



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

Jaekyoung Lee^a, Eun Jeong Jang^a, Hu Young Jeong^b, Ja Hun Kwak^{a,*}

^a School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 44919, Republic of Korea

^b UNIST Central Research Facilities (UCRF), Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 44919, Republic of Korea

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ABSTRACT

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 FeO_x 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 [23,32]. The second challenge lies in the preparation of a series of γ -Al₂O₃ samples with systematic variance 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

* Corresponding author.

E-mail address: jhkwak@unist.ac.kr (J.H. Kwak).

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 transferred into a 125 ml Teflon-lined autoclave, then sealed and kept in the electric oven at 200 °C. After 12 h, the pH was measured by pH meter. The variance of hydrazine monohydrate amounts led to the pH range from 8.3 to 10. Next, the precipitates were collected by centrifugation, repeatedly washed by DI water and isopropyl alcohol, and dried at room temperature with air blowing for 1 day. Another series of platelet Al₂O₃ were synthesized with addition of glacial acetic acid in controlled amounts, leading to the variance of pH from 4.3 to 7.6. The other procedures were same. The as-prepared powders were calcined in a muffle furnace at 600 °C for 3 h, resulting in the platelet γ -Al₂O₃.

2.2. Characterizations

XRD patterns were obtained on a Bruker D8 Advance A25 using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) in step mode between 2θ 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 obtained by 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 ²⁷Al-NMR experiments were performed at room temperature on a Varian VNMRS 600 MHz NMR spectrometer, operating at a magnetic field of 14.4 T. The corresponding ²⁷Al 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 spectra were externally referenced (i.e., the 0 ppm position) to a 1 M Al(NO₃)₃ aqueous solution. We normalized the ²⁷Al 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

(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].

2.3. 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 w_1 , w_2 and w_3 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 w_3/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

$$S_{110}, \text{ the area of } \{110\} \text{ facets} = w_3 \times h \text{ (rhombus) or } 2 \times w_1 \times h' \text{ (parallelogram)}$$

$$S_{111}, \text{ the area of } (111) \text{ facets} = 2 \times t \times (w_1 + w_2)$$

$$\text{Total area} = S_{110} + S_{111}$$

$$\text{The relative ratio of each facet (\%)} = 100 \times S_i / \text{total area}$$

Elongated particles

$$S_{100}, \text{ the area of } (100) \text{ facets} = 2 \times w_3 \times t$$

$$S_{110}, \text{ the area of } (110) \text{ facets} = 2 \times w_3 \times h + 2 \times w_1 \times w_2 \times \sin(\theta)$$

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