High Field ^{27}Al MAS NMR and TPD studies of active sites in ethanol dehydration using thermally treated transitional aluminas as catalysts

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Abstract

High field quantitative ^{27}Al single pulse (SP) MAS NMR combined with temperature programmed desorption (TPD) of ethanol are used to study the surface of $\gamma\text{-Al}_2\text{O}_3$ during phase transformation processes induced by calcination in the temperature range of 500 to 1300 °C. Following ethanol adsorption, ethylene is generated during TPD with a desorption temperature above 200 °C. The amount of ethylene decreases monotonically with increasing calcination temperature prior to TPD. Significantly, ^{27}Al SP MAS NMR reveals that the amount of penta-coordinated Al^{3+} ions also decreases with increasing calcination temperature. A quantitative (within experimental error) correlation between the amount of penta-coordinated Al^{3+} ions and the amount of strongly adsorbed ethanol molecules (i.e., the ones that convert to ethylene during TPD) is obtained. These results provide good evidence for a proposal that the penta-coordinated aluminum sites are the catalytic active sites on alumina surfaces during ethanol dehydration reaction across the entire course of γ -to- α Al_2O_3 phase transformations.

Keywords: penta-coordinated alumina; ^{27}Al MAS NMR; high magnetic field; TPD

Introduction

Transitional aluminas with medium to high surface areas have wide applications in catalysis and adsorption processes.[1, 2] Among them, γ - Al_2O_3 is the most prominent polymorph in catalytic applications due to its high surface area and structural stability enduring up to temperatures of 700-800°C. However, after a prolonged exposure to higher temperatures, γ - Al_2O_3 transforms into δ - and subsequently θ - polymorphs, and finally forms the thermodynamically stable structure, α - Al_2O_3 . [3, 4] A key consequence of these phase transformations, with generally detrimental implications for the use of Al_2O_3 in catalysis, is the dramatic reduction in surface area. Furthermore, the distribution of active centers (e.g., metals and oxides) on alumina support is intimately linked to Al_2O_3 surface properties and the chemical processes take place primarily on the surfaces of catalysts.[5] Therefore, the characterization of the chemical and physical properties of Al_2O_3 surfaces is crucially important for the correlation of catalytic properties with surface geometric and electronic structures.[6-8] However, the characterization of high surface area transition aluminas by well-established analytical techniques such as X-ray diffraction (XRD) is not straightforward, due to not only the surface insensitivity of these characterization techniques but also the poor crystallinity, small particle sizes, etc., of these phases.[9] Moreover, phase transformations can occur under catalytically relevant conditions (e.g., moderately high temperatures), making the characterization of the surface of this oxide especially difficult.

Many attempts have been made to understand the nature of alumina surfaces, especially the various Brønsted and Lewis acid sites which are considered as active centers in acid-catalyzed reactions.[10-16] It is generally accepted that the primary acid sites of high temperature dehydrated γ - Al_2O_3 are Lewis acidic, which are the active centers in alcohol dehydration

reaction.[14, 17] However, which aluminum site, i.e. three-, four-, or five-coordinated aluminum, is responsible for the catalysis is still a matter of some controversy. Chemical probes (i.e., surface reactions), can provide information about the nature of surface sites on catalysts, which then can be used to directly correlate catalytic properties with surface structure. For example, using ethanol temperature-programmed desorption (TPD) to study the active sites on γ - Al_2O_3 surface,[10] we proposed that Lewis-acidic surface Al atoms in 5-fold coordination (penta-coordinate Al^{3+} ions) were the active sites for ethanol dehydration. This conclusion was derived from a nearly 1-to-1 correlation between the number of dissociatively adsorbed ethanol molecules and the number of penta-coordinated Al^{3+} sites of calcined γ - Al_2O_3 . [6, 7, 10] Very recently, Larmier et al. have suggested again that five-coordinated Al sites were the active sites in isopropanol dehydration based on very good agreement between the activation enthalpies derived from experimental kinetic studies and those predicted from DFT transition state calculations.[18] However, other recent work, notably from computational studies performed by the Sautet[6, 11, 12] and Vlachos[13, 15, 16] groups, finds 5-coordinated Al sites in a number of hypothetical alumina models to be the least acidic of possible surface Lewis sites on γ - Al_2O_3 surfaces.

In this paper, quantitative ^{27}Al single pulse (SP) MAS NMR and ethanol TPD are used to study the surface aluminum species in Al_2O_3 as a function of calcination temperature (from 500 to 1300 °C), during which the material undergoes a number of phase transformations. A link between the number of surface aluminum species and the number of dissociatively adsorbed ethanol molecules was established from a set of Al_2O_3 samples with different concentrations of surface aluminum species. The results confirm a strong quantitative correlation between the amount of penta-coordinate Al^{3+} ions and the amount of desorbed ethylene, supporting our prior proposal that penta-coordinate Al^{3+} ions on the surface of transition aluminas are the active

sites in the ethanol dehydration reaction across the entire course of the γ -to- α phase transformations of Al_2O_3 .

