessary to activate the alumina, which is done by thermal dehydration of aluminum hydroxide or oxyhydroxide in a temperature range of 250 to 800 °C. In this dehydration a large number of transition aluminas is formed, whose structures can be identified by their XRD pattern. In the temperature range of 250 to 600 °C, γ-group aluminas are obtained, which include the ρ, χ, η, and γ forms. Their principal characteristics are lower crystallinities and more extensive porous structures of the aluminum oxide with large surface areas [1]. In alumina activation many factors, such as precursor type, structural properties (crystallinity, crystallite size, and impurities), mode of heating, and final temperature, affect the structural properties of the transition aluminas and modify their reactivities in organic reactions [2–5]. With respect to catalytic epoxidation, alumina was shown to be an efficient catalyst for a variety of nucleophilic olefins, such as linear, cyclic and substituted olefins and terpenes [6–8]. Among the advantages of using alumina as an epoxidation catalyst is that it is a nonpolluting compound and that it is possible to use the environmentally friendly oxidant hydrogen peroxide. The activation of hydrogen peroxide occurs probably through the reaction of weak acidic sites (Al–OH) of the alumina surface to form hydroperoxide groups, which are responsible for the transfer of oxygen to the olefin [9]. However, the properties which the alumina requires to have good catalytic activity are not yet well understood. The γ-aluminas prepared by different sol–gel routes show different catalytic activities in the epoxidation of cyclohexene and (S)-limonene using anhydrous H_2O_2 in ethyl acetate and the γ-alumina prepared from aluminum *sec*-butoxide, using oxalic acid as gelation catalyst, showed a significant higher epoxidation activity compared

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to commercial alumina [3]. However, different types of commercial chromatographic aluminas (acidic, neutral, and basic) had similar catalytic behaviors in the epoxidation of α-pinene [6]. The yield of epoxides in the alumina-catalyzed epoxidation is not affected by the exchange of anhydrous H_2O_2 by aqueous 70 wt% H_2O_2, which, on the other hand, improves the lifetime and the productivity of the catalyst [9]. In the present study, we synthesized ultrapure γ-alumina via the sol–gel route [3] and evaluated the influence of structural, textural, and chemical properties and the amount of water on the γ-alumina surface on its catalytic activity in the epoxidation of *cis*-cyclooctene.

2. Experimental

2.1. Synthesis of the catalysts

2.1.1. γ-Al_2O_3-1

The precursor of γ-Al_2O_3-1, Boehmite-1, was prepared by mixing aluminum *iso*-propoxide (9.39 g, Aldrich, $>$ 99.99%) with nitric acid (2.2 mL, 8 mol L^{-1}, Merck, p.a.) and deionized water (3.2 mL) at 75 °C for 30 min. No homogeneous solution was obtained. The gelatinous precipitate was dried for 3 days in air. The Boehmite-1 was treated under a flow of synthetic air at 100, 200, and 400 °C, sequentially, for 24 h each, generating γ-Al_2O_3-1.

2.1.2. γ-Al_2O_3-2

The precursor of γ-Al_2O_3-2, Boehmite-2, was prepared by the uncatalyzed hydrolysis of aluminum *iso*-propoxide (9.12 g, Aldrich, $>$ 99.99%) in deionizated water (22.3 mL) at 85 °C for 1 h. After this period, nitric acid (0.39 mL, 8 mol L^{-1}, Merck, p.a.) was added for peptization and the sol refluxed for 12 h. The water was removed by distillation and the solid was dried at 70 °C in an oven for 24 h to remove residual water. The Boehmite-2 was treated under a flow of synthetic air at 100, 200, and 400 °C, sequentially, for 24 h each, generating γ-Al_2O_3-2.

2.1.3. γ-Al_2O_3-3

The precursor of γ-Al_2O_3-3, Boehmite-3, was obtained by the hydrolysis of aluminum *iso*-propoxide (10.2 g, Aldrich, $>$ 99.99%) dissolved in isopropanol (15 mL, Merck, p.a.), catalyzed by an aqueous solution of oxalic acid (7.5 mL, 0.75 mol L^{-1}, Synth, p.a.) under vigorous stirring. The mixture was refluxed for 3 h. The gel was dried at 70 °C for 24 h and then the Boehmite-3 was treated under a flow of synthetic air at 100, 200, and 400 °C, sequentially, for 24 h each, generating γ-Al_2O_3-3.

2.1.4. γ-Al_2O_3-4

The precursor of γ-Al_2O_3-4, Boehmite-4, was prepared using the same procedure as for Boehmite-3, but substituting aluminum *iso*-propoxide by aluminum *sec*-butoxide (10.0 g, Aldrich, 99.99%) dissolved in *sec*-butanol (15 mL, Vetec, p.a.). To this solution was added under vigorous stirring an aqueous solution of oxalic acid (7.5 mL, 0.75 mol L^{-1}, Synth, p.a.). The gel was dried at 70 °C for 24 h and then the Boehmite-4 was treated under a flow of synthetic air at 100, 200, and 400 °C, sequentially, for 24 h each, generating γ-Al_2O_3-4.

