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A study of commercial transition aluminas and of their catalytic activity in the dehydration of ethanol



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1. Introduction

Since decades, transitional aluminas have been among the most used materials in any field of technologies. In spite of this, details of their physicochemical properties are still a matter of discussion and investigation [1]. The details of the crystal structure of the most common polymorph, γ -Al₂O₃, are still a matter of controversy, being a defective non-stoichiometric spinel [2,3] or other cubic or tetragonal structures with the occupancy of non-spinel cationic sites [4-7]. γ -Al₂O₃ starts to convert at ca. 773 K toward other transitional phases: However, also the sequence of alumina phases obtained upon calcination has been an object of disagreement [8]; while some authors report the direct conversion of γ - Al_2O_3 into θ - Al_2O_3 near 923 K, most studies find the formation of slightly different intermediate phases, closely related to that of γ -Al₂O₃, formed continuously in the range 773–923 K. Also for these intermediate phases, different spinel-type tetragonal superstructures, with the occupancy of spinel and/or non-spinel cationic sites, such as those denoted as δ -Al₂O₃ [9] and γ' -Al₂O₃ [10], have been reported by different authors. Only above ca. 923 K, the

ABSTRACT

Conversion of ethanol was investigated over four commercial aluminas prepared by different industrial procedures and one commercial silica-alumina. Characterization was performed by TEM, XRD, S_{BET} and porosity measurements, and IR spectroscopy of the surface OH groups and of adsorbed CO and pyridine. Different features are attributed to different phases (γ -, δ -, θ -Al₂O₃) and different impurities (Na⁺, Cl⁻). Total conversion of ethanol with >99% selectivity to ethylene is achieved at 623 K over the purer Al₂O₃ catalyst (Na < 0.002 wt%). The most active sites are believed to be Lewis acidic Al³⁺ sites in a tetrahedral environment located on edges and corners of the nanocrystals. Ethanol adsorbs dissociatively on Lewis acid-base pair sites but may also displace water and/or hydroxyl groups from Lewis acidic Al³⁺ sites forming the active intermediate ethoxy species. Surface ethoxy groups are supposed to be intermediate species for both diethyl ether and ethylene production. Silica-alumina also works as a Lewis acid catalyst. The slightly lower activity on surface area basis of silica-alumina than aluminas attributed to the lower density of Lewis acid sites and the absence of significant basicity.

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crystal chemistry of alumina becomes well established. In fact, at this temperature, θ -Al₂O₃ is formed, whose "beta-gallia" structure is completely determined. However, the formation of θ -Al₂O₃ is a complex phenomenon [11], and γ -Al₂O₃ and θ -Al₂O₃ could coexist in core and shell structures [12]. The only fully ascertained phenomenon is that all aluminas transform into α -Al₂O₃ (corundum) completely above 1473 K.

The predominant application of alumina in the catalysis field is as the support of metal and sulfide catalysts. However, pure or "modified" aluminas represent today also important bulk catalysts, such as those of most catalytic steps of the Claus process [13,14] and those for the synthesis of dimethyl ether [15] and methyl chloride [16] from methanol. Aluminas have also been used in the sixties for producing ethylene from dehydration of ethanol [17,18]. This reaction might find renewed interest in the future to convert bioethanol produced by fermentation into "bioethylene" [19,20] in the frame of a new industrial organic chemistry based on renewables. Ethanol dehydration has also been used recently as a test reaction for the investigation of the surface properties of aluminas [21–23].

In the present paper, we report the results of our studies on the conversion of ethanol over different commercial catalysts based on alumina. Our interest for this investigation is multiple: (i) in the



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frame of studies [24] concerning the feasibility of new schemes for the conversion of renewable raw materials into useful products; (ii) to complete the picture of our studies [25] on the conversion of ethanol with steam (steam reforming) over alumina-supported catalysts, where the support activity plays some role; (iii) and to characterize different aluminas and go deeper in understanding the physicochemical properties of this very important family of materials and the ethanol dehydration mechanism.

2. Experimental

2.1. Catalysts

Four commercial alumina and one silica-alumina samples were investigated, whose characteristics are summarized in Table 1. According to the information we have, the aluminas arise from three different preparation procedures. V200 is produced from boehmite (γ -AlOOH) [26] prepared by precipitation from sodium aluminate [27]; P200 and P90 arise also from heat treatment of boehmite, but in this case, γ -AlOOH is prepared Al alkoxides [28]; D100 is a "fumed" oxide, prepared by flame hydrolysis of AlCl₃ [29].

2.2. Transmission electron microscopy studies

Samples were prepared in aqueous suspension in an ultrasonic bath, and TEM was recorded with a Zeiss EM 900 instrument.

2.3. XRD

The XRD was performed on a Siemens D-500 diffractometer (CuK α radiation, Ni filter; operated in the vertical mode on 40 KV and 30 mA) equipped with the Diffract AT V3 software package. The patterns were recorded over the 2θ angle ranging from 10° to 70° at a scan rate of 4°/min.

2.4. Infrared spectroscopy (IR) experiments

IR spectra were recorded using Nicolet 380 FT-IR spectrometers. For skeletal studies, the samples were pressed into thin wafers with KBr and spectra were recorded in air.

Acidity measurements were taken using the pure powders pressed into thin wafers (~30 mg, surface area of 1.31 cm^2) and activated in the IR cell connected with a conventional outgassing/gas manipulation apparatus at 773 K. The activated samples were contacted with pyridine vapor ($p_{Py} \sim 1$ torr) at room temperature for 15 min; after which the IR spectra of the surface species were collected in continuous evacuation at room temperature with increasing temperature. CO adsorption was performed at 130 K (real sample temperature measured by a thermocouple) by the introduction of a known dose of CO gas inside the low temperature infrared cell containing the previously activated wafers. The sample was saturated with CO using sufficiently high CO pressure

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The properties of investigated catalysts.