Experimental Section

The γ - Al_2O_3 samples used in this study are high-purity commercial materials obtained from Sasol (Puralox, SBA 200) and used as received. The set of samples studied was prepared by calcination in dry air for 2 h in a muffle furnace at selected annealing temperatures in the range of 500-1300 °C.[19]After each calcination step the sample was cooled down to room temperature and analyzed.

The specific surface areas of the alumina samples were determined by the Brunauer-Emmett-Teller (BET) method[20] using an automated adsorption instrument (Micromeritics, TriStar-3000). Prior to N_2 adsorption, all alumina samples were flushed with UHP He at 150 °C for 3 h.

Alumina powders precalcined at various temperatures were then activated at 500 °C for 2 h under a 1.0 mL/s He flow, and subsequently transferred to sealed rotors in a glove box for the NMR measurements. ^{27}Al single pulse (SP) MAS NMR and 2D MQMAS experiments were performed at room temperature on a Varian-Inova 900 MHz NMR spectrometer, operating at a magnetic field of 21.1 T. The corresponding ^{27}Al Larmor frequency is 234.669 MHz. Unless otherwise specified, all of the SP spectra were acquired at a sample spinning rate of 24 kHz, using a commercial 3.2-mm pencil-type MAS probe. About 15 to 20 mg of samples was used for each measurement. A SP sequence with a pulse width of about 1.5 μs , corresponding to a $\pi/4$ (or 45°) pulse was used. Each spectrum was acquired using a total of 4000 scans with a recycle delay time of 10 s and an acquisition time of 25 ms. 2D ^{27}Al MQMAS NMR spectra were obtained

using a z-filter MQMAS pulse sequence at a sample spinning rate of 20 ± 0.002 kHz. The optimized pulse widths were $p1=4.25\ \mu\text{s}$, $p2=2.0\ \mu\text{s}$, $p3=10.0\ \mu\text{s}$. In the hypercomplex MQMAS experiment, 240 transients for either the real and imaginary F1 FID were collected for each of the 100 evolution increments. The recycle delay was 1 s and the acquisition time was 10 ms. Spectral widths for the F2 (acquisition) and F1 (evolution) dimensions were 100 and 40 kHz, respectively. ^1H - ^{27}Al CP/MAS NMR was conducted at a Varian-Inova 850 MHz NMR spectrometer at a spinning rate of 20 kHz using a commercial 3.2-mm pencil-type MAS probe and ^1H radio-frequency field strengths of 55.6 kHz for ^1H $\pi/2$ pulse. The method of ramped CP was used for cross-polarization.[21] The CP match condition, including determining the optimal length of contact time, that generates the highest CP signal at 20 kHz spinning rate was carefully set up using the sample of boehmite ($\gamma\text{-AlO}(\text{OH})$). Boehmite offers a ^1H - ^{27}Al CP/MAS NMR spectrum with good S/N using a single scan at 19.975 T field (the 850 MHz NMR spectrometer). Unless otherwise specified, a contact time of 1.5 ms and a recycle delay of 2 s were used with 10,000 to 30,000 scans being accumulated. All spectra were externally referenced (i.e., the 0 ppm position) to a 1 M $\text{Al}(\text{NO}_3)_3$ aqueous solution.

Since quantification of the relative peak area for each type of Al-sites is vitally important for establishing the correct correlation between the number of penta-Al sites and the number of ethanol dissociative adsorption, the potential distortion of the peak intensity as a function of the pulse angle is investigated and the results are summarized in Figure S1 of Supporting Information. Figure S1 shows the results of a single pulse experiment on 500 °C $\gamma\text{-Al}_2\text{O}_3$ by varying the tip angle of the excitation pulse width from 9 degree to 90 degrees with increment of 10 degrees at high field of 19.97 T, where the recycle delay time is 5 s that is longer than the T_1 value of $\gamma\text{-Al}_2\text{O}_3$ in the present study. Clearly, the use of any pulse tip angles from 9 to 90

degrees generates ^{27}Al MAS NMR spectra with centerband spectra similar both in line shape and in peak intensity distribution, indicating the results obtained by the 45 degree pulse in this study is quantitative primarily due to the very similar quadrupolar coupling constants for the various Al sites detected in this study [see Table S1 for details]. It should be pointed out that acquiring a quantitative ^{27}Al MAS NMR spectrum can be very challenging for a general case, in particular for those cases where there are a large variations in quadrupolar coupling constants in the same spectrum [22], where spinning sidebands from satellite transitions must be considered. Note that the benefit of high field by narrowing the second order quadrupolar lineshape for quadrupolar lineshapes with similar quadrupolar coupling constants has certainly improved the quantitation by using a single tip angle pulse excitation at high field.