2.2. Catalyst characterization

2.2.1. X-Ray power diffraction

X-ray diffraction patterns were determined with a Shimadzu XD-3A diffractometer, using Cu$K\alpha$ radiation and 2θ from 5 to 90°, with step sizes of 0.02° and counting times of 3 s. The apparent crystallite size of Boehmite-1 to Boehmite-4, synthesized by the different sol–gel routes, was determined using Scherrer's equation and the 020 reflection of the boehmite samples. Corundum with a crystallite size of 1 µm was used as internal standard.

2.2.2. Surface area analysis

The nitrogen adsorption–desorption isotherms of γ-Al_2O_3-1 to γ-Al_2O_3-4 were measured on a Micrometrics ASAP 2010 equipment. The surface area was determined by adsorption–desorption of nitrogen at 77 K. The pore volume and average pore diameter were calculated using the BET method.

2.2.3. Temperature-programmed desorption of ammonia and carbon dioxide

The temperature-programmed desorption (TPD) experiments were carried out in a lab-built equipment using a thermal conductivity detector (TCD). Typically, 100.0 mg of γ-alumina was treated under a flow of nitrogen (30 mL min^{-1}) at 400 °C for 1 h. The sample was allowed to cool to 100 °C under a flow of nitrogen. The adsorption of the probe molecule (ammonia or carbon dioxide) was accomplished at 100 °C for 1 h using a flow of 30 mL min^{-1} of a gaseous mixture of 10% (v/v) of the probe molecule in nitrogen. The excess of the probe molecule was removed by a flow of 30 mL min^{-1} of nitrogen for 1 h at 100 °C. Afterward, the sample was heated to 800 °C at a heating rate of 10 °C min^{-1} and the desorbed probe molecule quantified using the TCD detector. Blank TPD experiments were done for all γ-aluminas and their results were subtracted from the TPD curves obtained for the desorbed probe molecules.

2.2.4. Thermogravimetric analysis

Thermogravimetric (TG) analyses of Boehmite-1 to Boehmite-4 were carried out under an oxidative atmosphere (synthetic air, 100 mL min^{-1}) using a TA Micrometrics 2950 TGA instrument with a heating rate of 10 °C min^{-1} in the range of 30–900 °C. For TG analyses of γ-Al_2O_3-1 to γ-Al_2O_3-4 a heating rate of 20 °C min^{-1} in the temperature range of 25–875 °C was used.

2.2.5. *Elemental analysis*

Elemental analyses were carried out using a Perkin-Elmer Series II CHN S/O Analyzer Model 2400. Samples of Boehmite-1 to Boehmite-4 and γ-Al_2O_3-1 to γ-Al_2O_3-4 were mixed with an oxidant mixture (Pb_3O_4/NaF, 1:7) and the elemental analysis was performed by combusting the samples at 925 °C. The analyses were done in triplicate.

2.2.6. *Qualitative X-ray fluorescence analysis*

The γ-Al_2O_3-1 to γ-Al_2O_3-4 samples were analyzed by X-ray fluorescence, using a Shimadzu energy-dispersive X-ray spectrometer, Model EDX-700, a 10-mm collimator, and a Rh X-ray tube at 15 kV (for Na to Sc) and 50 kV (for Ti to U), under vacuum.

2.3. *Catalytic reactions*

The aqueous solution of hydrogen peroxide (70 wt%) was supplied by Peróxidos do Brasil S.A. (Solvay) and was used without further treatment. The other reagents were also used without further treatment.

A mixture of cyclooctene (10 mmol, Acros, 95%), hydrogen peroxide (20 mmol), di-*n*-butyl ether (5 mmol, internal standard, Fluka, $>$ 99%), and ethyl acetate (10 mL, Merck, p.a.) 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 γ-alumina (200.0 mg). Samples were taken at different reaction times and treated with a few milligrams of manganese dioxide, for decomposition of the peroxides, and then with anhydrous sodium sulfate, to remove residual water. The samples were analyzed using a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with an Alltech AT-WAX capillary column (20 m × 0.25 mm × 0.25 µm film thickness) and a flame ionization detector (FID). The cyclooctene epoxide was quantified using a calibration curve obtained with a standard solution. Selectivity is always given with respect to converted cyclooctene.

3. Results and discussion

The different routes of sol–gel synthesis yield boehmites with different crystallinities [10]. The fast hydrolysis of the aluminum isopropoxide, used in the synthesis of Boehmite-1, resulted in a material with very poor crystallinity. The noncatalyzed hydrolysis of aluminum isopropoxide followed by peptization in nitric acid resulted in a higher crystallinity (Boehmite-2). Boehmite-3 and Boehmite-4, which were synthesized by hydrolysis of aluminum isopropoxide and *sec*-butoxide, respectively, with oxalic acid as gelation catalyst, were obtained with intermediate crystallinities. The XRD patterns of these (pseudo)-boehmites are shown in Fig. 1.

