Critical role of (100) facets on γ-Al2O3 for ethanol dehydration: Combined efforts of morphology-controlled synthesis and TEM study

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A B S T R A C T
In this work, the effect of crystal facets on the catalytic behavior of γ-Al2O3 was investigated by X-ray diffraction, transmission electron microscopy, temperature-programmed desorption of ethanol, solid-state 27Al NMR, infrared spectroscopy, and ethanol dehydration reaction. A series of platelet γ-Al2O3 were synthesized, in which the relative ratio of (100) facets had been systematically increased. Ethylene formation increased with increasing (100) facets, clearly demonstrating the critical role of these facets as active sites for ethanol dehydration on γ-Al2O3. This systematic approach is helpful for a better understanding of facet-dependent catalytic properties of γ-Al2O3 that arise from the interaction between the supported metal and the crystal facets.

1. Introduction

γ-Al2O3 is an important catalytic material that has been used as a support for a wide range of applications in petroleum chemistry and automobile emission control [1–3]. Since γ-Al2O3 has an intrinsic acidity, it can participate in acid-catalyzed reactions such as alcohol dehydration [4]. For decades, numerous studies have been devoted towards understanding the fundamental nature of Al2O3 owing to its practical importance in catalysis [3,5–14].

The catalytic properties of oxides, such as activity, selectivity, and distribution of active phases on the support, are significantly affected by their surface characteristics because chemical processes mainly occur on the surface [8–12,14]. Thus, considerable research efforts have been made to study the surface characteristics of oxides in detail. In particular, the effect of a crystal facet on catalytic behavior has been thoroughly examined for oxides like TiO2, CeO2, and FeOx that have a well-defined crystalline structure [15]. However, it is difficult to understand the effect of each crystal facet of γ-Al2O3 on its catalytic properties due to undefined structures (defect-spinel or non-spinel), which is intrinsically complex [8,16,17]. Therefore, many studies have been performed by indirect methods such as surface science, theoretical calculations, or using relatively crystalline δ, θ, α phases of Al2O3 which are obtained by phase-transformation of γ-Al2O3 [8,9,18–20]. For example, Digne and Sautet et al. have suggested a non-spinel-based γ-Al2O3 simulated model and shown that surface dehydroxylation is closely related to both temperature and exposed facets [8,9]. In order to experimentally verify the influence of crystal facets on the catalytic properties of γ-phase, two issues must be addressed. The first issue deals with the sensitivity of the technique or instrument used for characterization of the crystal facets of γ-Al2O3. Various tools like X-ray diffraction (XRD) [16,21–23], NMR [14,24,25], FT-IR [3,26–29], transmission electron microscopy (TEM) [1,6,30], and other temperature-programmed techniques [31–33] can be utilized to characterize the Al2O3 surface. However, a quantitative measurement of the facet ratio using bulk techniques such as XRD is very difficult due to the low crystallinity and small domain size of γ-Al2O3 [32,33]. The second challenge lies in the preparation of a series of γ-Al2O3 samples with systematic variation in morphology. Recent advances in nanotechnology have made it possible to prepare various Al2O3 with different morphologies. Since the morphology of γ-Al2O3 is determined from boehmite (by topotactic transformation) [9,13,34], the synthesis of the precursor ALOOH were controlled to obtain specific morphologies such as needle, platelet, flower-like, and ellipsoid Al2O3 [35–39]. However, many studies focus on the characterization of boehmite instead of γ-Al2O3. Although some researchers have investigated the crystal facets of γ-Al2O3, these studies have been limited to comparisons between its drastically different morphologies, such as rod, platelet, and cuboctahedral [40,41]. Therefore, any approach towards understanding the effects of crystal facets on catalytic properties must involve well-defined γ-Al2O3 with systematic morphological change.

In this work, a series of platelet γ-Al2O3 samples were synthesized wherein the number of (100) facets increased systematically and then correlated with the catalytic behavior of γ-Al2O3 in ethanol dehydration. The catalytic activity of γ-Al2O3 in ethylene formation increased.
with an increase in the relative ratio of (100) facets. This result suggests that the (100) facets play a crucial role in the alcohol dehydration reaction; therefore, careful control of γ-Al₂O₃ morphology is an important aspect of catalyst design.