Rigorous fit of the quantitative 1D SP MAS NMR spectra using quadrupolar lineshapes by using the DMFIT program[23] were conducted as a function of thermal annealing of the $\gamma\text{-Al}_2\text{O}_3$ between 500 and 1300 °C. For the purpose of this work, both direct integration and deconvolution of each well resolved peak in the quantitative 1D SP MAS NMR spectrum were conducted to obtain quantitative integrated peak intensities, and the same quantitative results were obtained by both methods. It is important to emphasize here that 1D SP MAS NMR is the only method that offers rigorous quantitative results and is, thus, best-suited for establishing correlations between the number of penta-coordinated Al^{3+} ions (exclusively on surface) and surface chemistry-focused TPD results, discussed below.

XRD analysis was carried out on a Philips PW3040/00 X'Pert powder X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in step mode between 2θ values of 10 and 75°, with a step size of 0.02°/s. Data analysis was accomplished using JADE (Materials Data,

Inc., Livermore, CA) as well as the Powder Diffraction File database (2003 Release, International Center for Diffraction Data, Newtown Square, PA).

Ethanol TPD experiments were performed using the same protocol we described previously.[10] Prior to ethanol TPD experiments, 0.05 g of freshly calcined alumina powders were introduced to the TPD reactor and then, similar to the NMR experiments, activated at 500 °C for 2 h under a 1.0 mL/s He flow. Then the activated sample was cooled to room temperature, and ethanol adsorption was carried out for 30 min using a 2.0% ethanol/He gas mixture (1.0 mL/s), followed by a He purge for 1 h in order to remove most of the weakly bound ethanol molecules. Gas analysis during TPD was performed on a Hewlett-Packard 5890 gas chromatograph (GC). After stabilization of the flame ionization detector (FID) signal, TPD experiments were carried out in flowing He (1.0 mL/s) with a heating rate of 10 K/min, with the reactor outlet flowing directly to the FID (i.e., no GC column separation). Desorption amounts were determined from FID signal intensities, and the FID sensitivity factor was calibrated using 100 µL pulses of 2.0% ethanol in He. In this experimental configuration, only the total amount of desorbed hydrocarbons is measured. For the identification of specific desorption products in the TPD profiles, full gas chromatography (GC) analysis was performed at the maximum temperatures of the desorption peaks. It was found that ethylene was the only product detected during the high-temperature desorption ($T > 200$ °C) under the experimental conditions applied here. Thus, in the following text when we discuss the high-temperature ethanol desorption features in the TPD experiments, we are referring to ethylene evolution that is produced from dehydration of adsorbed ethanol.

The reasons for selecting a temperature of 500 °C for the activation step in all of the experiments described above are based on our earlier investigations[10]. At 500 °C,

the hydroxyl groups on the $\langle 100 \rangle$ facets were fully dehydroxylated and can serve as a reproducible starting point. On the other hand, calcination at temperature higher than 500 °C has the risk of inducing potential phase transformation[24]. For these two reasons, we select 500 °C as a reference condition for the TPD experiments[25].

Results and Discussion

The XRD data for the aluminas calcined at various temperatures are shown in Figure 1. By comparing the observed diffraction peaks to reference patterns[24, 26], the approximate temperatures for the emergence of various crystalline phases can be determined. At 500 °C, a set of broad peaks corresponding to the γ - Al_2O_3 phase is observed. The XRD patterns between 500 °C and 900 °C are similar and the very slight evolution of the XRD patterns between 500 and 900 °C could be analyzed in terms of gamma to delta evolution, as mentioned previously by P. Euzen *et al.*[27]. Nevertheless, detailed phase evolution at this temperature range cannot be inferred. The emergence of the θ -phase is identified at calcination temperatures from 950 to 1100 °C, where several new peaks at 2θ values of 31.8, 32.9, 51.1 and 60.3°, assigned to the θ - Al_2O_3 phase [28, 29], are observed. The intensities of these peaks grow with increasing temperature. At 1050 °C, the XRD pattern is characteristic of the θ -phase, similarly to that reported in prior literature[28, 29]. Finally, the evolution of α - Al_2O_3 phase commences at 1100 °C and becomes fully established by 1150 °C.

Figure 1. XRD patterns of annealed alumina samples as a function of calcination temperature.

The samples were calcined at each temperature for 2 hours.

Because of the nature of XRD, direct information is only obtained about the bulk crystalline structures of the various alumina phases, while structural information related to highly amorphous phases is very difficult to deduct, or is not detectable if the structures are at the alumina surface only. On the other hand, NMR is a local probe that detects all the structures regardless whether they are related to crystalline phase, amorphous phase or the alumina surface. The position and the lineshape associated with an NMR peak are highly sensitive to local structural changes. In contrast, long range periodicity of a lattice structure is required in order to generate a meaningful XRD pattern. However, it should be emphasized that the concept of various bulk crystalline alumina phases in Al_2O_3 samples has been established historically by XRD. To bridge this gap, in the following discussion on a ^{27}Al MAS NMR spectrum, we employ the strategy of assigning a particular ^{27}Al MAS NMR peak/feature to an alumina phase only when the corresponding XRD pattern is observed. Otherwise, we refer the peak to a local structure that has atomic coordination identical to the corresponding bulk crystalline phase

but lacks of long range ordering (i.e., lacks of periodicity) for those cases where a ^{27}Al MAS NMR peak/feature is located at the same position as that observed for the bulk crystalline phase.