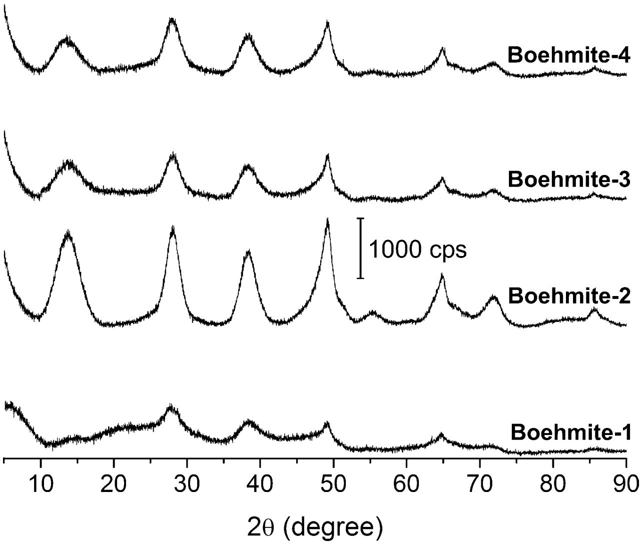

Fig. 1. Powder XRD pattern of the boehmites synthesized by different sol–gel routes.

Table 1
Apparent crystallite sizes of the boehmites synthesized by different sol–gel routes

Solid	*d* spacing (nm)	Apparent crystallite size (nm)
Boehmite-1	0.629	n.d.
Boehmite-2	0.644	5.1
Boehmite-3	0.648	4.5
Boehmite-4	0.650	4.7

n.d., not determined.

The apparent crystallite sizes of the boehmites, estimated using Scherrer's equation, are shown in Table 1. Boehmite-2 to Boehmite-4 are nanocrystalline solids [11]. The apparent crystallite size was not estimated for Boehmite-1, as this material is more amorphous than crystalline. Thus it was not possible to measure the width at half height of the 020 reflection.

The thermogravimetric curves of the boehmites synthesized by the different routes are shown in Fig. 2. According to these TG curves, the boehmites have four regions of weight loss: (i) room temperature to ca. 120 °C, due to desorption of physically bonded water and residual solvent; (ii) ca. 120 to 300 °C, corresponding to desorption of chemically bonded water and organic molecules between the interlayers; (iii) ca. 300 to 500 °C, corresponding to dehydroxylation during the phase transition of boehmite to γ-alumina and the burning of residual organic material; (iv) above 500 °C, due to dehydration of γ-alumina and posterior phase transitions ($\gamma \rightarrow \delta \rightarrow \theta$-alumina) [11,12].

The thermal behavior of the boehmites depends strongly on its crystallinity and on the crystallite size [1,13]. Boehmite-1 and Boehmite-2 have a similar profile of weight loss. However, due to the larger crystallite size of Boehmite-2 (Table 1), the desorption of chemically bonded water is slower, as can be seen by the smaller weight loss in the second region. The conversion of boehmite to γ-Al_2O_3 consists in dehydroxylation of the space between the boehmite double layers. In larger crystallites of boehmite, this is more dif-

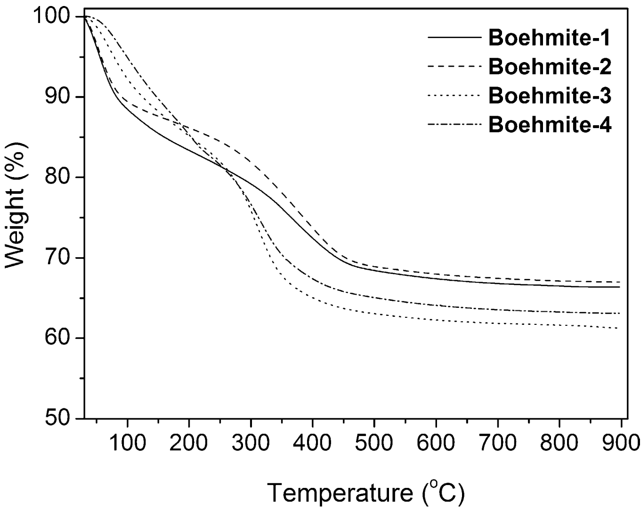

Fig. 2. TG curves of the boehmites.

Table 2
Carbon assay for the boehmites before and after calcination at 400 °C

Solid	Carbon assay (%)	
	Before calcination	After calcination
Boehmite-1	1.7	0.6
Boehmite-2	2.1	0.6
Boehmite-3	5.4	1.1
Boehmite-4	5.8	0.8

ficult because the chemisorbed water and organic molecules have longer diffusion paths, which suppress the phase transition of boehmite to γ-alumina [13]. The higher weight losses observed for Boehmite-3 and Boehmite-4 in the second and third region are due to decomposition of oxalic acid during the thermal treatment. Elemental analyses of the boehmites as prepared and after calcination at 400 °C show (Table 2) that almost all organic material was removed during calcination, since the carbon assay for the calcined materials is comparable to the instrumental error of the equipment (±0.5% for carbon).