(up to 20 Torr) until the intensity of the bands of the adsorbed species has reached the maximum. IR spectra were later collected under evacuation at increasing temperatures between 130 and 273 K.

In order to study the mechanism of reaction, pressed disks of the pure catalyst powders were activated *in situ* in the IR cell connected with a conventional gas manipulation apparatus before any adsorption experiment. IR spectra of the surface species as well as of the gas phase were recorded with increasing temperature in static conditions (starting $P_{EtOH} \sim 4$ torr).

2.5. Surface area and porosity

The BET surface areas and porosity were measured using N_2 adsorption/desorption at 77 K determined both volumetrically with a Micromeritics Gemini 2380 instrument and gravimetrically by a modified Sartorius symmetrical microbalance, described elsewhere [30].

2.6. Catalytic experiments

Catalytic experiments have been performed at atmospheric pressure in a tubular flow reactor using 0.5 g catalyst (60–70 mesh sieved) and feeding 7.9% v/v ethanol in nitrogen with total flow rate of 80 cc/min. The carrier gas (nitrogen) was passed through a bubbler containing ethanol (96%). The temperature in the experiment was varied stepwise from 423 K to 723 K.

Ethanol conversion is defined as usual:

 $X_{\text{EtOH}} = (n_{\text{EtOH}(\text{in})} - n_{\text{EtOH}(\text{out})})/n_{\text{EtOH}(\text{in})}$

While selectivity to product i is defined as follows:

$$S_i = n_i / (v_i (n_{\text{EtOH}(\text{in})} - n_{\text{EtOH}(\text{out})}))$$

where n_i is the moles number of compound *i*, and v_i is the ratio of stoichiometric reaction coefficients.

The outlet gases were analyzed by a gas chromatograph (GC) Agilent 4890 equipped with a Varian capillary column "Molsieve 5A/Porabond A Tandem" and TCD and FID detectors in series. In order to identify the compounds of the outlet gases, a gas chromatography coupled with mass spectroscopy (GC-MS) Thermo Scientific with TG-SQC column (15 m \times 0.25 mm \times 0.25 µm) was used.

3. Results

3.1. X-Ray diffraction

The X-Ray diffraction patterns of the four alumina samples are presented in Fig. 1. The pattern of P200 is typical of γ -Al₂O₃ (JCPDS card No. 43-1308), while that of V200 contains the same pattern with an additional broad component at low 2 θ likely due to some residual poorly crystalline pseudoboehmite (JCPDS card No. 21-1307). The pattern of P90 is typical of θ -Al₂O₃ (JCPDS card No. 35-0121) while that of D100 certainly contains the peaks of δ -Al₂O₃ (JCPDS card No. 47-1770) possibly with those of γ -Al₂O₃, in

Notation	Manufacturer	Preparation	$S_{\rm BET} (m^2/g)$	$V_p (\mathrm{cm}^3/\mathrm{g})$	Average particle size ^a (Å)	XRD phase	Na content (%)
P90 P200	Puralox Sba90 Sasol Puralox Sba200 Sasol	Calcination of P200 From boehmite via Al alkoxides	90 ± 5 190 + 10	0.13 0.45	160 100	θ -Al ₂ O ₃ γ -Al ₂ O ₂	0.002*
V200	Versal 250 UOP	From boehmite via ra dinomices	202 ± 5	0.47	90	γ -Al ₂ O ₃	<0.04*
D100 SA330	Strem (13 wt% Al ₂ O ₃)	From flame hydrolysis of AlCl ₃	100 ± 10 330 ± 10	0.10 -	-	γ,δ-Al ₂ O ₃ Amorphous	0.006 -

Data from the manufacturers.

^a From TEM data (Scherrer formula).



Fig. 1. XRD patterns of aluminas. The peaks marked with ■ are due to sample holder. Above, the position and intensities of the peaks of the pertinent alumina phases are reported according to the JCPDS cards.

agreement with other studies concerning this material [31]. The sample SA330 appears to be fully amorphous to XRD analysis, as typical for silica-aluminas with moderate alumina contents.

3.2. TEM analysis

Transmission electron micrographs of the alumina samples are presented in Fig. 2. While the morphology of the V200 sample is typically fibrous, as reported by the manufacturer [26], the other samples appear to have quite a globular morphology. Actually the lamellar morphology, usually arising from the topotactic decomposition of (pseudo) boehmites (which have a layered structure and typically a lamellar habit [5,32]), is not pronounced in the TEM of P200. This sample appears to be "prismatic," in agreement with the literature data published on the same material [28,31]. The fumed alumina D100 shows also a globular morphology, as reported previously [33,31].

From the data reported in Table 1, it can be observed that the average size of particles (from TEM) of the P90 and D100 samples is similar to each other and higher than those measured for the samples V200 and P200, in accordance with the lower surface area of the former ones with respect to the latter ones.

3.3. Porosity characterization

The data concerning morphological characteristics of all materials are summarized in Table 1 and in Fig. 3. The nitrogen adsorption/desorption isotherms (Fig. 3a) correspond to the type IV of the BDDT classification [34]. The isotherm of P200 exhibits an hysteresis loop intermediate between H2 and H4 (according to the IU-PAC classification) due to open tubular pores with circular or polygonal sections and a monomodal pore size distribution with a maximum frequencies of pore diameters between 6 and 10 nm. The isotherm of V200, which has a similar surface area, can be classified as type IV and H1 (cylinder shape). The pores show a monomodal pore size distribution with a maximum frequency of pore diameters near 9 nm. The pore volume of V200 (0.47 cm³/g) is similar to that of P200 (0.45 cm³/g).



Fig. 2. TEM micrographs of aluminas.