A series of ^{27}Al MAS NMR spectra collected on the thermally treated Al_2O_3 samples is displayed in Figure 2, and the corresponding full spectra are displayed in Figure S2. These spectra indicate that significant changes in the coordination sphere of Al^{3+} ions occur during thermal treatment of $\gamma\text{-Al}_2\text{O}_3$ that are associated, at least in part, with the local structural changes occurring during phase transformations. Compared with recently reported high field MAS NMR spectra of $\gamma\text{-Al}_2\text{O}_3$, [30-32] the spectral resolution achieved in this study at the ultra-high field of 900 MHz is considerably enhanced, allowing these structural changes to be more accurately followed. After 2 h of annealing at 500 °C, Al^{3+} ions in octahedral (Al_O), pentahedral (Al_P) and tetrahedral (Al_T) coordination are present, giving rise to three well resolved broad peaks centered at about 12, 35 and 69 ppm, respectively. These broad peaks are characteristic of the highly disordered $\gamma\text{-Al}_2\text{O}_3$ phase. [33] Consistent with the thermal stability of the $\gamma\text{-Al}_2\text{O}_3$ phase [Fig. 1], no changes in the 500-800 °C calcination temperature range are evident in the NMR spectra. As such, NMR spectra recorded from the alumina samples calcined at 550, 600, 650, 700 and 750 °C are not displayed in this figure.

Figure 2. The centerband spectra of SP^{27}Al MAS NMR spectra of samples annealed at different temperatures. Full spectra are provided in the Supporting Information. All the spectra were acquired at a spinning rate of 24 kHz except the 950, 1000, 1150 and 1200 °C calcined samples, where sample spinning rate at 22.5, 21, 22 and 22.1 kHz was used respectively. Thus the peak at ≥ 90 ppm in their corresponding spectrum is due to spinning side bands.

The NMR spectrum obtained for the 850 °C calcined sample shows the appearance of a shoulder at the high chemical shift side of the tetrahedral Al^{3+} feature at around 76 ppm and becomes very obvious at 900 °C. In general, increasing the calcination temperature from 800 to 1100 °C brings about significant changes in the NMR spectra. Specifically, the relatively broad

but nearly symmetric peak of the Al_O initially centered at around 12 ppm becomes highly asymmetric, and encompasses at least three distinct components at ~10, ~12 and ~16 ppm chemical shifts. Concomitantly, the Al_T peak centered at ~70 ppm gradually loses intensity, while the shoulder at 76 ppm gains intensity, indicating the formation of a new, specific alumina structure. Previously reported ^{27}Al NMR spectra [34] have identified these changes with the formation of new phases, and specifically the Al_O peak at 10 ppm and the Al_T break point peak (associated with a typical quadrupolar line shape) at 76 ppm with the θ - Al_2O_3 phase [35]. The intensities of these two peaks grow with increasing calcination temperature until 1050 °C, where these features dominate the NMR spectrum. However, significant shoulder peaks centered at about 12 and 16 ppm are observed at the Al_O sites for the 1050 °C sample, which likely indicate that this sample is not a single phase. At 1150 °C, the α -phase is fully established, accompanied by the disappearance of the tetrahedral aluminum species, where essentially only the well-defined hexagonal corundum containing a single octahedral site, i.e., α - Al_2O_3 , remains. During the calcination process, the center of these peaks moves gradually, suggesting small and continuous structural rearrangements of aluminum ions with increasing calcination temperature. As shown in Table 1, when transition aluminas undergo phase transformation from γ - to α - Al_2O_3 , significant primary particle growth occurs as reflected by the decrease of the BET surface area, a result consistent with prior reports. [36]

Further insights into the detailed structural changes as a function of calcination temperature can be obtained by evaluating the fitted spectra summarized in Figure 3. The quadrupolar line shape associated with each fitted peak and the minimum number of peaks used for fitting both the Al_O and Al_T in each spectrum are determined by consulting the corresponding

