



Ethanol dehydration on γ -Al₂O₃: Effects of partial pressure and temperature

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ABSTRACT

Ethanol dehydration was investigated using platelet γ -Al₂O₃ over a wide range of reaction temperature (180–300 °C) and ethanol partial pressure (0.5–2 kPa) by X-ray diffraction, ethanol Temperature-programmed desorption and reactions. The turnover frequencies for commercial and platelet γ -Al₂O₃ were almost identical (1.2 – 1.3×10^{-2} ethanol/site s) when normalized to the number of ethoxide quantified by ethanol TPD. The desorption barrier of ethoxide was 183.6 kJ/mol, similar to the activation barrier of ethylene formation. These results demonstrate that ethoxide is a key intermediate rather than molecular ethanol, possibly suggesting an E1 mechanism for ethylene formation, consistent with recent spectroscopic studies. Detailed kinetic measurements demonstrate the nature of the species on alumina surface varied with reaction temperature. At low temperature (180 °C), the ethanol dimer, one of which would be the ethoxide, saturated the surface, leading to the inhibition of ethylene formation and constant ether formation rates with ethanol pressure. At high temperature (260 °C), the ethanol monomer became dominant, consistent with the constant ethylene formation rates and increased ether formation rates with ethanol pressure. The apparent activation energies also changed with reaction temperature and ethanol partial pressure. Especially, the inhibition by ethanol dimer clearly contributed the increased apparent activation barrier at 180 °C.

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1. Introduction

γ -Al₂O₃ is one of the most important catalyst support materials in heterogeneous catalysis [1–3]. Due to its high surface area and thermal stability, it is used in many chemical processes from petroleum refining to automobile emission control. In addition, γ -Al₂O₃ itself is used as an acid catalyst, for example in alcohol dehydration reactions [4–29]. As alcohol dehydration over alumina has been known since the end of the 18th century, considerable research efforts had been focused on understanding the nature of active sites and the involved reaction mechanisms which related with the rational dehydration chemistry and elucidated the surface characteristics of alumina [6–25,28,29]. Furthermore, it is expected to give insight to acid-catalyzed deoxygenation which is one of the important chemical routes to remove oxygen from biomass compounds [4,5,15–20,23,26].

Alcohols are dehydrated mainly by two pathways: intra-molecular dehydration to form olefins and inter-molecular

dehydration to produce ethers. Considerable efforts have been focused on clarifying the reaction mechanisms for each products [8,9,14,16–21,23,27,29]. For olefin, Knözinger et al. [9] and Shi et al. [30] suggested E2 mechanism based on their kinetic isotope experiments. Recently, Larmier et al. also reported that isopropanol dehydration preferred an E2 mechanism [29]. Based on theoretical studies on various facets of alumina, e.g. (100), (110) and (111) facets, the authors concluded that E2 mechanism is preferred for olefin formation [18–20]. On the other hand, E1 mechanism was proposed for the 2-butanol dehydration reaction based on kinetic measurements and the results were supported by theoretical calculations [27]. Very recently, we found that the ethylene formation rates were inversely proportional to the desorption temperature of dissociative ethanol (T_d) irrespective of modification origin of the alumina surface [31]. Based on the correlation between T_d and ethylene formation rates, we suggested that ethoxide is a key intermediate in ethanol dehydration on alumina. E1 mechanism was also reported over other solid acids such as zeolite, oxides and mixed oxides [32–36]. Ether formation is much more complex than ethylene formation due to inter-molecular dehydration. Although the reaction mechanism is not fully understood yet, ether is mainly assumed to proceed via surface alkoxide [8,18–20,23,29,37–41].

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Especially, Shi et al. used S(+)-2-butanol to suggest that ether is formed through S_N2 mechanism [37]. Later, Busca et al. reported that ethoxide was the key intermediate for ether formation by Infrared (IR) study [23]. Recent theoretical investigations also support S_N2 mechanism [19–21,29], but the nature of active sites (Al sites or O sites) still remained to be clarified.

As alcohol dehydration occurs on the alumina surface, its characteristics is critical to the reaction. Previous studies have shown that surface properties of alumina were mainly determined by the activation temperature which directly influences surface dehydroxylation [24,42–45]. Based on their own γ - Al_2O_3 model, the theoretical studies of Digne and Sautet et al. showed that the coverage of surface hydroxyls strongly depended on the activation temperature [42]. Furthermore, they suggested that the chemical properties of surface hydroxyls were affected by the exposed crystalline facets [43]. Their recently reported experimental work showed that thermal treatment of γ - Al_2O_3 resulted in different surface hydroxyl coverages, greatly affecting the activation of probe molecules, such as N_2 , H_2 , CH_4 [44,45]. Not only the activation temperature but also the reaction temperature will influence the surface dehydroxylation, leading to different surface coverage of water and alcohol during the dehydration of alcohols. This will ultimately affect the catalytic behavior of the alumina surface in alcohol dehydration. However, many studies with different reaction temperature, partial pressure etc., led to difficulties of comprehensive understanding due to diverse test conditions.