Boehmite-1 to Boehmite-4 were transformed into γ-Al$_2$O$_3$-1 to γ-Al$_2$O$_3$-4, respectively, after calcination at 400 °C as shown by the typical XRD patterns in Fig. 3 [14]. The XRD patterns show very broad peaks indicating small crystallite sizes and/or not well crystallized materials. γ-Al$_2$O$_3$-1, γ-Al$_2$O$_3$-2, and γ-Al$_2$O$_3$-4 exhibit a similar XRD pattern; however, γ-Al$_2$O$_3$-3 is better described as an amorphous solid, as indicated by a broad band at 2θ between 20 and 40°. The crystallite size of the calcined γ-aluminas were not calculated due to the absence of well-defined peaks below $2\theta = 40°$.

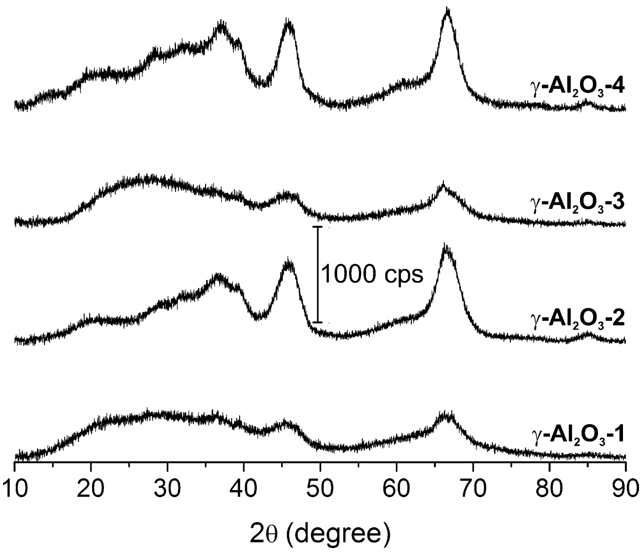

Fig. 3. XRD pattern of the aluminas calcined at 400 °C.

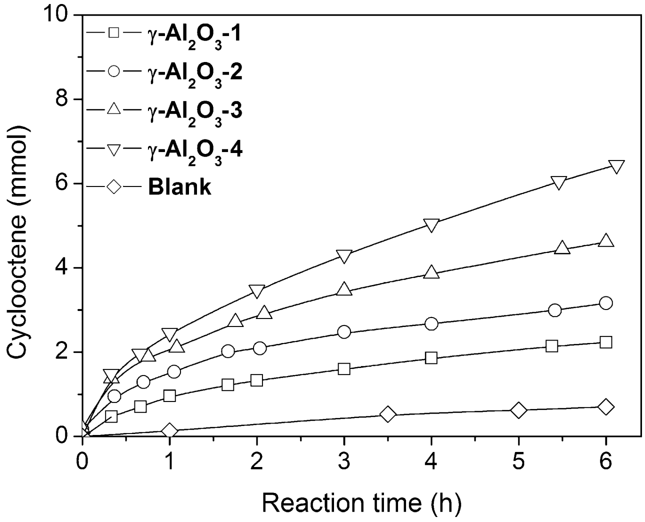

Fig. 4. Alumina-catalyzed epoxidation of *cis*-cyclooctene. Reaction conditions: 200 mg of γ-alumina, 10 mmol of cyclooctene, 20 mmol of hydrogen peroxide, under reflux.

Despite the similarities of the XRD pattern of γ-Al$_2$O$_3$-1, γ-Al$_2$O$_3$-2, and γ-Al$_2$O$_3$-4 their activities in the epoxidation of *cis*-cyclooctene are totally different, as shown in Fig. 4. The structural characteristics of the γ-alumina do not seem to have any direct correlation with their catalytic activity. The most active alumina is γ-Al$_2$O$_3$-4, which gives a yield of cyclooctene epoxide of ca. 65% after 6 h, followed by alumina γ-Al$_2$O$_3$-3 (ca. 45%), γ-Al$_2$O$_3$-1 (ca. 30%), and γ-Al$_2$O$_3$-1 (ca. 20%). The blank reaction without catalyst gives a yield of ca. 7%, indicating that alumina is really catalyzing the epoxidation. For all reactions the selectivity for cyclooctene epoxide was higher than 99%. The same selectivity was observed for more strained epoxides, such as cyclohexene epoxide [3,9] and (*S*)-limonene epoxides [3], indicating that there are no strong acid sites on the alumina surface under the reaction conditions used [9]. The catalytic activity of the γ-aluminas is not due to impurities. As already noted, the carbon content of the calcined aluminas is low and dispersive X-ray fluorescence analyses showed only traces of iron, in low ppm quantities, so low that no reproducible results could be obtained.