2D ^{27}Al MQMAS spectrum shown in Figure S3, where the 1000 °C and the 1100 °C samples are used as 2D MQMAS examples. Briefly, one peak is used to fit well the Al_P peak in a SP MAS spectrum across the entire calcination temperature range. For the 500 °C sample, a minimum number of 3 peaks are needed for fitting the Al_O and 3 other peaks are needed for the Al_T . While for the Al_T , 3 peaks can be used to fit all the spectra from 500 to 1100 °C samples, for the 800-1100 °C samples an additional peak centered at about 16 ppm is needed. The quadrupolar coupling constant associated with each peak resulted from the fitting are summarized in Table S1 of Supplemental Material. Since the 1050 °C sample is dominated by $\theta\text{-Al}_2\text{O}_3$ phase (XRD results from Fig. 1), the Al_O at about 10 ppm and the most downfield Al_T peak featured at about 76 ppm can be assigned to the $\theta\text{-Al}_2\text{O}_3$ phase for samples with calcination temperatures of 950 to 1100 °C. As the XRD patterns (Fig. 1) do not show the signature features for the $\theta\text{-Al}_2\text{O}_3$ phase for the 500 to 900 °C samples, based on the principles of NMR it is reasonable to assign the Al_O at about 10 ppm and the Al_T peak featured at about 76 ppm observed from the 500 to 900 °C samples to the nucleation sites with local structure similar to that of the $\theta\text{-Al}_2\text{O}_3$ phase but without long range ordering. Likewise, the Al_O at about 16 ppm observed from the 800 to 1000 °C samples can be attributed to the nucleation sites with local structure similar to that of the $\alpha\text{-Al}_2\text{O}_3$ phase but again without long range ordering. This is because the $\alpha\text{-Al}_2\text{O}_3$ phase is observed from 1050 °C and above by XRD [Fig. 1]. While the Al_O centered at about 12 ppm and the Al_T centered at about 69 ppm can be assigned to the $\gamma\text{-Al}_2\text{O}_3$ phase for the 500 to 1100 °C samples based on their dominant abundance in the 500 to 850 °C samples where the corresponding XRD patterns indicate exclusively a $\gamma\text{-Al}_2\text{O}_3$ phase (Fig. 1), the assignments of the most upfield Al_O peak centered at about 5 ppm and the most upfield Al_T peak centered at about 64

ppm are not possible due to the lacking of characteristic XRD patterns [35, 37] for other phases such as δ - or θ - Al_2O_3 phase at calcination temperature from 500 to 850 °C and thus left unassigned. Further dedicated research is needed to understand the nature of these two unassigned peaks.

Figure 3. The quadrupolar lineshape simulated 1D NMR spectra of the annealed samples at various calcination temperatures. “ N_α ” indicates Al nucleation sites that eventually evolve into the α - Al_2O_3 phase. “ N_θ ” indicates Al nucleation sites that eventually evolve into the θ - Al_2O_3 phase. “ O_{un} ” and “ T_{un} ” are octahedral and tetrahedral Al sites that are unassigned. The peak with chemical shifts ≥ 90 ppm is due to spinning side bands (see Figure 2).

With the assignments made above, the phase transition across the entire calcination temperature range can be refined and be briefly summarized below. Compared with the 500 °C sample, at a calcination temperature of 800 °C for 2 h, Al nucleation sites with local coordination structure similar to α -Al₂O₃ phase but without long range ordering are formed, accompanied by the increasing amount of nucleation sites with local structure similar to that of θ -Al₂O₃ phase. With further increasing calcination temperature from 800 to 900 °C, the number of nucleation sites for both the α - and the θ -Al₂O₃ phases increase. At 950 °C, θ -Al₂O₃ phase is first observed while the initial α -Al₂O₃ phase is observed at a much higher calcination temperature of 1050 °C and then become fully established with nearly 100% of abundance at 1150 °C. During the transition of the various alumina phases, the alumina surface changes dramatically that will be tightly related to the amount of Al_p sites to be discussed below.

Table 1. BET surface areas of the calcined alumina samples (BET surface area data of the 500 °C annealed sample was not measured but manufacturer's data indicate that it should be ~200 m²/g).

Calcination Temperature/°C	BET Surface Area/(m ² /g)
800	185.7
850	179.8
900	168.3
950	157.1
1000	138.4
1050	112.1
1100	59.7

1150	12.8
1200	10.7
1250	8.9
1300	8.8

Compared with the 500 to 850 °C samples, the intensity loss of the Al_P peak in the 950 °C calcined sample is consistent with a similar decrease in surface area as a result of high temperature calcination since Al_P ions have been shown to be located exclusively on the surface.[10] Previously, the intensity of the Al_P peak has been proposed to be a reflection of the extent of disorder in alumina samples since no Al_P sites should exist in any of the ideal crystalline Al_2O_3 phases.[36] Thus, the intensity loss of the Al_P sites may indicate both a surface area loss and a concomitant increase in the crystalline order. The latter is also reflected by the gradually decreasing intensity of the tail on the low frequency side (highlighted by the red dash line in Figure 2 and the fitted unassigned octahedral, O_un , and tetrahedral, T_un , peaks in Fig. 3) of the Al_O signal. However, the Al_P sites never completely disappear, not even after annealing at a temperature of 1300 °C for 2 hours (see the expanded insertion in Figure 2), indicating the existence of 5-coordinated Al ion surface defects even at 1300 °C. Note that ^{27}Al MAS NMR at low to moderate field strength is not able to provide this level of analysis due to the overlap of the penta-Al peak with peaks of tetra- and octahedral coordinated Al ions that are much broader at lower field strengths.