2. Experimental section

2.1. Preparation of facet-oriented γ-Al₂O₃

A series of platelet Al₂O₃ were synthesized based on previous reports with modification [39,42]. First, Al(NO₃)₃·9H₂O (SAMCHUN, 98.0% purity, 7.15 g) was dissolved in distilled water (80 ml) to form a transparent solution. Then, hydrazine monohydrate (N₂H₄·H₂O, SAMCHUN, 80% minimum purity) diluted in water was dropped into the solution, leading to a milky precipitate. The resultant mixture was diluted in water and the reactor outlet was cooled down to the room temperature. The pretreatment conditions were confirmed by obtaining the spectrum of commercial γ-Al₂O₃ (Puralox SBA-200). The IR spectrum collected from Puralox SBA 200 after the same treatment showed that the hydroxyl groups were consistent results with previous study (Supporting information) [12]. Then, the spectrum was collected at 25 °C under 3 ml/min of He flow by using harshly dried KBr as a background. Each obtained spectrum was the average 1024 scans at a resolution of 4 cm⁻¹. The each spectrum was normalized with the intensity of 3728 cm⁻¹ peak which was assigned to be located on the (110) surface by Digne et al. [8].

2.2. Characterizations

XRD patterns were obtained on a Bruker D8 Advance A25 using Cu Ka radiation (λ = 1.54 Å) in step mode between 20 values of 5° and 75°, with a step size of 0.02°/s. The morphologies of Al₂O₃ were confirmed by TEM (JEOL JEM-2100). The bright field transmission electron microscopy (BFTEM) image and electron diffraction pattern were acquired on a FEI Titan3 G2 60–300 at an accelerating voltage of 80 kV. The specific surface area was determined by the Brunauer–Emmett–Teller method using BELSORP-Max instrument. Solid ⁷⁷Al-NMR experiments were performed on a Varian VNMRs 600 MHz NMR spectrometer, operating at a magnetic field of 14.4 T. The corresponding ⁷⁷Al Larmor frequency was 156.299 MHz. All the spectra were acquired at the spinning rate of 25 kHz, using a 1.6 mm pencil-type MAS probe. Each spectrum was acquired using a total of 256 scans with a recycle delay time of 1 s. All the spectra were externally referenced (i.e., the 0 ppm position) to a 1 M Al (NO₃)₃ aqueous solution. We normalized the ⁷⁷Al MAS spectra with the same total NMR peak area for the ease of comparison.

Ethanol TPD was carried out using the same experimental procedures as described in our previous report [33]. Prior to ethanol TPD experiments, 0.05 g of alumina was calcined at 500 °C for 1 h under 20% O₂/He flow (1.0 ml/s). After calcination, the sample was cooled down 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 30 min in order to remove weakly-bound ethanol molecules. After stabilization of the flame ionization detector (FID) signal of an Agilent 7820A gas chromatograph (GC), a TPD experiment was carried out in flowing He (1.0 ml/s) with a heating rate of 10 °C/min, and the reactor outlet flowing directly to the FID (i.e., no GC column separation).

The in situ diffuse reflectance infrared spectroscopy (DRIFTS) experiments were performed on a Nicolet iS10 FTIR spectrometer equipped with a mercury cadmium telluride (MCT) detector. Al₂O₃ samples were loaded into a high temperature reaction chamber (Harrick Scientific) using ZnSe windows, which is installed in a Praying Mantis diffusion reflection accessory. The loaded sample in the DRIFTS reactor was purged at 500 °C for 2 h with 3 ml/min of He and then cooled down to the room temperature. The pretreatment conditions were confirmed by obtaining the spectrum of commercial γ-Al₂O₃ (shown in Supporting information). Therefore, the initial reaction rates were estimated by extrapolation (shown in Supporting information).

2.3. Catalytic activity measurements

Ethanol dehydration tests were performed in a quartz flow reactor (outer diameter 1/4” and inner diameter 3.6 mm) using 0.01 g samples (60–100 mesh) supported by quartz wool. Samples were treated under 20% O₂/He flow at 500 °C for 1 h. The carrier gas (He) was passed through a bubbler containing ethanol (99.5%, Sigma Aldrich) kept at 24 °C and ambient pressure. The ethanol concentration (2%) was controlled by relative He flow rate (total flow rate of He was 2.0 ml/s). Under this reaction flow condition, external diffusion could be neglected [43]. The outlet gases were analyzed by a GC (Agilent 7820A) using a HP-FFAP column and FID. The overall activity for ethanol dehydration were compared at 180 °C and apparent activation energies were obtained in the temperature region ranging from 170 °C to 190 °C under differential condition (<10% conversion). Another series of activity measurements were carried out at 300 °C with the same protocols. Under these condition, catalyst exhibited some deactivations. Therefore, the initial reaction rates were estimated by extrapolation (shown in Supporting information).