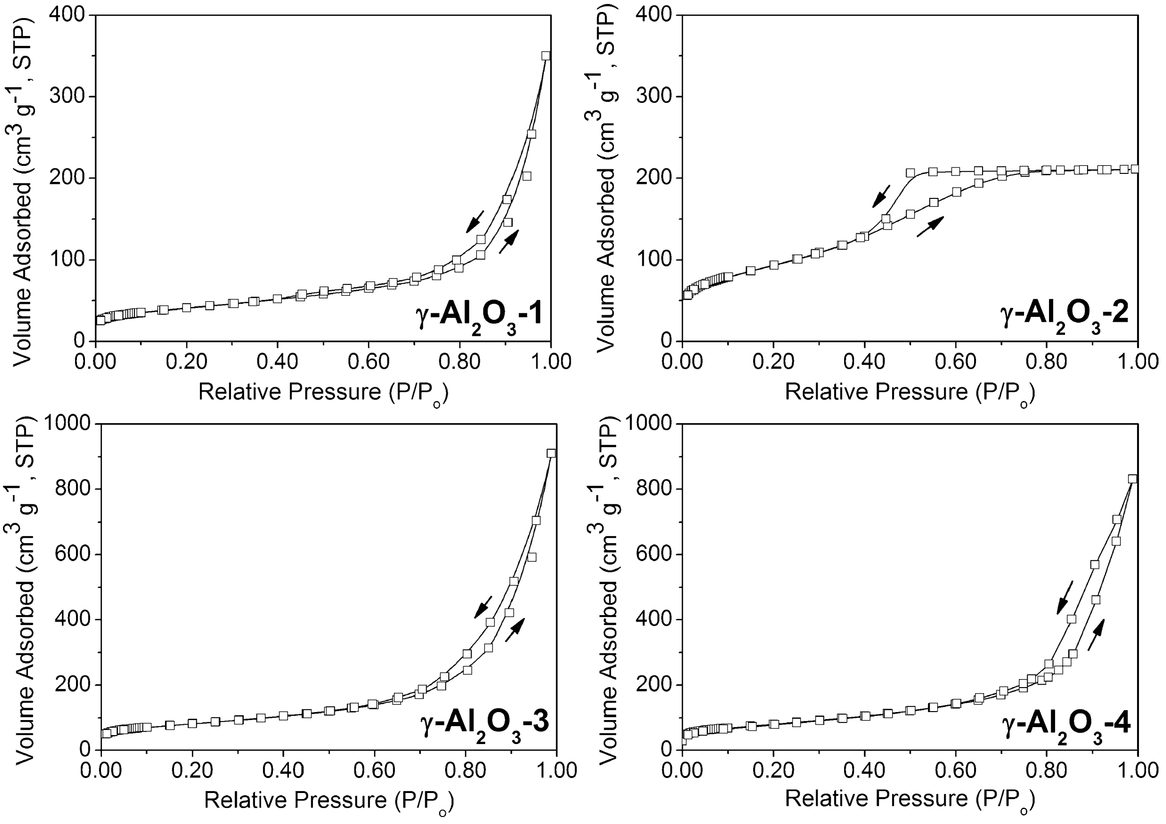

Fig. 5. Nitrogen adsorption–desorption isotherms at 77 K of the γ-aluminas.

The textural properties of the catalysts are another relevant factor for the catalytic activity of alumina, since the number of active sites, their geometry, and their reactivity depend mainly on the geometry of the void space inside the particles, as well as between them [15]. The textural properties of these γ-aluminas were determined by nitrogen adsorption–desorption isotherms at 77 K, which are shown in the Fig. 5.

Adsorption isotherms of type II were observed for γ-Al_2O_3-1, γ-Al_2O_3-3, and γ-Al_2O_3-4, indicating that they are nonporous solids. However, these isotherms have a type H3 hysteresis, indicating that nonstructural mesopores are present, which are formed by particle packing. This type of hysteresis is found for slit-shaped pores between plate-like particles, which are so large that capillary condensation happens only at a relative pressure close to $P/P_0 = 1$ [16]. However, γ-Al_2O_3-2 has a type IV isotherm with a type H2 hysteresis, indicating the existence of ink bottle-shaped mesopores. The surface area (A_{BET}), pore volume, and average pore diameter of the aluminas are given in Table 3.

Table 3
Textural properties of aluminas calcined at 400 °C

Alumina	A_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
γ-Al_2O_3-1[a]	143	0.54	15.1
γ-Al_2O_3-2	330	0.37	3.9
γ-Al_2O_3-3[a]	288	1.41	19.6
γ-Al_2O_3-4[a]	286	1.29	18.0

[a] Nonstructural porosity.