To explore the surface properties of aluminas, we use ethanol as a chemical probe in a series of TPD experiments. As in our previous study,[10] each TPD profile of the calcined samples in Figure 4(a) shows three main desorption peaks (i.e., TPD peak temperatures) at ~70 and ~90 °C, with the third one above 200 °C. The positions of the two low-temperature

desorption peaks are very similar and are independent of the alumina phases present (calcination temperature), and are assigned to weakly bound (i.e., physisorbed) ethanol.[10] Indeed, GC analyses of the desorbing products in this low (<150 °C) temperature range confirms that the desorbing species was, indeed, molecular ethanol. The difference of TPD profiles between our results and the ones recently reported by Lee *et al.* [38] are mainly due to the difference in calcination times (3 h in Lee *et al* paper and 2 h in this study). It should also be pointed out that although similar TPD experiments were used in reference[36], there are significant differences between the current investigation and those of Lee *et al*'s work, including but not limited to the followings. (i) The objectives are different. In this work, our focus is to provide good evidence to support the proposal that the penta-coordinated aluminum sites are the catalytic active sites on alumina surfaces during ethanol dehydration reaction across the entire course of γ -to- α Al_2O_3 phase transformations. While in reference[36], the focus was on morphology-dependent bulk phase transformation of γ - Al_2O_3 into different bulk phases, where at 1100 °C commercial γ - Al_2O_3 phased transformed into α - Al_2O_3 phase (from 200 m^2/g to 25 m^2/g). Platelet-shaped γ - Al_2O_3 transformed into θ -phase while the rod-shaped γ - Al_2O_3 transformed into δ -phase. (ii) In the current manuscript, our emphasize is on quantitative penta-Al site detection, where ultra-high field of 900 MHz made this possible. In reference[36], the ^{27}Al MAS NMR spectra were acquired on a 600 MHz NMR spectrometer, due to the second order quadrupolar line broadening the penta-Al site is severely overlapped with the tails of the octahedral-Al and tetrahedral-Al peaks. Therefore, no discussion on penta-Al sites was reported in reference [36].

Figure 4. Ethanol TPD profiles of the annealed alumina samples after calcination at various temperatures. (a) TPD from the samples with calcination temperatures ranging from 500 to 1100 °C. (b) Comparison of the TPD profiles from γ -Al₂O₃ (i.e., the 500 °C sample) and α -Al₂O₃ (i.e., after calcination at 1300 °C; curve multiplied by a factor of 40). (c) Temperature of the TPD peak maximum for the high temperature ethylene TPD peaks in (a) as a function of calcination temperature.

In discussing the higher temperature (> 200 °C) peak, it is important to note that the adsorption of ethanol in these TPD experiments was carried out at room temperature on calcined alumina samples that were activated at 500 °C for 2 h under a He flow immediately prior to ethanol absorption (similar to the pretreatment procedure used to prepare samples just prior to NMR experiments). In particular, chemisorbed water and -OH groups associated with the surface penta-Al ions are essentially completely removed by activation at 500 °C, while the Al-OH related to other surface alumina species likely remain intact.[6, 7] On the basis of similar ethanol TPD studies on γ -Al₂O₃ samples dehydrated at various temperatures ≤ 600 °C, the desorption peak at $T \sim 225$ °C was found to be due to ethylene via GC analysis, with ethylene formed during TPD by the dehydration of adsorbed ethanol.[10] In these previous studies,

the ethylene TPD peak at $T \sim 225\text{ }^{\circ}\text{C}$ increased in intensity as the Al_P sites were formed (via removal of water and/or $-\text{OH}$ groups). On this basis, we proposed that the reaction of ethanol to ethylene occurred mainly on Lewis acidic surface penta-coordinated $\text{Al}^{3+}(\text{Al}_\text{P})$ sites. In support of this conclusion, a quantitative comparison of the number of dissociatively adsorbed ethanol molecules that produce ethylene in TPD and the number of Al_P sites measured by NMR showed that these two values are essentially equal.[10]

Our previous study also revealed that, as long as the $\gamma\text{-Al}_2\text{O}_3$ sample did not undergo phase transformation, the ethylene maximum desorption temperature and desorption amounts remained unchanged following a $500\text{-}600\text{ }^{\circ}\text{C}$ pretreatment prior to TPD.[10] However, as shown in Figure 4a-c, with an increase in Al_2O_3 calcination temperatures where phase transitions begin to occur, the ethylene desorption temperature increases. Although certainly not a direct measurement, the gradual increase in the temperature of the ethylene desorption peak accompanied by phase transformations (Figure 4c) suggests that the dehydration of ethanol on the alumina surface is sensitive to the surface structure change as continuous structure rearrangements occurring during the calcination process. An important question remains whether our prior proposal that ethylene formed only on Al_P sites for $\gamma\text{-Al}_2\text{O}_3$, also holds for other transition phases formed at higher calcination temperatures.