P90 has an incipient H4 hysteresis loop with a small pore volume and an irregular pore size distribution between 10 and 15 nm. In D100, the pore volume is very low, essentially zero.

3.4. Skeletal IR spectra

The skeletal IR spectra of the catalysts are presented in Fig. 4. The spectrum of sample P200 is typical for γ -Al₂O₃, mostly charac-



Fig. 3. (a) Nitrogen adsorption/desorption isotherms at 77 K in aluminas, and (b) pore size distribution curves of aluminas.

terized by two very broad poorly resolved bands in the medium IR region at 550 and 830 cm⁻¹, which may show some complexity [35–38]. The spectrum of the sample V200 is roughly similar, but with some distinct difference in the shape of the broad absorption. Slight difference is mainly observed at high frequency, where the LO components, arising from the splitting of the transverse and longitudinal optical modes (TO/LO splitting), are located. The extent of TO/LO splitting is somehow dependent from crystal morphology; thus, this difference might reveal a "morphological" effect on the skeletal IR spectrum. The spectrum of P90, showing several components superimposed to a broad background, is typical of θ -Al₂O₃ [36,37], while the spectrum of D100 (also with several components but much less defined) may agree with the structure of δ -Al₂O₃ superimposed to that of γ -Al₂O₃. The spectrum of SA330 is, instead, typical of silica based materials and, in particular, of amorphous silica [36].

3.5. Surface acidity characterization by IR spectroscopy of adsorbed probe molecules

3.5.1. Surface hydroxyl groups

The IR spectra of the four alumina samples as well as that of SA330 in the region of the surface hydroxyl groups, all recorded after outgassing at 773 K, are presented in Fig. 5. The spectra of the two γ -Al₂O₃s, P200 and V200, show the typical bands of the surface OHs of transitional aluminas, as discussed in many papers

[1,39,40]. In particular, the bands at ca. 3790, 3770, 3740–3720, 3700–3660, and 3580 cm⁻¹ are detectable in both cases. The main difference in the OH stretching spectra between these two samples resides in the lower relative intensity of the component near 3770 cm⁻¹ in V200, which has in fact been noted to be selectively reduced by sodium impurities [41] which are more abundant in V200. For all other bands, except the band near 3770 cm⁻¹, a similar relative intensity is observed in the spectra of the two samples, typical for γ -Al₂O₃, irrespective of the evident difference in their morphology (a fibrous morphology for V200 and a globular morphology for P200).

The same bands are also evident in the spectra of the other samples, but the relative intensities differ significantly. In particular, the spectrum of the D100 sample shows clearly much more intense the band at ca. 3670 cm^{-1} respective to the others. This spectrum has been reported by other authors for similar fumed samples [42,43]. This difference implies a significant effect of the difference either in morphology (different exposed planes, corners, and edges) or in the structure (presence of the δ -Al₂O₃ phase), or in the amount and type of impurities. Indeed, it seems likely that the different spectrum of this sample might be associated with chlorine impurities (particularly abundant in fumed samples), due to chloride ions replacing some surface hydroxyl groups, thus reducing the intensities of the bands other than that at ca. 3670 cm^{-1} [44,45]. The spectrum of the sample P90 is similar to that reported by Lodziana et al. [46] for θ -Al₂O₃ samples, showing the band at ca. 3725 cm⁻¹ very strong and sharp, with an evident



Fig. 4. FT-IR skeletal spectra (KBr pressed disks) of (a) P90, (b) P200, (c) V200, (d) D100, and (e) SA330.



Fig. 5. FT-IR spectra of aluminas after activation at 773 K (vOH region): (a) P90, (b) P200, (c) V200, (d) D100, and (e) SA330.

component at higher frequency, and the component at ca. 3760 cm^{-1} weaker than in the other samples.

The spectrum of the SA330 sample shows, as usual for amorphous silica-alumina [47,48], a single band at 3744 cm^{-1} with a tail at lower frequencies, attributed to terminal silanol groups.

We may remark here that some authors denote the hydroxyl groups of alumina as "Brønsted acid sites," to distinguish these sites from the Lewis acid sites [21]. Here, we want to underline that part of hydroxyl groups of silica-alumina have acidity strong enough to protonate pyridine (see below), while those of alumina are weaker acids and do not protonate pyridine. For this, it is usually reported that alumina does not carry Brønsted acidity. Thus, the use of the term "Brønsted acid sites" for the OHs of alumina is ambiguous.

3.5.2. CO adsorption

The characterization of the surface acidity of aluminas has been frequently performed using IR spectroscopy of adsorbed CO as a probe molecule [31,49]. In Fig. 6, the spectra of CO adsorbed on our catalysts at 173-273 K after previous outgassing at 773 K are reported. In the case of all alumina samples, a main band due to \dot{CO} interacting with Al^{3+} ions is observed: This band presents the maximum at ca. 2180 cm⁻¹ at the higher coverages and decreases in intensity, while its maximum shifts progressively to ca. 2200 cm⁻¹. Only over P200, we distinctly find at the lowest coverages a very weak component at 2220 cm⁻¹ with another component at 2206 cm⁻¹. In the other three cases at the lowest coverages, the maximum is very near 2202 cm^{-1} . Interestingly, over the SA330 catalyst, instead, the presence of a band at 2230 cm⁻¹ is very evident with a much weaker component slightly lower than 2200 cm⁻¹. These data would indicate that stronger Lewis sites should exist at the surface SA330 than on aluminas. As for aluminas, the strongest Lewis acid sites are found on P200, while for the other aluminas, the strongest Lewis sites are slightly weaker.

We can mention that our result for the D100 sample is slightly different from that reported, for a same material, by Gribov et al. [31]. These authors in fact show the same band but, additionally, at the lowest coverage, a very weak double band at ca.