The lower catalytic activity of γ-Al_2O_3-1 can be directly related to its small surface area, when compared with the more active γ-Al_2O_3-3 and γ-Al_2O_3-4. However, alumina γ-Al_2O_3-2 has a slightly larger surface area than γ-Al_2O_3-3 and γ-Al_2O_3-4 and its epoxide yield is only 3 mmol after 6 h. On the other hand, Al_2O_3-2 is a mesoporous material without slit-shaped pores between the plate-like particles as observed for γ-Al_2O_3-1, γ-Al_2O_3-3, and γ-Al_2O_3-4. The lower yield of epoxide for γ-Al_2O_3-2 is probably due to the entrapment of water in the ink bottle-shaped mesopores during the reaction, not allowing the approach of the hydrophobic olefin to the active sites. The surface area and porous system of γ-Al_2O_3-3 and γ-Al_2O_3-4 are very similar. However, after 6 h the yield of epoxide is ca. 6.5 mmol for alumina γ-Al_2O_3-4 and only ca. 4.5 mmol for alumina γ-Al_2O_3-3, indicating that the catalytic activity of the alumina cannot be totally explained by its textural properties.

In order to analyze the acidic and basic properties of the γ-aluminas we performed temperature-programmed desorption of ammonia and carbon dioxide (TPD-NH_3 and TPD-CO_2, respectively). Fig. 6 shows the profiles of the TPD-NH_3 curves for γ-Al_2O_3-1, γ-Al_2O_3-2, γ-Al_2O_3-3, and γ-Al_2O_3-4.

The strength of interaction between ammonia and the acidic sites determines the desorption temperature. How-

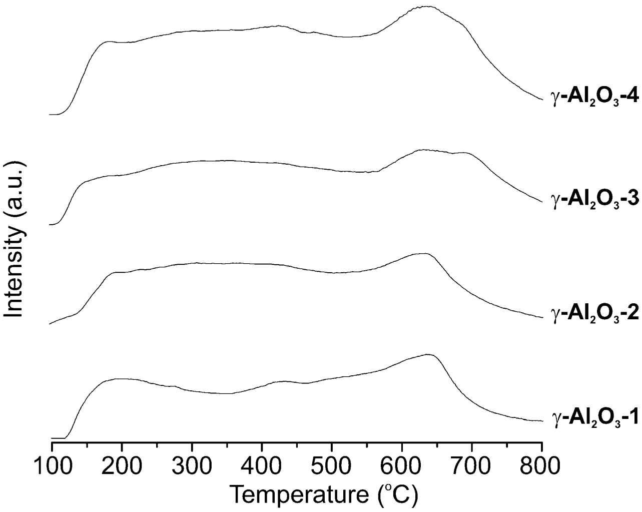

Fig. 6. TPD-NH_3 profiles for aluminas calcined at 400 °C.

Table 4
Distribution of acidic sites on the alumina surfaces

Alumina	Amount of acidic sites, a.u./g (relative amount, %)		
	Weak to moderate acidic sites[a]	Strong acidic sites[b]	Total per gram
γ-Al_2O_3-1	243 (60)	161 (40)	404
γ-Al_2O_3-2	251 (68)	118 (32)	369
γ-Al_2O_3-3	264 (60)	176 (40)	440
γ-Al_2O_3-4	363 (64)	208 (36)	571

Desorption temperatures: [a]100–550 °C and [b]550–800 °C.

ever, besides its chemical nature, the strength of the acidic sites depends also on the neighbors that surround it [17,18]. For crystalline solids, these neighbors are the same in all directions of the lattice, creating acidic and basic sites with distinct strengths, as was shown by Peri [19] and Knözinger and Ratnasamy [4]. On the other hand, for poorly crystalline or amorphous solids, the neighbors are not the same, creating a wide range of strengths of different acidic and basic sites. Therefore, the poorly crystalline structures of the γ-aluminas (Fig. 3) are the reason for the very broad and superimposed peaks in the TPD-NH_3 profiles that are shown in Fig. 6. Table 4 shows the distribution of acidic sites on the alumina surfaces. Surprisingly, the relative amounts of acidic sites with different acid strengths are similar for all these γ-aluminas. In contrast, the total amounts of acidic sites are different and can be directly correlated with the activity in the epoxidation of *cis*-cyclooctene for γ-Al_2O_3-2, γ-Al_2O_3-3, and γ-Al_2O_3-4. However, γ-Al_2O_3-1, which has more acidic sites than γ-Al_2O_3-2, shows lower activity.

The sol–gel routes for the preparation of γ-alumina precursors also create different populations of basic sites on the γ-alumina surfaces, as can be seen in the TPD-CO_2 profiles shown in Fig. 7. No basic sites are observed on the γ-Al_2O_3-1 surface. On the other hand, γ-Al_2O_3-1 shows weak as well as strong basic sites and γ-Al_2O_3-3 and γ-Al_2O_3-4 possess only strong basic sites, giving similar TPD profiles. However, these basic sites are "neutralized" under reaction conditions by ethyl acetate or small amounts of acetic acid which may be formed by hydrolysis of the solvent [2]. Therefore, the participation of these sites in the catalytic epoxidations is believed to be unimportant under these reaction conditions.