Table 2. Amount and density of penta-coordinate Al^{3+} sites and adsorbed ethanol on alumina calcined at various temperatures.

Calcination Temperature ($^{\circ}\text{C}$)	Al_P sites ($\times 10^4 \text{ mol/g}$)	Dissociative adsorption ($\times 10^4 \text{ mol/g}$)	Total adsorption ($\times 10^4 \text{ mol/g}$)	Al_P /dissociative ethanol	Al_P density ($\text{sites}\cdot\text{nm}^{-2}$)	Dissociative adsorption sites density ($\text{sites}\cdot\text{nm}^{-2}$)
500	4.7	3.2	7.3	1.5	-	-
800	4.9	3.2	8.1	1.5	0.26	0.17

850	3.9	2.6	6.7	1.5	0.22	0.14
900	4.2	2.7	6.9	1.5	0.25	0.16
950	2.2	2.3	6.3	1.0	0.14	0.15
1000	1.7	1.8	5.1	0.9	0.12	0.13
1050	1.7	1.6	4.3	1.1	0.15	0.14
1100	0.9	0.8	2.4	1.1	0.15	0.13

Generally, the area underneath a TPD curve for saturation coverage of an adsorbate is directly related with the concentration of surface binding sites that are, in turn, related to the surface area of the sample. Indeed, we find that the overall area underneath the TPD curves decreases (Figure 4a), indicating an overall reduction in surface area of the samples, which is qualitatively consistent (Figure S4) with BET results given in Table 1. The amount of penta-coordinated Al^{3+} sites is calculated according to the equation: Penta sites = $(1\text{g}/\text{MW}(\text{Al}_2\text{O}_3)) \times (\text{penta-Al fraction}) \times 2$, where the penta-Al fraction is obtained as the area ratio of the penta-Al centerband peak over the total centerband peak area by deconvoluting the centerband ^{27}Al MAS NMR spectrum. The amount of penta-coordinated Al^{3+} sites and adsorbed ethanol molecules on the surface of various calcined aluminas is shown in Table 2. The average ratio of Al_p sites/dissociatively adsorbed ethanol is 1.2 ± 0.3 , very close to the expected value 1.0. Note that the perhaps slightly higher Al_p sites/dissociatively adsorbed ethanol, especially for lower temperature calcined samples, may result from the penta-coordinated aluminum sites located in inaccessible defects/pores within the alumina primary particles.[37] Besides this strong quantitative comparison, it is especially striking that the correlation between the amount of desorbed ethylene molecules and penta-coordinate Al^{3+} ions maintains over the entire γ -to- α phase transformation process as shown in Figure 5. On this basis, we conclude that, during the phase transformation process, Lewis acidic Al_p sites remain the active sites for the ethanol dehydration reaction. However, the interaction between Al_p sites and ethanol molecules becomes

stronger at higher calcination temperatures as evidenced by the increasing desorption temperature for ethylene. This result can be rationalized as a reflection of the changing local coordination of the Al_P sites as the surface structure changes due to the changes in the bulk structure of the Al_2O_3 phases. As noted above, these phase changes also lead to crystal grain growth, causing decreases in both the surface area and the number of Lewis acidic Al_P sites. The reduction in the number of active sites and the increased desorption temperature will cause the diminishing ethanol dehydration activity for the alumina catalyst.

Figure 5. Correlation between the amount of dissociative ethanol (ethylene) during ethanol TPD experiments and the amount of penta-Al sites from quantitative ^{27}Al MAS NMR results at various annealing temperatures.

Finally, although very recent experimental and computational studies are consistent with the conclusions we make here,[18] there remains an apparent discrepancy with conclusions by others based on DFT calculations.[6, 11-13, 15, 16] The latter studies indicate that Al_P sites are the weakest Lewis acidic centers on the various surfaces of $\gamma\text{-Al}_2\text{O}_3$. In particular, both 3- and 4-coordinate surface Al^{+3} ions provide stronger adsorption sites and correspondingly lower barriers

