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.

Keywords: γ -Al₂O₃, Ehtanol-TPD, Metal oxide modification, Acid/Base property.

Introduction

γ - Al_2O_3 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 Al_2O_3 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 - Al_2O_3 [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 - Al_2O_3 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 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.

Experimental

The γ -Al₂O₃ samples used in this work were obtained from Condea (surface area = 200 m²g⁻¹). A series of Pt- and BaO/ γ -Al₂O₃ 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 γ -alumina and was calcined at each temperature (100 °C, 300 °C, 500 °C and 700 °C) for 2 hrs under He flow (1.0 ml/sec) (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/sec), 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/sec) 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- μ l pulses of 2.0 % ethanol in He prior to each TPD experiments.

A various metal oxide loaded on γ -Al₂O₃ 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.

Results and Discussions

We first performed series of ethanol TPD experiments over γ -Al₂O₃ samples that were pre-calcined at 100 °C, 300 °C, 500 °C and 700 °C, and the results obtained are displayed in Figure 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 γ -Al₂O₃ [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 γ -Al₂O₃, 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 ethanol desorption peak shifted to higher temperature after activation at 700 °C is related with the phase transformation and so the surface characteristics changes. All these results were consistent with our previous reports, proving ethanol TPD could be a very sensitive technique to follow the changes in the physicochemical properties of alumina surfaces, such as activation temperatures and phase transformations [6, 27, 28].

Our next questions are how the oxide modification affects the physicochemical properties of alumina surfaces. Before moving on to this, we need to establish the experimental conditions of ethanol TPD for even comparison of oxide modifications by excluding the effects of preparation protocols such as impregnation, precursors and activation. For that, we prepared 1% Pt and 1% BaO loaded alumina samples by simple impregnation methods and performed ethanol TPD after activation at 100 °C, 300 °C, 500 °C and 700 °C. Figure 2 shows the ethanol TPD profiles obtained with reference ethanol TPD collected from pure alumina after activation at 500 °C. Interestingly, Pt- and BaO-modified alumina showed completely different ethanol desorption behavior, especially the desorption peak of dissociatively adsorbed ethanol varied significantly. The ethanol desorption peak on Pt/Al₂O₃ after activation at 100 °C was very small and showed a maximum at significantly lower temperature (~ 190 °C) than pure alumina (~ 250 °C) treated under the same conditions. Ethanol desorption peak intensity increased significantly as the activation

temperature increased to 300 °C and 500 °C, but desorption temperatures didn't change much which might be related with the dehydroxylation of alumina surfaces and also decomposition of tetra-ammine platinum nitrate precursors. After 500 °C activation, decomposition of Pt precursors is complete and the ethanol desorption peak, due to the presence of Pt, shifts to 200 °C on Pt/Al₂O₃ from 225 °C on alumina [44]. It is very interesting that the presence of a relatively very small amount of Pt (1%) resulted in 25 °C change on ethanol desorption temperature [43, 45]. After 700 °C activation, the desorption peak shifted to ~ 230 °C which is slightly higher than that on alumina after activated at 500 °C and, at the same time, the desorption peak intensity decreased significantly. In our previous report we showed that the alumina surface changed after activated at 700 °C and the desorption peak shifted to higher temperature (~ 235 °C) [27]. Therefore, we can safely interpreted these results as after activation at 700 °C, Pt will be significantly sintered, leading to no effect on the physicochemical properties of the alumina surface. In addition, at this high temperature the phase of the alumina surface might have also changed a little to delta or theta. In contrast with Pt on alumina, BaO loaded alumina showed completely different behavior as shown in figure 2(b). After 100 °C activation, the 1% BaO/Al₂O₃ sample showed significantly higher ethanol desorption temperature (~ 280 °C) compared with alumina (~ 250 °C). The 300 °C-activated BaO/Al₂O₃ also showed much higher desorption temperature (~ 265 °C) than alumina (~ 240 °C). Barium nitrate decomposition takes place above 400 °C [46]. But even after barium nitrate decomposition as BaO formed after 500 °C activation, the ethanol desorption peak temperature was significantly higher than that on alumina (255 °C to 225 °C). Therefore, these consistently higher ethanol desorption temperatures on the BaO-loaded alumina may come from the modification of the electronic properties of the alumina support surface by BaO. Interestingly, after 700 °C activation the ethanol desorption peak shift to 285 °C which might be related with the formation of barium aluminate (However, we never detected barium aluminate formations below 4 wt.% BaO loading on Al₂O₃ not even after 1000 °C activation [42]. But surface barium aluminate-like species can probably form above 700 °C, the temperatures of BaAl₂O₄ formation on 20% BaO/Al₂O₃. It also proves the power of surface sensitive techniques such as ethanol TPD compared with bulk analytical techniques such as XRD. Anyhow, all the ethanol desorption peak after BaO loading shifted to significantly higher temperatures, while after Pt loading it shifted to lower temperatures. So, the key question is why the ethanol desorption peak shifted to higher (BaO/Al₂O₃) or to lower (Pt/Al₂O₃) temperatures than that on alumina. For fair comparison,

we chose an activation temperature of 500 °C which is high enough to decompose the metal precursors, but low enough to prevent initiation of phase transformation of alumina or reaction of supported metal with alumina. One remaining issue we need to point out is alumina surface modification by water. In a recent report on the tomography of platelet-shaped model gamma alumina we showed that the alumina surfaces were significantly modified by water or alcohol treatments [21]. Those results suggest that the 300 °C activated samples do not show the characteristics of oxide modified aluminas due to amorphous layer on alumina surface, as well as the incomplete decomposition of metal precursors like barium nitrate.