2.4. Calculation of the facet ratio by TEM measurements

Length and thickness of platelet γ-Al₂O₃ particles were measured on TEM images at low magnification. 50 particles were counted for each platelet γ-Al₂O₃ synthesized at different pH condition (4.3–10). Usually, the main facets of γ-Al₂O₃ are discussed based on (100), (110) and (111) facets. So, we measured the length and thickness of each particle in order to obtain the relative facet ratio of (100), (110) and (111) facets. The needed length parameters are defined on Scheme 1. The parameter w₁, w₂ and w₃ are the lengths for each corresponding sides on exposed planes. t is the thickness of particles. h is the diagonal of (110) facet. h’ is the height of (110) facet. θ is the angle between (111) facets on elongated platelet. The aspect ratio was defined as w₁/h (rhombus) and a/h (elongated). The calculation of the facet ratio was done based on the measured parameters. Simply, we can divide into two groups; rhombus and elongated platelet. For rhombus particles, no apparent (100) facet existed. So, (110) and (111) facet was only considered. Although the previous TEM study shows that the (100) facet exists on the rhombus platelet γ-Al₂O₃ due to surface roughness on (110)/(111) facets or internal surface of pore [45], the detailed understanding is out of the scope in this work. For elongated particles, (100), (110) and (111) facets all are considered.

Rhombus particles
\[ S_{110}, \text{ the area of (110) facets = } w_1 \times h \text{ (rhombus) or } 2 \times w_1 \times h’ (parallelogram) \]
\[ S_{111}, \text{ the area of (111) facets = } 2 \times t \times (w_1 + w_2) \]
Total area = \( S_{110} + S_{111} \)

The relative ratio of each facet (%) = 100 × Sᵢ/total area

Elongated particles
\[ S_{100}, \text{ the area of (100) facets = } 2 \times w_2 \times t \]
\[ S_{110}, \text{ the area of (110) facets = } 2 \times w_3 \times h + 2 \times w_1 \times w_2 \times \sin(\theta) \]
3. Result and discussion

Fig. 1 shows the structural and morphological characteristics of Al₂O₃ synthesized by controlling pH with acetic acid and hydrazine. XRD patterns confirmed the formation of orthorhombic γ-AlOOH (JCPDS no. 74-1895) under the entire range of pH used. The different morphologies of AlOOH at selected pH are shown in Fig. 1b. Representative TEM images for all series of AlOOH synthesized at pH 4–10 are shown in Fig. S2. Boehmite synthesized at pH 10 primarily showed a rhombus shape. Under neutral conditions, hexagonal shapes were obtained and elongated platelets that were truncated at one-side were synthesized under acidic conditions. With decreasing pH, growth in a specific direction was observed.

After thermal treatment at 600 °C, boehmite phase-transformed to become γ-Al₂O₃ (JCPDS no. 10-425), as confirmed by XRD (Fig. 2a). It is noteworthy that there are no apparent differences in the XRD peaks of boehmite and γ-Al₂O₃, even though some differences can be observed for as-prepared γ-AlOOH samples. This observation illustrates the difficulties in applying bulk techniques such as XRD for γ-Al₂O₃, which arise due to its low crystallinity and small domain sizes. The transformation of AlOOH into γ-Al₂O₃ is known to be topotactic, which means that the facets on γ-Al₂O₃ inherit their characteristics from the starting AlOOH [9,13,34]. Compared with initial morphologies of AlOOH, the overall morphology of γ-Al₂O₃ platelet is maintained (Fig. S4). This is

\[ S_{111} \text{, the area of (111) facets} = 2 \times t \times (w_1 + w_2) \]
\[ \text{Total area} = S_{100} + S_{110} + S_{111} \]
\[ \text{The relative ratio of each facet (\%)} = 100 \times \frac{S_i}{\text{total area}} \]
consistent with topotactic phase transformation (Fig. 2b). At pH 10, the particles have a rhombus shape with length of 30–70 nm. After the shape changes to hexagonal under neutral conditions, Al₂O₃ finally becomes an elongated platelet with the elongated side measuring 30–90 nm and the shorter side 8–25 nm. The aspect ratio of synthesized γ-Al₂O₃ was also measured for more quantitative information, as shown in Fig. 2c. A high aspect ratio is observed under acidic conditions, indicating the presence of elongated platelet morphology. Thus, several γ-Al₂O₃ platelet with different morphologies were synthesized by systematically controlling the pH during their synthesis (Table 1).