2230 cm⁻¹ and near 2215 cm⁻¹. They found the same spectrum for a γ -Al₂O₃ sample. These additional features are the result of the higher activation temperature these authors used (1020 K), which allowed more extensive de-hydroxylation and made free additional sites. According to Gribov et al. [31], the weak features at 2230 cm⁻¹ and near 2215 cm⁻¹ are due to CO adsorbing on tri-coordinated Al³⁺ located on corners and edges of the crystal surface, while the band shifting from ca. 2180 cm⁻¹ to ca. 2200 cm⁻¹ is due to CO adsorbing on tri-coordinated Al³⁺ located on flat surfaces. Assuming the same assignments, with which we agree, and that are supported by the calculations of Wischert et al. [50], we may conclude that on P200 much more edges and corners should exist with respect to P90, D100, and V200, where the higher frequency features are essentially not evident in our conditions.

These data somehow contradict the idea of Kwak et al. [21] that active Lewis sites on alumina are only penta-coordinated Al ions observed by ²⁷Al MAS NMR.

In any case, it seems interesting to remark that on silica-alumina SA330 even stronger Lewis sites would exist than on aluminas, very likely associated with coordinatively unsaturated tetrahedral Al³⁺ "embebbed" in the silica network.

3.5.3. Pyridine adsorption

The use of stronger basic molecules (we can say true bases) is also applied to characterize catalyst surfaces, allowing also a definite determination of the existence of Brønsted acidity. Traditionally, the most used basic probe is pyridine. The spectra recorded after adsorption of pyridine on SA330, P200, and V200 are presented in Fig. 7. On their surfaces, the typical features of Lewisbonded pyridine can be observed. Over P200, three 8a components observed at 1589–95, 1610–16, and 1624 cm⁻¹ reveal the existence of at least three different families of Lewis acid sites, as discussed previously for transitional aluminas [1,39,40,51,52]. The typical assignments for the first and the last of these three components are to pyridine bonded to octahedral and tetrahedral Al cations, respectively, both with a single coordinative unsaturation, thus being tri- and penta-coordinated, respectively, before pyridine adsorption. The band in the middle may be due to pyridine species interacting either with Al ions in coordination five (four



Fig. 6. FT-IR spectra of CO adsorbed on aluminas and silica-alumina after outgassing at increasing temperature.

before adsorption), or, in any case, to sites having Lewis acid strength slightly lower than canonical tri-coordinated cations. These sites may be tri-coordinated too, but with a nearest cation vacancy. The shifts observed for the maxima of the 8a band, as well as of the 19b mode (1440–1456 cm⁻¹) upon desorption, provide evidence of the high heterogeneity of each family these sites. The spectra observed on the other aluminas (P90, D100, V200) are very similar, as also are most spectra reported in the literature for pyridine adsorbed on aluminas [53]. Again, these data contrast the opinion of Kwak et al. that report that only penta-coordinated Al ions are active Lewis sites on alumina [21].

In the case of sample V200, the features of pyridine adsorption are almost the same with P200. However, the 8a band at 1590– 1595 cm⁻¹ seems to be slightly stronger and broader on V200 than on P200. This is possibly due to pyridine molecule adsorbed on weakly Lewis acidic Na⁺ cations, slightly more abundant on V200 [54], contributing to the band, i.e. superimposing to the band due to pyridine on penta-coordinated Al^{3+} ions.

In the spectra of the sample SA330, the features of pyridine adsorbed on very strong Lewis sites are also evident: The spectral components (8a mode at 1623 cm⁻¹, 8b mode at 1579 cm⁻¹, and 19b mode at 1454–6 cm⁻¹) are the same as for pyridine adsorbed on the strongest Lewis sites of aluminas, thus being attributed to pyridine adsorbed on coordinatively unsaturated Al³⁺ "embebbed" in the silica network. Interestingly, this band does not shift with coverage and outgassing, thus suggesting that these species are "homogeneous" on SA330. Additionally, bands due to more weakly bonded molecular pyridine are also observed (8a mode at 1597 cm⁻¹ and 19b mode at 1446 cm⁻¹), which may be due to strongly H-bonded pyridine.

Indeed, some authors have calculated the adsorption of pyridine Lewis-bonded on Al-oxide clusters and found that the calculated



Fig. 7. FT-IR spectra of surface species arising from pyridine adsorbed on (a) SA330, (b) P200 and (c) V200.

shifts of the vibrational modes of pyridine adsorbed on tri-coordinated Al³⁺ (thus forming a tetrahedral complex) [55,56] agree with those we have measured for pyridine adsorbed on the strongest Lewis sites of alumina and silica-alumina (1624 and 1456 cm⁻¹).

Additional to Lewis-bonded pyridine, on SA330, also the bands are associated with pyridinium ions at 1633–31 cm⁻¹, 8a, and 1545 cm⁻¹, 19a [57]. This corresponds to the well-known Brønsted acidity of part of the hydroxyl groups of silica-alumina [48].

Thus, studies performed using IR spectroscopy of adsorbed probe molecules show that the four alumina samples display slightly different Lewis acid sites. P200 seems to have stronger sites than other samples, which may have similar Lewis acidity. The silica-alumina sample SA330 has Lewis acidity similar or even stronger with respect to P200, and, additionally, also Brønsted acidity.

3.6. Catalytic activity in ethanol dehydration

In table 2, the data concerning the catalytic activity of the five catalysts in ethanol dehydration are summarized. While ethanol conversion in the blank experiment (only silica glass in the reactor) starts to be detectable only at 673 K, in the presence of all alumina samples, ethanol conversion is already significant at ca. 473 K and total at 673 K (Fig. 8a), providing evidence of their catalytic activity. In the experiment performed using the same catalyst weight, the more active catalyst is P200 followed by SA330 and by P90. V200 shows the lowest conversions. In the experiments performed using beds with the same catalyst area (Fig. 8b), evidence is provided for the lower activity of SA330 with respect to P200, P90,

Table 2

Ethanol conversion and product selectivities upon ethanol dehydration (experiments with the same catalyst weight, WHSV 1.43 h^{-1}).