for the ethanol dehydration reaction.[16] 3-fold coordinated sites might be expected to provide a very small contribution due to fairly high barriers for the removal of hydroxyl groups, and, even at optimized conditions, their site density is only 0.03 site-nm⁻². [6, 7, 10, 12] 4-fold Al³⁺ ions seem likely to be present after the pretreatment we used just prior to ethanol TPD. However, it is not possible to correlate the ²⁷Al SP NMR peaks with such structures because they exist both on the surface and in the bulk of the alumina particles, with the number of the latter being considerably greater than the former. To emphasize the change of surface Al species, ¹H→²⁷Al CP/MAS NMR was conducted with the spectra shown in Figure S5, since most protons exist at the surface. Indeed, the significant enhancement of the relative signal intensity of penta-coordinated Al³⁺ is observed. However, no significant change of penta-coordinated Al³⁺ is observed for the samples calcined at 800 and 1000 °C, where the quantitative results from ²⁷Al SP MAS NMR spectra indicate the amount of penta-coordinated Al³⁺ decreases from 0.26 to 0.12 sites nm⁻², which is reasonable as CP/MAS NMR is not an effective quantification technique. Thus, it remains possible that the concentration of surface 4-fold Al³⁺ ions changes in the same manner as the observed change in concentration of the 5-fold (Al_P) Al³⁺ ions. While we cannot rule this out, it does seem to be at least somewhat improbable because the concentrations of the under-coordinated 4- and 5-fold Al³⁺ ions are a strong function of the exposed surface facets, and these various surface facets seem unlikely to decrease in concentration uniformly with calcination temperature. Furthermore, we might expect to observe some evidence in the TPD if multiple coordinations of Al³⁺ ions, with varying Lewis acidity, were able to carry out the ethanol dehydration reaction. However, the TPD data seem to consist of a single fairly sharp ethylene desorption feature in all of the experiments reported here; a result at least qualitatively inconsistent with multiple sites for ethanol dehydration with varied reaction barriers.

In considering the strong correlation shown in both Table 2 and Figure 5, between the number of active sites for ethanol dehydration during TPD and the areas for the Al_p NMR peak, we also note a recent report by Sautet and co-workers [39] that discusses the challenge of quantifying all Al species (particularly at the surface) present in a $\gamma\text{-Al}_2\text{O}_3$ sample. This study points out that very high magnetic fields and high sample spinning rates in ^{27}Al MAS NMR experiments are especially useful for overcoming the problem of “invisible” Al due to the quadrupolar nature of its nucleus. However, these issues remain for NMR invisible sites such as 3-fold coordinated or highly distorted Al which may be stronger Lewis-acids. It appears to not be possible to directly probe the reactivity of these sites and provide their quantification by the use of ^{27}Al MAS NMR experiments. Despite this, we believe that the quantitative (within experimental error) 1-1 correspondence between ethylene TPD peak areas and the NMR peak areas for Al_p structures shown in Table 2 and Figure 5 is not a fortuitously misleading artifact of the experiments. Of significance in this regard, we reiterate the results given in our prior publication, [10] where the amount of ethylene produced increased with $\gamma\text{-Al}_2\text{O}_3$ dehydration temperature, and moreover, the quantified aluminum sites $0.22\text{-}0.26\text{ sites nm}^{-2}$ in $\gamma\text{-Al}_2\text{O}_3$ (800-900 °C calcination in Table 2) is comparable to the reported 0.2 sites nm^{-2} derived by in situ titration for ethanol dehydration to ethylene. [40] In this case, the pretreatments at varying temperatures less than 600 °C just prior to TPD partially dehydrated the $\gamma\text{-Al}_2\text{O}_3$ sample and, at these pretreatment temperatures, the only surface sites predicted to be dehydrated [6, 10] were 5-fold Al ions. Thus, both the formation of these sites by dehydration (our prior study) and their removal by phase transformations (results given here) directly correlate with the number of active sites for ethanol dehydration during TPD. In addition, BaO was previously shown to selectively anchor at the penta-coordinate Al^{3+} sites on $\gamma\text{-Al}_2\text{O}_3$ surfaces. [41, 42] Our prior

study of methanol dehydration on BaO/ γ -Al₂O₃ with BaO loadings of 0–4 wt% clearly shows a monotonic decrease in the catalytic activity with increasing BaO loading.[10] Considering this, we believe that the present results are a strong confirmation of our earlier proposal that Al_P sites are the primary active centers for the ethanol dehydration reaction. Additionally, we note again the similar conclusions made in a very recent experimental and computational study.[18]

Conclusions

Ultra-high magnetic field ²⁷Al MAS NMR combined with temperature programmed desorption of ethanol are used to study the surface and phase evolution of γ -Al₂O₃ during calcination in the temperature range from 500 to 1300 °C. Similar to our prior results for γ -Al₂O₃, [10] a quantitative correspondence between surface Lewis acidic Al_P sites and dissociatively adsorbed ethanol molecules is found across the entire γ - to α -Al₂O₃ phase transformation process, supporting the proposal that Lewis acidic Al_P sites are the active sites for the ethanol dehydration reaction independent of the phase of the transition alumina. With increasing calcination temperature, the alumina phase transformation also results in a decrease in surface area and, as such, the amount of active surface Lewis acidic Al_P sites is reduced. Interestingly, the interaction between adsorbed ethanol molecules and active Al_P sites increases likely reflecting changes in their local coordination geometry as the bulk structure of alumina is changing.

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