In order to identify the detailed crystallographic orientation of synthesized γ-Al₂O₃, bright-field TEM (BFTEM) and electron diffraction studies were performed on individual particles and the results are shown in Fig. 3. Usually, the (010) facet is known to be the most dominating of all facets on AlOOH because the interfacial tension of this facet is the lowest and also independent of the pH [44]. The BFTEM images and selected area electron diffraction (SAED) pattern of AlOOH given in Fig. 3a show that all particles are aligned to the main basal planes perpendicular to the [010] direction. The diagonal planes of the platelet formed at pH 10 are parallel to the (202) facets. The newly elongated planes formed with decreasing pH were found to be parallel to (001), which illustrates the specific growth along (001) facets. After thermal treatment, the SAED pattern for γ-Al₂O₃ (Fig. 3b) showed that the main basal planes were perpendicular to the [110] direction, indicating the change of the (010) facet on AlOOH into a (110) facet of γ-Al₂O₃. The lateral faces of (202) and (002) facets in AlOOH also changed into (111) and (004) facets of γ-Al₂O₃ respectively. These

![Fig. 2. (a) XRD patterns and (b) TEM images for γ-Al₂O₃ synthesized at different pH levels. (c) Aspect ratio of γ-Al₂O₃ at selected pH (4.3, 7.6 and 10). The aspect ratio is defined as a/h on the inlet.](image)

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<td>1.16</td>
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indicating the presence of elongated platelet morphology. Thus, several γ-Al₂O₃ platelet with different morphologies were synthesized by systematically controlling the pH during their synthesis (Table 1).
observations are consistent with previous structural correlations between AlOOH and γ-Al₂O₃ [9]. The crystal facets of γ-Al₂O₃ that are mainly discussed in literature are (100), (110), and (111) facets [9]. Detailed TEM studies were performed to determine the ratio of each of these facets in fifty Al₂O₃ particles. The BFTEM images were analyzed based on the structural model shown in Fig. 4a and the results are summarized in Fig. 4b. The rhombus γ-Al₂O₃ synthesized under basic conditions showed no apparent (100) facet. Previous HR-TEM study of platelet γ-Al₂O₃ reveals that the alumina have the internal surfaces of pore/voids defined by (100) and (111). And based on epitaxial relationship between Pt and platelet gamma alumina, external surface mainly defined as (110) and (111) facets have (100) facets also, which correlated with some degree of roughness on the (111)/(110) surfaces [44,46]. However, detailed understanding should be further investigated. Considering the apparent morphology, it may be concluded that the (100) facet ratio increased up to 23% with decreasing pH. Thus, there was a systematic increase in (100) facets on γ-Al₂O₃ but the (110) and (111) facet ratio decreased with decreasing pH. Hence, γ-Al₂O₃ synthesized in this work may be considered a suitable model system to investigate the role of (100) facet on the catalytic behavior of γ-Al₂O₃.

Diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopic analysis was performed to investigate the typical properties of the synthesized alumina surface and the changes in surface hydroxyl groups with increase in the (100) facet ratio. Fig. 5a shows the hydroxyl region of the DRIFT spectrum. It is noteworthy that the peaks at
3766 cm$^{-1}$ and 3660 cm$^{-1}$ increase with increasing (100) facet ratio. Here, 3580 cm$^{-1}$ peak which is hydroxyl group affected by water might cause doubts about the reliability of the results. So, we also compared the spectra collected at 500 °C treatment where the broad band at 3580 cm$^{-1}$ being minimized (Fig. S8). The results clearly demonstrate the overall tendency of two peaks at 3766 cm$^{-1}$ and 3660 cm$^{-1}$ in the spectra collected at 500 °C was consistent with the above results.