Catalyst	Temp. (K)	TC ^a	Sdiethylether	Sethylene	Sethane	Sbutene
P90	423 473 523 573 623 673 723	0.0 5.3 66.6 85.6 100.0 100.0 100.0	- 100.0 93.2 67.7 0.0 0.0 0.0	- 0.0 6.8 32.0 99.4 99.6 98.8	- 0.0 0.0 0.0 0.6 0.4 1.2	- 0.0 0.0 0.0 0.0 0.0 0.0 0.0
P200	423 473 523 573 623 673 723	0.2 20.8 78.6 97.7 99.7 99.9 100.0	100.0 99.1 79.7 0.3 0.0 0.0 0.1	0.0 0.9 20.2 99.7 100.0 99.8 98.9	0.0 0.0 0.1 0.0 0.0 0.0 0.8	0.0 0.0 0.0 0.0 0.0 0.1 0.0
V200	423 473 523 573 623 673 723	0.0 2.2 41.2 77.8 97.4 99.8 99.8	- 100.0 97.1 52.1 0.2 0.0 0.0	- 0.0 2.8 47.6 99.1 99.4 99.4	- 0.0 0.1 0.3 0.7 0.5 0.5	- 0.0 0.0 0.0 0.0 0.1 0.1
D100	423 473 523 573 623 673 723	0.0 2.5 49.8 72.1 99.3 99.9 100.0	- 100.0 96.5 51.1 0.1 0.1 0.2	- 0.0 3.5 48.9 99.9 99.8 99.4	- 0.0 0.0 0.0 0.0 0.0 0.0 0.3	- 0.0 0.0 0.0 0.0 0.1 0.1
SA330	423 473 523 573 623 673 723	0.8 15.7 67.5 96.0 99.8 100.0 100.0	100.0 86.3 64.9 0.3 0.0 0.0 0.0	0.0 13.7 35.1 99.6 100.0 100.0 99.9	0.0 0.0 0.1 0.0 0.0 0.0	0.0 0.0 0.0 0.0 0.0 0.0 0.0

^a TC = total conversion.

and D100. D100 shows slightly lower activity than P200 and P90 whose catalytic activity per surface area is quite similar.

In all cases, diethyl ether is formed with high selectivity at low temperature (<523 K), when conversion is low, as shown also by Kwak et al [21]. In contrast, ethylene is produced almost quantitatively at high temperature (>573 K) when conversion approaches 100%. Over all catalysts except V200 (where conversion is slightly lower), the yield in ethylene is above 99% at 623 K with WHSV 1.43 h^{-1} in our diluted conditions. Very small amounts of ethane and butene are found as by-products.

As shown in Fig. 9, the selectivities to ethylene depend on ethanol conversion in similar way for the alumina samples. In the case of silica-alumina, the selectivity to ethylene is higher, at low conversion, than for aluminas.

The experiments performed with the same catalyst at the same temperature but with different space velocities (compare Tables 2 and 3) show, as expected, higher conversion at lower space velocities. Only in the case of D100 at 523 K and 573 K, the conversion is slightly higher at slightly higher SV. This anomalous datum is associated with a slightly lower repeatability of catalytic results on this sample, likely associated with its high chlorine impurities. This behavior may be associated with a chlorine/hydroxide exchange reaction occurring in parallel with ethanol dehydration, or to more heterogeneity in different portions of the same batch. In any case, the results obtained at different SVs show that, at moderate conversion, the higher the ethanol conversion, the higher the ethylene selectivity; the lower the ethanol conversion, the higher the diethyl ether selectivity. At full conversion, diethyl ether is not formed at all. This suggests that the ethanol partial pressure available is a key factor favoring diethyl ether (at low conversion, with more ethanol available) or ethylene (at high conversion): In fact, the dependence of the diethyl ether synthesis is expected to have a higher reaction order with respect to ethanol than ethylene synthesis, as actually found experimentally [23].



Fig. 8. Conversion of ethanol over aluminas and silica-alumina as a function of reaction temperature: (a) experiments performed using the same catalyst weight, and (b) experiments performed using the same catalyst surface area.



Fig. 9. Selectivities of ethylene as a function of total ethanol conversion.

3.7. Infrared studies of ethanol dehydration

In Figs. 10–12, the IR spectra recorded during the experiment of ethanol dehydration performed in the IR cell are reported. The surface species observed on the P200 catalyst during ethanol conversion are presented in Fig. 10. The main bands at 1116 and 1073 cm⁻¹ observed upon heating are attributed to the asymmetric and symmetric stretching modes of the C-C-O system of surface ethoxide species. The spectrum of gaseous ethanol shows a dominant roto-vibrational peak at ca. 1060 cm^{-1} in this region, while liquid ethanol shows two bands at 1089 and 1053 cm⁻¹ [58]. Two features similar to those of undissociated ethanol are found, weak, in the spectrum recorded at r.t. (room temperature) just after outgassing at r.t. The band at 1167 cm^{-1} is essentially a CH₃ rocking mode also having a CO stretching character [59], while the maxima at 1450 cm⁻¹ (δ_{as} CH₃) and 1390 cm⁻¹ (δ_{sym} CH₃) are due to deformation modes of the CH₃ group to which the CH₂ scissoring mode is superimposed. The presence of a weak broad band centered at 1297 cm⁻¹, due to the COH deformation mode of undissociated adsorbed ethanol, provides further evidence of the predominance of dissociated ethanol adsorbed in the form of ethoxide groups but also of the copresence of adsorbed undissociated species in small amounts. By increasing the temperature, the spectrum is essentially unchanged up to 473 K. The bands of adsorbed ethoxide species essentially decrease in intensity later, up to almost disappear at 573 K when two bands at 1582 and 1462 cm⁻¹ grow. These bands are associated with acetate species. The spectrum in the OH stretching region (see Fig. 10) shows the full disappearance of the higher frequency surface hydroxyl group (3800-3700 cm⁻¹) after contact with ethanol, persisting even after outgassing at 423 K, while a complex absorption in the region 3600-3500 cm⁻¹ may be associated with the presence of weakly Hbonded undissociated ethanol as well as to new triply bridged OHs formed as a result of ethanol dissociation. After progressive heating in the range 423–573 K, at least part of the OH bands (in particular the band at ca. 3740 cm⁻¹) reappear in parallel to the decrease in the bands due to ethoxy groups. This occurs well before the disappearance of the absorption at $3600-3500 \text{ cm}^{-1}$, showing that the disappearance/reappearance of the bands of the free hydroxyl groups is not due to a reversible shift associated with Hbonding. The spectra indicate that a mutual disappearance/reappearance of hydroxyl and ethoxy groups occurs.

