



Modification of the acid/base properties of γ -Al₂O₃ by oxide additives: An ethanol TPD investigation



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ABSTRACT

The electronic properties of oxide-modified γ -Al₂O₃ surfaces were investigated by using ethanol TPD. Ethanol TPD showed remarkable sensitivity toward the surface structures and electronic properties of the aluminas modified by various transition metal oxides. Maximum desorption rates for the primary product of ethanol adsorption, ethylene, were observed at 225 °C on non-modified γ -Al₂O₃. Desorption temperature of ethanol over a γ -Al₂O₃ samples with different amounts of BaO linearly increased with increasing loading. On the contrary, ethanol desorption temperature on Pt modified γ -Al₂O₃ after calcined at 500 °C linearly decreased with increasing Pt loading. These results clearly suggested that the acid/base properties of the γ -Al₂O₃ surface can be strongly affected by ad-atoms. For confirming these arguments, we performed ethanol TPD experiments on various oxide modified γ -Al₂O₃ and normalized the maximum desorption temperatures based on the same number of oxide dopants. These normalized ethanol desorption temperatures linearly correlate with the electronegativity of the metal atom in the oxide. This linear relationship clearly demonstrates that the acidic properties of alumina surfaces can be systematically changed by ad-atoms.

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1. Introduction

γ -Al₂O₃ is one of the most important materials in heterogeneous catalysis. It has been widely used both as an active catalyst and as a support for a variety of catalytically active phases (metals and oxides). The widespread applications of such catalysts range from petroleum refining to automotive emission control [1–3].

The catalytic properties (activity, selectivity, distribution of supported catalytic materials) of oxides (e.g., alumina) are intimately linked to their surface properties, because these chemical processes take place primarily on the surfaces of catalysts [4–20]. Therefore, the chemical and physical characterization of Al₂O₃ surfaces is crucially important for the correlation of catalytic properties with surface geometric and electronic structures [5,15,17,21–24]. However, the characterization of transition alumina surfaces by well-established analytical techniques is not straightforward, due to the intrinsic properties of these phases, such as low crystallinity, small particle size [3,24,25]. Especially, the alumina surface can go through phase transformations even under catalytically

relevant conditions (e.g., moderately high temperatures), leading to the difficulties of detailed characterizations of the surface [26–28].

For decades, various physicochemical and theoretical approaches have been devoted to understanding the surface properties of γ -Al₂O₃ [5,21–24,29–41]. Its surface consists of various types of Lewis and Brønsted acid sites. Knözinger and Ratnasamy reported an empirical alumina model based on detailed IR studies which identified five hydroxyl groups on the surface [5]. Later, Busca et al. suggested different assignments of IR bands of surface hydroxyl groups of Knözinger model [29,30]. They assigned previously bridging hydroxyl groups between two Al_{oct} into single Al_{oct} site. Also, they changed triply bridging OH groups into bridging between two Al sites, where one site is tetrahedral. Recently, Digne and Sautet et al. suggested a γ -Al₂O₃ model based on DFT simulations by considering temperature dependent surface hydroxyl group coverages [31,32]. They also showed the number and chemical properties of those surface hydroxyls were significantly affected by their crystalline facets [32]. Although their model is most popular one, accurate assignments are still debated and attempts to get more accurate model of the alumina surface are continuously going on.

Recently, we have reported that temperature programmed desorption (TPD) of ethanol is a very sensitive method to follow changes in the γ -Al₂O₃ surface during thermal

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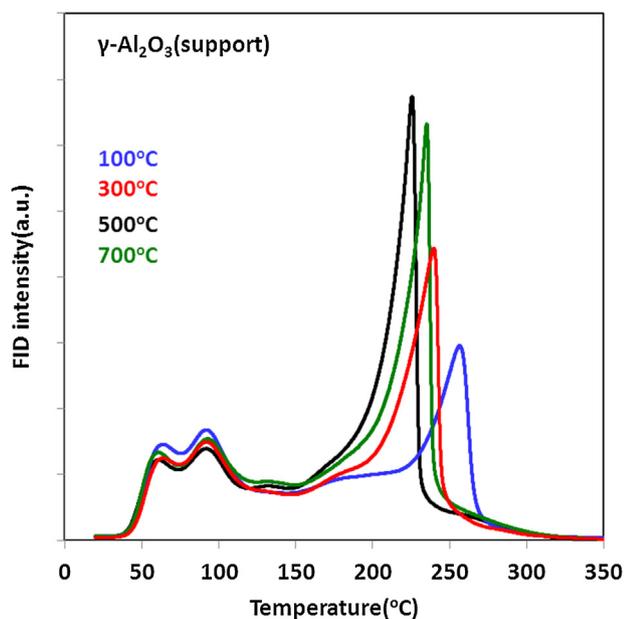


Fig. 1. Ethanol TPD profiles of supporting $\gamma\text{-Al}_2\text{O}_3$ after activated at 100 °C, 300 °C, 500 °C and 700 °C for 2 h.

dehydration/dehydroxylation [6,28]. We also reported that ethanol TPD was very sensitive to the surface structure and/or electronic properties which might be directly correlated with the acid–base properties of gamma-alumina surfaces [27,28].

Here we report on how the ad-atom changes ethanol desorption temperature significantly and that the ethanol desorption temperatures show strong correlation with the electronegativities of ad-atoms which clearly demonstrate that the acid–base properties of alumina surfaces can be controlled systematically by oxide modifiers.