Three types of OH groups are known to exist on the surface of γ-Al$_2$O$_3$: isolated OH ($\mu_1$), bridged ($\mu_2$) or triply-bridged OH ($\mu_3$), but their exact assignments are still controversial [3,5,8,9,26,29]. Digne et al. have assigned the bands at 3766 cm$^{-1}$ and 3660 cm$^{-1}$ to the isolated hydroxyl group ($\mu_1$) and triply bridged OH groups ($\mu_3$) on the (100) facet, respectively [8]. Meanwhile, Busca et al. has suggested that the band at 3766 cm$^{-1}$ is either associated with or indicates the active sites, and originates from penta-coordinated Al$^{3+}$ cations, or OH groups present in the vicinity of vacant sites, or in the exposed (100)/(110) corners [3]. Although the accurate origin of band for hydroxyl group observed at 3766 cm$^{-1}$ should be studied further, it is clear that these hydroxyl groups are related to the (100) facet ratio (Fig. 5b). These results are somewhat different to those obtained by Dyan et al. and Busca et al. who have suggested that there are no significant changes in the hydroxyl groups of alumina with different morphologies or exposed surfaces [3,47]. The results of temperature-programmed desorption (TPD) of ethanol, which will be discussed later, suggest that the increase in intensity of 3766 cm$^{-1}$ and 3660 cm$^{-1}$ peaks with the elongation of the (100) facet may be related to the easier desorption as ethylene and increased number of active sites. It has already been shown that specific OH groups located on the surface are related to the alumina facets. Therefore, the acid-base properties of synthesized alumina are affected by the systematically controlled surface facet ratio, as evident by the consistently changing IR spectrum. The surface characteristics of faceted γ-Al$_2$O$_3$ were also investigated by ethanol TPD (Fig. 6). Previous studies reported by our group have shown the ethanol TPD is a sensitive method that can be used to characterize the alumina surface [32,33,48]. Desorption profiles showed two peaks, one is observed below 150 °C, corresponding to the weakly bound ethanol and the other one (> 150 °C) is dissociatively-adsorbed ethanol, which desorbed as ethylene. Fig. S11 showed that the dissociative EtOH sites/nm$^2$ increased from 1.17 to 1.45 sites/nm$^2$ with increasing ratio of (100) facets. On the other hand, the maximum desorption temperature of dissociative ethanol ($T_d$) showed a systematic decrease from 221.4 °C to 206.8 °C with increasing number of (100) facets. The increase in (100) facet ratio led to both easier desorption as ethylene and increased number of active sites. With increase in this ratio, it was also expected to change the number of penta-coordinated Al$^{3+}$ sites which are formed by the dehydroxylation of isolated hydroxyls on octahedral Al sites of (100) facets [8,24]. So, we performed solid-state $^{27}$Al-NMR shown in Fig. S12 for more quantitative information of (100) facets from the number of penta-coordinated Al sites. All samples showed both tetrahedral and octahedral Al$^{3+}$ sites around ∼10 ppm and ∼69 ppm chemical shifts. The amount of tetrahedral Al$^{3+}$ sites were around 35% (the percentage of the total number of Al$^{3+}$ sites), consistent with typical γ-Al$_2$O$_3$ spectrum [24,41]. Penta-coordinated Al$^{3+}$ sites at 35 ppm chemical shift were also observed for three γ-Al$_2$O$_3$. However, the meaningful difference and quantification of penta-coordinated Al$^{3+}$ sites were difficult due to lack of sensitivity (600 MHz) and low surface area of platelet γ-Al$_2$O$_3$. Thus, various characterization techniques confirmed a systematic increase in (100) facets on platelet γ-Al$_2$O$_3$. Next, it is important to investigate the influence of (100) facets on the catalytic activities on γ-Al$_2$O$_3$. For this purpose, ethanol dehydration was chosen as the model reaction. Ethanol dehydration on Al$_2$O$_3$ proceeds via two pathways, with one producing ethylene via intramolecular dehydration and the other producing ether via intermolecular dehydration [4]. Despite considerable efforts, the nature of the active sites for alcohol dehydration on γ-Al$_2$O$_3$ is still unclear [4,12,33,49–56]. Fig. 7 shows the activity of faceted γ-Al$_2$O$_3$ for ethanol dehydration reaction at 180 °C and using 2% ethanol. Under these reaction conditions, the dominant product was ether (> 98%). Interestingly, overall conversion increased from 2% to 3.9% with increasing (100) facet ratio. In addition, ethylene yield almost doubled at the maximum but selectivity didn’t show significant difference (1.8–2% – Fig. S13). We also carried out ethanol reaction measurements at 300 °C, where ethylene was the major product (Fig. S14). Fig. S14 showed increase of conversion with increasing (100) facet. Under high temperature reaction condition, C$_2$H$_4$ yield clearly increased from 36.5% to 54.6% with increasing (100) facet. C$_2$H$_6$ selectivity also increased from 51.9% to 70%. Increased selectivity to ethylene is consistent with ethanol TPD which showed easier desorption as ethylene for elongated platelet than rhombus platelet. Note that rhombus platelet where no apparent (100) facets exist showed catalytic activity for ethanol dehydration. Although no apparent (100) facets are shown in rhombus particles, (100) facets related to surface roughness on (110)/(111) facets or internal surface of pore might be related to catalytic activities for ethanol dehydration. The existence of 3766 cm$^{-1}$ on rhombus platelet also might be related to these facets. The increase in catalytic activity for ethanol dehydration is closely related to the intense hydroxyl bands around 3766 cm$^{-1}$. Srinivasan et al. have demonstrated a correlation between the intensity of band at 3770 cm$^{-1}$ with the most reactive transition alumina studied by them.