Looking at the gas-phase spectra, presented in Fig. 11, we can remark that some amount of gas-phase water is observed after absorbing ethanol (note that the spectrum of gas-phase ethanol

Table 3
Ethanol conversion and products selectivities upon ethanol dehydration (experiments with the same catalyst surface area).

Catalyst	Temp. (K)	TC ^a	Sdiethylether	Sethylene	Sethane	Sbutene
P90 1.43 h ⁻¹ WHSV	423	0.0	-	-	-	-
	473	5.3	100.0	0.0	0.0	0.0
	523	66.6	93.2	6.8	0.0	0.0
	573	85.6	67.7	32.0	0.0	0.0
	623	100.0	0.0	99.4	0.6	0.0
	673	100.0	0.0	99.6	0.4	0.0
	723	100.0	0.0	98.8	1.2	0.0
P200 2.97 h ⁻¹ WHSV	423	0.0	-	-	-	-
	473	9.5	99.1	0.9	0.0	0.0
	523	61.5	91.4	8.8	0.1	0.0
	573	91.5	5.5	94.1	0.4	0.0
	623	99.2	0.1	98.9	1.1	0.0
	673	100.0	0.0	99.4	0.5	0.1
	723	99.7	0.0	99.2	0.7	0.1
D100 1.66 h ⁻¹ WHSV	423	0.0	-	-	-	-
	473	2.8	100.0	0.0	0.0	0.0
	523	57.6	95.5	4.4	0.1	0.0
	573	80.4	38.5	61.2	0.3	0.0
	623	96.3	0.2	98.8	1.0	0.0
	673	100.0	0.0	99.6	0.4	0.1
	723	100.0	0.0	99.7	0.2	0.1
SA330 4.95 h ⁻¹ WHSV	423	0.3	100.0	0.0	0.0	0.0
	473	3.7	87.6	12.4	0.0	0.0
	523	26.0	69.5	30.5	0.0	0.0
	573	73.8	32.5	67.5	0.0	0.0
	623	99.0	0.4	99.6	0.0	0.0
	673	100.0	0.0	100.0	0.0	0.0
	723	100.0	0.0	100.0	0.0	0.0

^a TC = total conversion.



Fig. 10. FT-IR spectra of surface species arising from ethanol adsorbed on P200 at r.t., and at increasing temperature (gas-phase and activated catalyst spectra were subtracted). In the insert: non-subtracted spectra of the activated catalyst (full line) and after outgassing at 423 K after ethanol adsorption (broken line).

is subtracted in Fig. 11, at 373 K). The formation of diethyl ether is evident at 473 K and, much more, at 523 K, when its C–O–C asymmetric stretching band is observed at 1142 cm⁻¹, together with the CH stretchings at 2989 and 2870 cm⁻¹ [60]. This gas-phase species disappears at 573 K, when ethylene (3105, 2988, and 949 cm⁻¹) is observed in the gas. The beginning of the disappearance of the bands of surface ethoxy groups corresponds to the formation of diethyl ether in the gas phase, while the end of this process corresponds to the formation of gas-phase ethylene.



Fig. 11. FT-IR subtraction spectra of gas phase of ethanol adsorbed on P200.

The IR results suggest that ethanol adsorbs, at least in part, by replacing hydroxyl groups forming ethoxy groups and gas-phase water (Scheme 1). Another part of it likely dissociatively adsorbs on Lewis acid-base pairs forming ethoxy groups and new OHs. It can be proposed that surface ethoxy groups are intermediate species for both diethyl ether and ethylene production. The IR data may be interpreted indicating that diethyl ether may form by a nucleophilic substitution reaction where ethoxy groups attack as nucleophiles the carbon atom of either gas-phase ethanol, or, more likely, of H-bonded adsorbed undissociated ethanol (Scheme 1). This reaction, reversible, vanishes in favor of ethoxy group decomposition to ethylene when the concentration of available undissociated ethanol is very low. These mechanisms may agree with the zero order found for ethanol conversion to ethylene (due to the strong adsorption of ethanol as ethoxy group nearly saturating the surface at least at low temperature) and the positive but frac-



Fig. 12. FT-IR spectra of surface species arising from ethanol adsorbed on aluminas and silica-alumina at outgassing at r.t.

tionary reaction order found for diethyl ether formation (associated to the need of weakly undissociatively adsorbed ethanol to react with ethoxy groups), as reported recently [23]. They also agree with the competition effect observed by water adsorption. The results obtained with the other alumina samples are very similar to those described for P200. In Fig. 12, the IR spectra of the surface species observed over the four alumina and silica-alumina samples are compared. The spectra are all very similar, with very slight differences. In particular, it seems evident a difference for the spectra recorded on V200 sample, where the C–C–O stretching modes are slightly shifted with a more evident additional component at 1100 cm⁻¹, and also the lower frequency CH stretching and deformation components at 2933 and 1390 cm⁻¹ are definitely lowered in intensity. It seems reasonable to attribute these differences to the formation of slightly different ethoxide species, possibly bridging between Al³⁺ and Na⁺ cations, due to the larger amount of sodium on this catalyst.