Based on these results we set the activation temperature as 500 °C and varied the Pt and BaO loading to identify the effect of the number of dopants on the ethanol desorption behavior. As we have shown above, the addition of Pt or BaO clearly affected the surface properties of the alumina, this effect should systematically vary as the loading of the modifier gradually increased. As the results of Figure 3 reveal, both the desorption temperature and the amount of desorbed ethylene decreased with increasing Pt loading, while the desorption temperatures increased with increasing BaO loading on the alumina support. Although the desorption temperature increased systematically with increasing BaO loading, the correlation between the amount of desorbed ethylene and BaO loading was not linear. This might be explained by the findings of our recent study in which we have shown that room temperature adsorption of ethanol (and formation of water on the surface) can interrupt the interaction between BaO and the alumina surface [6]. Figure 3(c) shows that the desorption temperature linearly increased with BaO loading while it linearly decreased with Pt loading. It is clear that the alumina surface is modified by Pt and/or BaO but in a completely opposite direction. Significant increase of ethanol desorption temperature has been found recently by Roy et al. in a mechanistic study of alcohol dehydration on γ -Al₂O₃ [47]. In that report, they showed that the alcohol desorption temperature on γ -Al₂O₃ decreased almost 150 °C by NH₄⁺ ion exchange and subsequent activation at 500 °C. Their results also revealed that amount of Na⁺ impurity was reduced significantly by NH₄⁺ treatment which would be one of the reasons for the change in ethanol desorption temperature. Furthermore, their DFT calculation showed the alcohol dehydration barriers shifted to higher energies with increasing Na⁺ content due to decreased basicity of basic centers in their model. We believe their

results are completely consistent with ours, in that the alcohol desorption temperature is affected by surface modifications, in their case by Na^+ and in our case by Ba^{2+} .

The final question is why the surface modification drives the ethanol desorption temperature to completely different directions when the alumina support is modified by Pt and BaO. In order to answer this question, we prepared a series of metal oxide-loaded alumina samples and performed ethanol TPD experiments after activation at 500 °C. Interestingly, some oxides increased the ethanol desorption temperatures while others decreased, as shown in figure 4(a). Especially, ethanol desorbed almost at 350 °C from 1% K-modified alumina. Intuitively it suggests that the acid/base properties of alumina changed significantly by oxide modification. Ethanol desorption product at high temperature is solely ethylene which is formed by uni-molecular dehydration of ethanol, a well-known acid-catalyzed reaction [4, 6, 43, 47-51]. Therefore, it is reasonable to assume that changes in the temperature of dissociative ethanol desorption should correlate with the acid/base property changes of the alumina surface brought upon by the surface modifiers. For rationalizing this argument we found that the electronegativity of ad-atoms correlated well with the variations observed in the acid/base properties of the alumina support. We normalized the ethanol desorption temperatures to same number of metal atoms added to the support (1×10^{-4} mole/g_{alumina}). Other oxides also showed the same linear relationships between desorption temperature and metal loading as we have seen for Pt and BaO. The results plotted in figure 4(b) show a reasonably linear correlation between the temperature of maximum ethylene desorption rate and the electronegativity of the metal atom of the oxide. This correlation clearly demonstrates that the acid/base properties of alumina surfaces can systematically be modified by ad-atoms and, more importantly, these effects might be one of the origins of promotional effects on supported metal clusters.

Conclusions

In this work, we investigated the effect of surface properties modification of $\gamma\text{-Al}_2\text{O}_3$ by metal and metal oxide dopants on the ethylene desorption temperature in ethanol TPD. Maximum desorption rates for the primary product of ethanol adsorption, ethylene, were observed at 225 °C on non-modified $\gamma\text{-Al}_2\text{O}_3$. Desorption temperature of ethanol over a $\gamma\text{-Al}_2\text{O}_3$ samples with different amounts of BaO linearly increased with increasing loading.

On the contrary, ethanol desorption temperature on Pt modified γ -Al₂O₃ after calcination at 500 °C linearly decreased with increasing Pt loading. These results clearly suggested that the acid/base properties of 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 on same number of oxide dopants. These normalized ethanol desorption temperatures linearly correlate with the electronegativity of the metal in the oxide dopant. These linear relationship clearly demonstrate that the acidic properties of alumina surfaces can be systematically varied by ad-atoms.

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Figure captions

Figure 1. Ethanol TPD profiles of supporting γ -Al₂O₃ after activated at 100 °C, 300 °C, 500 °C and 700 °C for 2hrs.

Figure 2. Ethanol TPD profiles of 1% Pt (a) and 1% BaO (b) on γ -Al₂O₃ after activated at 100 °C, 300 °C, 500 °C and 700 °C for 2hrs.

Figure 3. Ethanol TPD profiles of Pt (a) and BaO(b) on γ -Al₂O₃ with different loading after activated at 500 °C for 2hrs and (c) the plot of maximum ethanol desorption temperature vs Pt (red) and BaO (black) loadings, respectively.

Figure 4. Ethanol TPD profiles of various metal oxide supported on γ -Al₂O₃ after activated at 500 °C for 2hrs (a) and normalized (1×10^{-4} mol of metal/g_{alumina}) maximum ethanol desorption temperatures vs electronegativity (b).

Figure 1.

Figure 2(a)

Figure 2(b)

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 4(a)

Figure 4(b)