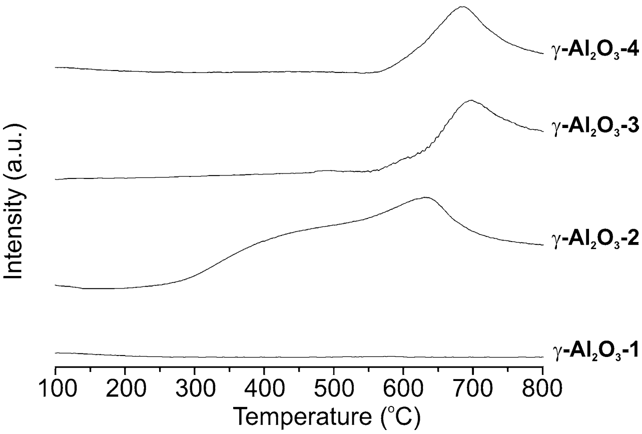

Fig. 7. TPD-CO_2 profiles for aluminas calcined at 400 °C.

The acidic and basic properties of the γ-alumina surfaces, determined by the TPD experiments, are only valid for a "cleaned" surface, obtained in the pretreatment (heating at 400 °C for 1 h) used in the TPD experiments. The alumina surface under reaction conditions, however, is completely rehydrated as aqueous H_2O_2 is used. Thus the Lewis acid sites, –O–Al^+–O–, are transformed into Brønsted acid sites, Al–OH or Al–$OH_2{}^+$. The acid strength of these sites is weak to moderate, as strong acid sites are expected to react with the epoxide forming ring-opened by-products, which were not observed.

An important factor that may restrict the reactivity of the alumina surface is its hydrophilicity. It is known that the epoxidation catalyst used industrially by Shell for the production of propylene oxide (Ti(IV)/SiO_2) cannot be used with H_2O_2, because this would create a water layer on its surface, making the approach of the olefin difficult and poisoning the active sites (Ti(IV)) [7,20]. Particularly effective Ti(IV)/SiO_2 catalysts are obtained when the deposition of titanium(IV) on silica is followed by further treatment with an organic silylating agent to remove the residual Brønsted acidity arising from Si–OH [21]. In contrast, the remarkable reactivity of TS-1 in catalytic epoxidation with aqueous 30 wt% H_2O_2 is due to the hydrophobicity of its surface that allows the approach of the olefin to the active sites even in the presence of water [7].

The surface of the calcined alumina, when exposed to water (from atmospheric air or from the reaction mixture), undergoes rehydration. The extension of this process depends on the structural and textural properties of the alumina. Thermogravimetric analyses of the γ-aluminas as used in the catalytic reactions (calcined at 400 °C and rehydrated in air) were carried out in order to evaluate the amount of physical and chemically bonded water on their surfaces (Fig. 8).

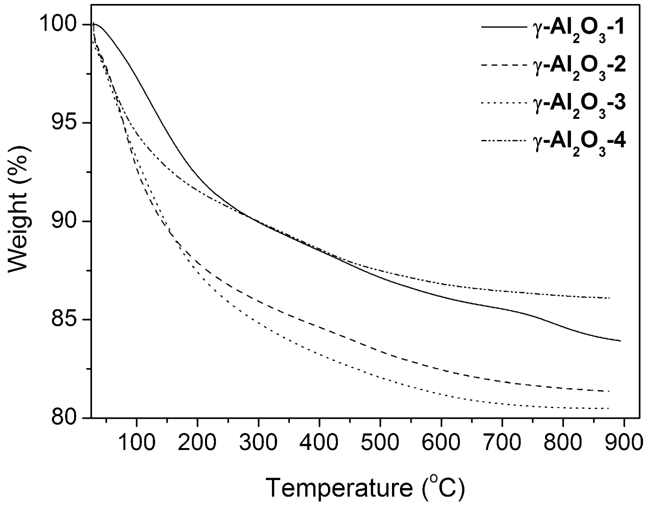

Fig. 8. TG curves of aluminas calcined at 400 °C.

The weight loss observed for alumina calcined at 400 °C (Fig. 8) can be assigned to the desorption of physically (up to ca. 200 °C) and chemically (above 200 °C) bonded water from the surface. These values are only approximate, as other compounds may also be evolved; however, deviations should be small as the carbon content is low and statistically the same for all γ-aluminas used in this study (Table 2). On the other hand, the amount of water evolved cannot be directly correlated to the hydrophilicity of the alumina surfaces as the surface areas vary considerably (Table 3). A better way is to consider the amount of water desorbed per unit of surface area of the alumina. The number of the water molecules per square nanometer of the alumina surface was calculated using

$$W(T\,^{\circ}\mathrm{C}) = \frac{\Delta m}{M_{\mathrm{H_2O}}}\frac{1}{A_{\mathrm{BET}}\cdot m_{\mathrm{i}}}N_{\mathrm{A}}, \tag{1}$$

where $W(T\,^{\circ}\mathrm{C})$ is the number of water molecules per square nanometer of alumina surface at a given temperature; Δm is the weight loss in grams at a given temperature (g); m_{i} is the initial weight of the alumina sample (g); $M_{\mathrm{H_2O}}$ is the molar mass of water (18.0153 $\mathrm{g\,mol^{-1}}$); N_{A} is the Avogadro constant ($6.022 \times 10^{23}\ \mathrm{mol^{-1}}$); A_{BET} is the surface area determined by the BET method ($\mathrm{nm^2\,g^{-1}}$).