Fig. 5. (a) DRIFT spectrum of platelet γ-Al$_2$O$_3$ measured for the entire pH range after activation at 500 °C and (b) the relative absorbance ratio of 3766 cm$^{-1}$ band with respect to 3728 cm$^{-1}$ band as a function of increased portion of (100) facets. The 3728 cm$^{-1}$ band was shown as (*) on Fig. 5(a).
In this work, the ratio of (100) facet was increased by controlling the morphology of γ-Al2O3, which also led to the intense band at 3766 cm⁻¹ (Fig. 5b) and increase in catalytic activity for ethanol dehydration. These results clearly demonstrate the catalytic role of (100) facet for ethanol dehydration reaction on γ-Al2O3. It has been proposed that (100) facet is the active site of the alcohol dehydration reaction. This was confirmed by showing that there is one-to-one correlation between the number of dissociative ethanol and the penta-coordinated Al sites created by dehydroxylation of hydroxyls on (100) facets [25,33]. Recently, Larmier et al. have reported based on a combination of experimental and DFT studies that the reaction pathways involved in isopropyl alcohol dehydration require the active sites on (100) facets [52]. However, experimental evidence of facet-dependent activities for ethanol dehydration on Al2O3 was still missing. The strong correlation between (100) facet ratio and ethanol dehydration activity given in this work provides the direct evidence of the critical role of the (100) facet for ethanol dehydration on γ-Al2O3. Here, we can’t exclude the possibility of catalytic role for defect sites (edge/corner) suggested by Busca group [3,12]. However, these edges of corner are also closely related with (100) facets. The edges of (100)/(110) also consistently increase with increasing (100) facets on elongated platelet (Fig. S16). In conclusion, (100) facets are closely related to the catalytic activity for ethanol dehydration.

4. Conclusion

We investigated the effect of crystal facets on the catalytic behavior of platelet γ-Al2O3 by X-ray diffraction, transmission electron microscopy, temperature-programmed desorption of ethanol, solid-state 27Al NMR, infrared spectroscopy, and ethanol dehydration reaction. A series of platelet γ-Al2O3 were synthesized with a systematic increase in (100) facet ratio confirmed by TEM. FT-IR results also showed consistent results supporting systematic change of (100) facets from the linear relationship between (100) facet and the intensity of 3766 cm⁻¹ peak. Ethanol dehydration activity measurements showed that ethylene formation increased with increasing (100) facets, clearly demonstrating the critical role of these facets as active sites for ethanol dehydration on γ-Al2O3. The increased (100) facet ratio led to easier desorption as ethylene evidenced by the lower Td for dissociative ethanol sites from the ethanol TPD study, and increased catalytic activities for ethanol dehydration. These results clearly demonstrated the catalytic role of (100) facet for ethanol dehydration on γ-Al2O3. These results contribute to the fundamental understanding of crystalline facets on γ-Al2O3 and other industrially important catalytic material.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.02.018.

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