2. Experimental

The $\gamma\text{-Al}_2\text{O}_3$ samples used in this work were obtained from Condea (surface area = $200\text{ m}^2\text{ g}^{-1}$). A series of Pt- and BaO/ $\gamma\text{-Al}_2\text{O}_3$ catalysts with different loadings were prepared by conventional impregnation methods described elsewhere using tetra-ammine platinum nitrate and barium nitrate precursors, respectively [17,35,42].

Ethanol TPD experiments were performed using the same protocol we have described in a previous report [6]. Prior to ethanol TPD experiments, 0.05 g of $\gamma\text{-alumina}$ and was calcined at each temperature (100 °C, 300 °C, 500 °C and 700 °C) for 2 h under He flow (1.0 ml/s) (note that every TPD run was carried out on a freshly calcined alumina sample). 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 1 h in order to remove most of the weakly bound ethanol molecules. After stabilization of the flame ionization detector (FID) signal of a Hewlett-Packard 5890 gas chromatograph (GC), a TPD experiment was carried out in flowing He (1.0 ml/s) with a heating rate of 10 °C/min, with the reactor outlet flowing directly to the FID (i.e., no GC column separation). FID sensitivities were calibrated by using 100- μl pulses of 2.0% ethanol in He prior to each TPD experiments.

Various metal oxide loaded on $\gamma\text{-Al}_2\text{O}_3$ catalysts with different loadings were also prepared by similar incipient wetness methods using responsible precursors and performed ethanol TPD experiments with same protocols describe above.

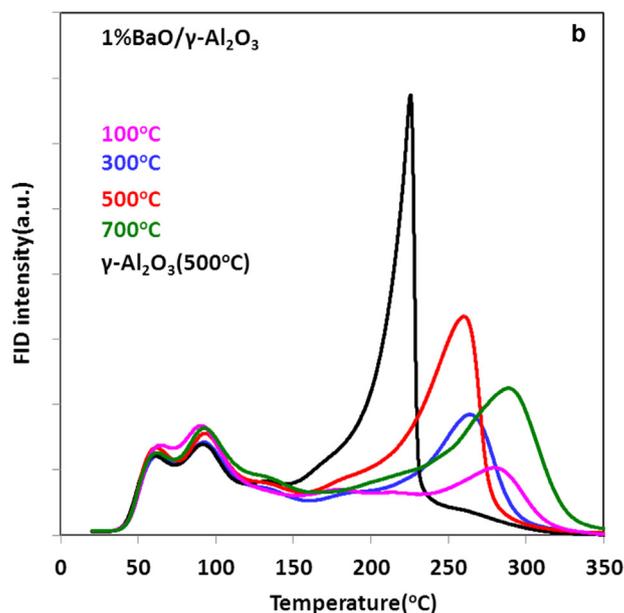
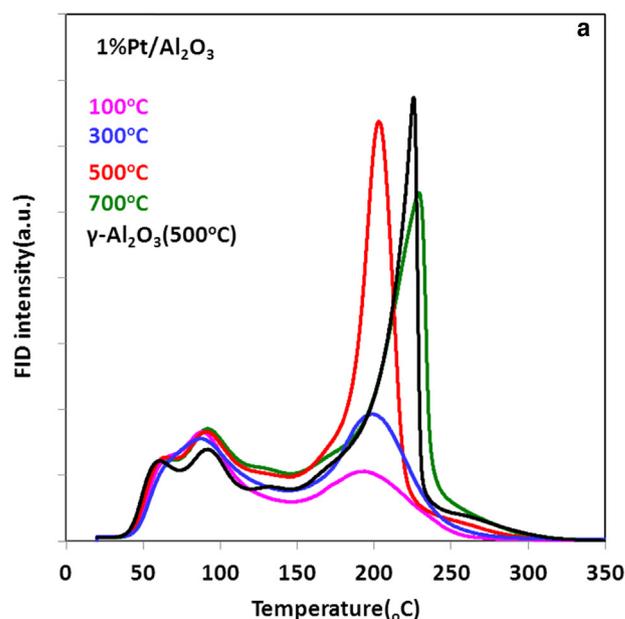


Fig. 2. Ethanol TPD profiles of 1% Pt (a) and 1% BaO (b) on $\gamma\text{-Al}_2\text{O}_3$ after activated at 100 °C, 300 °C, 500 °C and 700 °C for 2 h.

3. Results and discussions

We first performed series of ethanol TPD experiments over $\gamma\text{-Al}_2\text{O}_3$ samples that were pre-calcined at 100 °C, 300 °C, 500 °C and 700 °C, and the results obtained are displayed in Fig. 1. Each TPD profile shows three main desorption peaks with maximum desorption rates at ~70 °C, ~90 °C and above 200 °C, consistent with our previously reported results for ethanol TPD on $\gamma\text{-Al}_2\text{O}_3$ [6,27,28]. The positions of the two low temperature desorption peaks are very similar regardless of calcination temperatures, and are assigned to weakly bound (molecularly adsorbed) ethanol [43]. High temperature desorption peaks at 250 °C and 225 °C in ethanol TPD after activation at 100 °C and 500 °C are related with the dissociative ethanol adsorption on Brønsted and Lewis acid sites on $\gamma\text{-Al}_2\text{O}_3$, in other words, hydroxylated and dehydroxylated surfaces, respectively. The ethanol desorption peak at ~240 °C after calcination at 300 °C is related with partially dehydroxylated surfaces. The

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