In this study, ethanol dehydration was carried out on platelet γ - Al_2O_3 as catalyst over a wide range of reaction temperature (180–300 °C) and ethanol partial pressure (0.5–2 kPa). Ethanol dehydration reaction measurements and TPD demonstrate that the ethoxide is a key intermediate for ethylene formation by ethanol dehydration on Al_2O_3 , consistent with our very recent work [31]. This possibly suggests an E1 mechanism for ethylene formation. The reaction order for both ethylene and ether formation increased with increasing reaction temperature. The apparent activation energy also changed with reaction temperature and ethanol partial pressure. These results demonstrate the change of surface coverage in the catalytic active sites for alcohol dehydration as reaction temperature varies.

2. Experimental section

Commercial γ - Al_2O_3 was obtained from Sasol (Puralox SBA-200) and platelet alumina was synthesized based on previous reports [25,46]. The gamma phase and morphology of platelet alumina were confirmed by XRD (Bruker D8 Advance) and Transmission electron microscopy (JEM-2100, JEOL). The specific surface area of platelet alumina was $86\text{ m}^2/\text{g}$ determined by the Brunauer-Emmett-Teller method using ASAP 2420 instrument (Micromeritics).

To characterize surface properties of platelet and commercial alumina, ethanol TPD experiments were carried out using the same experimental procedures as described in our previous reports [24,25]. Prior to ethanol TPD experiments, 0.05 g of alumina was calcined at 500 °C for 1 h under 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 kPa 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). In order to get the activation barrier for desorption of ethylene, the

heating rate was varied systematically from 2.5 to 15 °C/min with commercial γ - Al_2O_3 and other TPD procedures were same.

Ethanol dehydration reaction tests were performed in a quartz flow reactor using 0.01 g catalysts supported by quartz wool. Samples were treated prior to reaction test in flowing 20% O_2 /He at 500 °C for 1 h. The carrier gas (He) was passed through a bubbler containing ethanol (99.5%, Sigma Aldrich) kept at 20 °C and ambient pressure. The ethanol concentration (0.5–2 kPa) was controlled by relative He flow rate (total flow rate of He was 2.0 ml/s). The outlet gases were analyzed by a GC (Agilent 7820A) using a HP-FFAP column and FID. For confirming the external diffusion issues in our reaction condition, the total flow was varied from 0.3 ml/s to 4.0 ml/s. In our reaction system from 1.0 ml/s to 4.0 ml/s, the external diffusion could be neglected and in this study we chose a total flow of 2.0 ml/s in all ethanol dehydration tests. For reasonable conversion level (<10%), we used platelet alumina and diluted with quartz chips if needed. Blank test using quartz chip showed 0.15% conversion (maximum) at 300 °C in 2 kPa ethanol which accounted for <5% error when we dilute the catalysts 50 times with quartz. All reaction data were used as initial rates by linear extrapolation and averaged more than three times to reduce experimental errors.

3. Results and discussion

In this study, we used commercial (Puralox SBA-200 from Sasol) and platelet γ -alumina synthesized according to previous studies [24,25,47]. Before we investigated the ethanol dehydration on γ -alumina in detail, we confirmed whether platelet alumina can be used as a representative model system for the commercial γ - Al_2O_3 . The XRD pattern of platelet alumina (Fig. 1(a)) confirmed that the synthesized crystalline alumina was γ -phase. The specific surface area of platelet alumina was $86\text{ m}^2/\text{g}$, significantly lower than that of the commercial one ($200\text{ m}^2/\text{g}$). The morphologies were confirmed by TEM on our previous work [25].

The surface characteristics of platelet and commercial γ - Al_2O_3 were evaluated by ethanol TPD shown in Fig. 1(b). The obtained desorption profiles clearly showed two desorption peaks: one below 150 °C, assigned to molecularly adsorbed ethanol and the other above 200 °C representing the products of dissociative ethanol adsorption [24]. Commercial and platelet γ - Al_2O_3 showed very similar ethanol desorption profiles with exactly the same maximum desorption temperature at 225 °C, indicating that these two aluminas have the same surface characteristics. The smaller total desorption amount of ethanol on platelet alumina might be related with the lower surface area of this material in comparison to the commercial one (86 vs. $200\text{ m}^2/\text{g}$). The normalized amount of ethanol desorbed, based on BET surface areas, on platelet alumina was 1.7 ethanol/ nm^2 , slightly higher than that on the commercial one (1.4 ethanol/ nm^2) [25]. The slight difference in the amount of ethanol desorbed is related to the different facet ratios of commercial and platelet aluminas [25,31,47]. These results suggest that both aluminas show practically the same surface characteristics and therefore, they should show the same catalytic behavior in ethanol dehydration.

To further confirm that the two aluminas possess comparable catalytic properties in alcohol dehydration, we tested ethanol dehydration at 180 °C under identical reaction condition (total flow 2.0 ml/s, $P_{EtOH} = 2\text{ kPa}$). Fig. 1(c) shows that the reaction reached steady-state over both aluminas, showing 3.1% (commercial) and 2.0% (platelet) overall ethanol conversion at 180 °C. The total turnover frequency normalized to the BET surface area was higher for platelet than commercial (platelet -2.2×10^{-2} ethanol/ $\text{nm}^2\text{ s}$ and commercial -1.7×10^{-2} ethanol/ $\text{nm}^2\text{ s}$) alumina. But, the TOF normalized to the dissociative ethanol detected from ethanol TPD was 1.3×10^{-2} ethanol/sites for platelet and

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