The values of $W(25\,^{\circ}\mathrm{C})$ and $W(200\,^{\circ}\mathrm{C})$ of the calcined aluminas, as well as the parameters used in the calculations, are given in Table 5.

Analyzing the values of $W(25\,^{\circ}\mathrm{C})$, it is possible to order the rehydrated γ-aluminas according to their hydrophilicities: γ-Al_2O_3-1 > γ-Al_2O_3-3 > γ-Al_2O_3-2 > γ-Al_2O_3-4. The highly hydroxylated surface of γ-Al_2O_3-1 (37.4 H_2O/nm^2) is believed to be the responsible factor for its lowest catalytic activity, as the water layer formed becomes a kinetic barrier for olefin approach to the active sites on the surface. Considering the γ-aluminas with the same nonporous surfaces (γ-Al_2O_3-1, γ-Al_2O_3-3, and γ-Al_2O_3-4), the catalytic activity can be directly related to the population of water on the surface. However, although γ-Al_2O_3-2 is less hydrophilic than γ-Al_2O_3-3, its catalytic activity is low, probably due to its ink bottle-shaped mesopores, which entrap water during the reaction, thus strongly reducing the active surface area of the alumina.

The values obtained for the dehydration of the γ-alumina surface at 200 °C are in the same order of magnitude as those determined by De Boer et al. [22] and Peri [23] for γ-alumina after evacuation at 25 °C for 100 h or after drying at 120 °C (13 and 8.25 water molecules per 1 nm^2, respectively). Around 200 °C, approximately all physically adsorbed water is liberated and the aluminas γ-Al_2O_3-2, γ-Al_2O_3-3, and γ-Al_2O_3-4 have approximately the same population of water on their surface. In contrast, γ-Al_2O_3-1 has much more water on its surface. The $W(25\,^{\circ}\mathrm{C})/W(200\,^{\circ}\mathrm{C})$ ratio is approximately the same for γ-Al_2O_3-2, γ-Al_2O_3-3, and γ-Al_2O_3-4 (~ 2.8); however, it is much lower for γ-Al_2O_3-1 (1.9) which is much more hydrophilic and, therefore, strongly binds water on its surface.

This result is certainly very interesting, as in an earlier paper [6] we surprisingly found that commercial chromatographic aluminas of different types (weakly acidic, acidic, neutral and basic) showed similar catalytic activities in the epoxidation of α-pinene. The reasons for this result are now well understood as all commercial aluminas used were Brockmann grade I [24], which means that the hydrophilicities of these aluminas were approximately the same. However, the alumina prepared from aluminum *sec*-butoxide, using oxalic acid as gelation catalyst, showed a better catalytic activity in the epoxidation of cyclohexene, *cis*-cyclooctene, and (S)-limonene compared with commercial alumina [3] due to the lower hydrophilicity of its surface.

4. Conclusions

The structural properties of the γ-aluminas do not seem to be very important for their activities in the catalytic epoxidation of *cis*-cyclooctene with aqueous H_2O_2. The textural

Table 5
Number of water molecules per nm^2 of alumina surface

Alumina	m_{initial}	$m_{T=200\,^{\circ}\mathrm{C}}$	m_{final}	Water molecules per nm^2		$W(25\,^{\circ}\mathrm{C})$
	(mg)	(mg)	(mg)	$W(25\,^{\circ}\mathrm{C})$	$W(200\,^{\circ}\mathrm{C})$	$W(200\,^{\circ}\mathrm{C})$
γ-Al_2O_3-1	12.592	11.622	10.579	37.4	19.4	1.9
γ-Al_2O_3-2	25.250	22.194	20.546	18.9	6.6	2.9
γ-Al_2O_3-3	8.803	7.695	7.086	22.6	8.0	2.8
γ-Al_2O_3-4	9.152	8.388	7.880	16.2	6.5	2.5

properties, however, are important; the γ-aluminas should have a large surface area and an open structure. An open structure is important in order to avoid the entrapment of water in the porous system, what makes the diffusion of the olefin to active sites difficult. The relationship of acidic properties, such as Brönsted acidity, with textural properties can be expressed in terms of the hydrophilicity of the surface, which should be sufficient to guarantee a fast reaction with hydrogen peroxide forming Al–OOH groups on the surface, but should not be too high in order to allow a fast approach of the olefin to the active sites for the oxygen transfer to the olefin. Under the conditions used in this study, the sol–gel alumina γ-Al_2O_3-4 best fulfills these requirements.

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