4. Discussion

Four different commercial alumina samples have been characterized by XRD, TEM, BET surface area and porosity measurements, and IR spectroscopy of the skeletal vibrations, of the surface hydroxyl groups and of adsorbed probe molecules. According to our information, the samples are prepared with three different procedures, as cited in the experimental section.

The sample P200 appears to be a highly pure γ -A₂O₃, with a distribution of Lewis acid sites characterized by high strength. According to the assignments of Gribov et al. [31], we believe that the sites evidenced by CO adsorption producing bands well above 2200 cm⁻¹ are tri-coordinated Al³⁺ cations located on corners and edges on the nanocrystal surface. We reveal these sites even by outgassing at 773 K, i.e. at lower outgassing temperature than that used by Gribov et al. [31]. In our opinion, the same sites are revealed by pyridine adsorption even after milder activation treatments, corresponding to the strongest adsorbed species absorbing at 1623 cm⁻¹ (8a mode) and at 1456 cm⁻¹ (19b mode). In fact, pyridine is a much stronger base than CO. Pyridine is also stronger as a base than water, thus being able to shift water or hydroxyl groups, at least partially, from the strongest Lewis acid sites or acid-base pairs.



Scheme 1. Proposed adsorption and reaction mechanisms.

A predominant role of corner and edge sites as carriers of highly coordinatively unsaturated cationic sites, well established for other oxides such as magnesia [61], is obviously very likely also on alumina [1]. In fact on these "defective" situations, the most coordinatively unsaturated cationic sites are expected to exist. The likely role of edge sites on alumina is further supported by the recent observation by high-resolution TEM studies that also the (110) exposed faces, supposed by most authors to be predominant on γ -Al₂O₃ nanocrystals, are not atomically flat but undergo a significant reconstruction, forming nanoscale (111) facets [62] thus with a very high density of edges.

The same sites are evident on the other alumina samples by pyridine adsorption but are less evident, if at all, in our experimental conditions using CO adsorption. We suggest that this is due to the higher amount of such sites on P200, as a result of its higher surface area with respect to P90 and D100, and also a higher defect typical of the surface of γ -Al₂O₃ [63], partially reduced in the case of δ -Al₂O₃, and virtually absent in the non-defective structure of θ -Al₂O₃. In the case of V200, the lower amount of these sites can be associated with the higher amount of sodium impurities in this sample, which can result in the poisoning of some of them by the balancing oxide ions or to a decrease in their acid strength due to increased basicity of the oxide ligands (inductive effect).

Above, the spectra of the surface hydroxyl groups of the four samples have been discussed and compared. While the spectrum observed for P200 is the typical one of γ -Al₂O₃, a role of different impurities is likely in causing a modification of the relative intensities of the bands, in the case of V200 (sodium) and D100 (chlorine). The spectrum of P90 seems to be more typical of θ -Al₂O₃, with the almost total disappearance of the band at ca. 3770 cm^{-1} , and the mode at ca. 3730 cm^{-1} sharper than usual for γ -Al₂O₃. This is likely associated with the crystallization of θ - Al_2O_3 from γ - Al_2O_3 , with the loss of the typical defectivity of the latter. These data confirm that the analysis of the OH stretching spectrum is interesting as a typical fingerprint of the alumina phase (in particular θ -Al₂O₃ and γ -Al₂O₃). On the other hand, we agree with Dayn et al. [63] that showed (also in agreement with the previous work of Tsyganenko and Mardilovich [64]) that many kinds of different hydroxyl groups can be hypothesized to occur on partially dehydroxylated alumina surfaces, thus suggesting that an assignment of a "family" structure of the bands is more reliable than the tentative identification of the planes on which they should be located. Another remark is that the P200 and D100 materials, assumed by Wischert et al. to be essentially similar [50], are actually very different in terms of phases, morphology, surface area, impurities, and IR spectra of the surface hydroxyl groups.

Also for at least part of the surface hydroxyl groups, as for Lewis sites, their location on edges and corners, more than on plane faces, is very likely in our opinion, for the same reasons. In fact, the most stable OH groups are likely bonded to highly uncoordinated hydroxyl groups. In this case, the (H)O-Al bond is expected to be stronger and more covalent, thus being decomposed with more difficulty. We may also mention that an OH group can quite likely be bonded to an aluminum ion that also carries coordinative unsaturations (e.g., an OH bonded to a Al^{3+} ions with overall coordination four), and this may very likely occur on edges. Thus, Lewis sites and OHs may, in some way, contribute to the same active site.

The catalytic data summarized above confirm that transitional aluminas are excellent catalysts for the conversion of ethanol to ethylene, in substantial agreement with the literature [21–23]. Yield to ethylene approaches 100% for all samples at 623 K in the conditions of our experiments. The comparison of the data obtained with aluminas and with silica-alumina suggests that Lewis acidity represents the key property for these catalysts when applied to this reaction. In spite of the significant differences between the surface properties of the four alumina samples, evidenced

