



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



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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 - Al_2O_3) and different impurities (Na^+ , Cl^-). Total conversion of ethanol with >99% selectivity to ethylene is achieved at 623 K over the purer Al_2O_3 catalyst ($\text{Na} < 0.002$ wt%). The most active sites are believed to be Lewis acidic Al^{3+} 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 Al^{3+} 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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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 - Al_2O_3 , 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 - Al_2O_3 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 - Al_2O_3 , 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 - Al_2O_3 [9] and γ' - Al_2O_3 [10], have been reported by different authors. Only above ca. 923 K, the

crystal chemistry of alumina becomes well established. In fact, at this temperature, θ - Al_2O_3 is formed, whose “beta-gallia” structure is completely determined. However, the formation of θ - Al_2O_3 is a complex phenomenon [11], and γ - Al_2O_3 and θ - Al_2O_3 could coexist in core and shell structures [12]. The only fully ascertained phenomenon is that all aluminas transform into α - Al_2O_3 (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 AlCl_3 [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 $4^\circ/\text{min}$.

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 ($p_{\text{Py}} \sim 1$ 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

(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 $P_{\text{EtOH}} \sim 4$ 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 ($15 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) 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 - Al_2O_3 (JCPDS card No. 43-1308), while that of V200 contains the same pattern with an additional broad component at low 2θ likely due to some residual poorly crystalline pseudoboehmite (JCPDS card No. 21-1307). The pattern of P90 is typical of θ - Al_2O_3 (JCPDS card No. 35-0121) while that of D100 certainly contains the peaks of δ - Al_2O_3 (JCPDS card No. 47-1770) possibly with those of γ - Al_2O_3 , in

Table 1
The properties of investigated catalysts.

Notation	Manufacturer	Preparation	S_{BET} (m^2/g)	V_p (cm^3/g)	Average particle size ^a (\AA)	XRD phase	Na content (%)
P90	Puralox Sba90 Sasol	Calcination of P200	90 ± 5	0.13	160	θ - Al_2O_3	0.002 [*]
P200	Puralox Sba200 Sasol	From boehmite via Al alkoxides	190 ± 10	0.45	100	γ - Al_2O_3	0.002 [*]
V200	Versal 250 UOP	From boehmite via precipitated NaAlO_2	202 ± 5	0.47	90	γ - Al_2O_3	<0.04 [*]
D100	Aeroxide Degussa/Evonik	From flame hydrolysis of AlCl_3	100 ± 10	0.10	150	γ, δ - Al_2O_3	0.006
SA330	Strem (13 wt% Al_2O_3)		330 ± 10	–	–	Amorphous	–

^{*} Data from the manufacturers.

^a From TEM data (Scherrer formula).

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