above, the differences in the catalytic behavior in ethanol dehydration are slight, showing that this reaction is not very sensitive or demanding. Indeed the higher activity of the Puralox materials P200 (when considered in terms of catalyst weight) and P200 or P90 (when considered in terms of catalyst surface area) is likely due to the high purity of these materials, resulting in high surface acidity. IR spectra show the formation of ethoxy groups which decompose to ethylene and water at the same temperature at which we reveal the high catalytic activity to ethylene in the flow reactor. It seems interesting to remark that the catalytic activity is observed in the presence of water (which is a reaction product) at quite a low temperature (473-673 K), i.e. in conditions where the studies of the adsorption of CO does not reveal the presence of Lewis acidity. We have, however, already remarked that pyridine reveals strong Lewis sites also on largely hydroxylated samples. due to its higher basicity with respect to not only CO but also water. Indeed, we found that ethanol can adsorb as ethoxy groups not only by dissociative adsorption on Lewis acid-base sites, but also substituting hydroxyl groups on hydroxylated surfaces, causing desorption of water. In fact, light alcohols have similar acidobasicity as water [53], and also similar volatility. This means that the adsorption/desorption of water and ethanol are competitive. In other words, ethanol can displace water and hydroxyl groups producing ethoxy groups without any previous dehydroxylation. Thus, the appearance of Lewis acidity does not need dehydroxylation if the basic probes are able to displace water. The same for reactants: reactants which have sufficient basicity to compete with water can be activated by alumina also in the presence of water. This is not the case of reactants having very low basicity such as hydrocarbons, whose conversion on alumina is usually inhibited by water.

Our data and our interpretation does not disagree with the data reported by Kwak et al. [21] that found ethylene evolution from ethanol during TPD experiments at slightly different temperatures depending on the previous alumina pretreatment. These authors identified the TPD peak found at 498 K on samples pretreated at higher temperature to the evolution of ethylene from ethanol adsorbed on Lewis sites, and that found at 523-533 K on samples pretreated at lower temperature to the evolution of ethylene from ethanol adsorbed on hydroxyl groups (they roughly define as "Brønsted acid" sites). Indeed, the two peaks may reflect the difference resulting from the overall hydroxylation state of the surface on the ethylene desorption step. It seems in any case likely that the difference between two more or less dehydroxylated surface should be progressively removed on stream, due to the effect of readsorption of water produced by the reaction and the desorption of the pre-existing water, depending on the reaction temperature. Our data well show that previous catalyst dehydroxylation is not needed to produce ethylene from ethanol.

Characterization studies show that both Lewis and Brønsted acidity are present over silica-alumina, while Lewis acid sites only are present at the surface of aluminas. On the other hand, the strength of the Lewis acid sites on silica-alumina is similar or even stronger than that of the strongest Lewis sites of alumina. Nevertheless, silica-alumina is nearly as active as the most active alumina in terms of catalyst weight, but is significantly less active in terms of catalyst surface area. Thus, it is supposed that similar active sites (Lewis sites) but a lower active site density exist at the surface of silica-alumina with respect to alumina. On the other hand, we can remark that at low ethanol conversion, silica-alumina is more selective toward ethylene than aluminas, that at low conversion produce more diethyl ether. We suggest that this is due to the presence, at the surface of alumina, of slightly stronger basic sites than on silica-alumina. To produce ethyl ether, in fact, one ethanol molecule must be activated as ethoxy groups, thus producing a nucleophilic species. The interaction of a second ethanol molecule nearby is useful to increase the electrophilicity of the alcoholic carbon atom to favor the nucleophilic substitution to produce the ether (Scheme 1).

5. Conclusions

The conclusions of this work can be summarized as follows:

- 1. The physicochemical properties of commercial aluminas closely depend on the preparation process and in the impurities left.
- 2. Very different morphologies are found even for samples that have similar surface areas (e.g. prismatic, fibrous) showing that the patterns of exposed faces and defects may be more complex than reported in some recent literature (based on predominant 110 face).
- 3. The strongest Lewis acid sites revealed by IR spectroscopy of CO adsorbed on highly dehydroxylated samples, and of pyridine adsorbed also after milder dehydroxylation, are associated to very low coordination Al cations, such as tri- and tetra-coordinated Al ions. This suggests that models based on ²⁷Al MAS NMR results, which only reveal penta-coordinated Al ions, give an incomplete picture of the aluminas surfaces, not revealing lower coordination sites.
- 4. The interpretation of the data suggest that highly uncoordinated sites are located on corners and edges of the crystal surface. Thus modeling of such defect sites should be more important than that modeling of exposed faces.
- 5. Although the IR spectra of the surface hydroxyl groups is formed by the same bands in all cases, several differences in the relative intensities are found from fumed and different precipitated samples, providing evidence of the role of the main impurities (Cl vs Na), of the crystal phase (γ -Al₂O₃, δ -Al₂O₃, θ -Al₂O₃) and of morphologies. Also hydroxyl groups are supposed to be at least in part located on corners and edges, more than on plane faces.
- 6. Aluminas are effective catalysts for producing ethylene from ethanol at 473-673 K. Slight differences between different aluminas are attributed mainly to different impurities present.
- 7. Ethoxy groups are formed not only by dissociative adsorption on Lewis acid-base sites but also by substitution of hydroxyl groups with evolution of water. In both cases, the strong Lewis acidity of the Al ions bonded to ethoxy groups is the main factor favoring ethylene synthesis.
- 8. Ethoxy groups are thought to be intermediates in both ethylene and diethylether formation. Ethanol residual partial pressure is proposed to be determinant in favoring diethylether synthesis, thus obtained with high selectivity at low to moderate ethanol conversion.
- 9. The alumina catalysts which in the reported experiments have not been activated previously, certainly work in a highly hydroxylated state, also due to the formation of water as a reaction product coupled with the low temperature needed for the reaction. This shows that dehydroxylation is not a requisite for Lewis acid activity when reactants or probes have comparable acidity and volatility with respect to water.
- 10. Silica-alumina is also active in ethanol dehydration working as a Lewis acid catalyst in this reaction. Its activity is similar with respect to the most active aluminas on weight base, but less on surface area basis, because of the lower density of Lewis sites and the absence of significant basicity.

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