Controlling the Acid-Base Properties of Alumina for Stable PtSn-based Propane Dehydrogenation Catalysts

Eun Jeong Jang, Jaekyoung Lee, and Ja Hun Kwak*
Ulsan National Institute of Science and Technology, Ulsan, Korea
*jhkwak@unist.ac.kr

Introduction

Demand for light olefins including propylene has increased because of their applications as raw materials in petrochemical industry.[1] For meeting the growing demand for propylene, propane dehydrogenation (PDH) has gained attention for propylene production utilizing shale gas. Platinum-based catalysts supported on alumina are widely used in the PDH due to their excellent activity and selectivity. However, it requires high reaction temperatures causing severe catalyst deactivation by metal sintering and coke deposition. To improve the thermal stability with high activity and selectivity, considerable research efforts were focused to modify the properties of the support with various additives. However, a fundamental understanding of surface properties of Al_2O_3 for improving catalytic properties in alumina-based PDH catalysts was not well established. Herein, we reported how does the surface properties of γ-Al_2O_3 affected the metal sintering and coke deposition using specifically synthesized γ-Al_2O_3 exhibited significantly different surface properties from commercial γ-Al_2O_3, despite the same bulk structure. PtSn loaded on synthesized alumina that have stronger but less amounts of Lewis acid sites showed significantly improved stability and coke resistance. We also correlated the coke behavior with the Lewis acid sites, using DRIFTs experiments at low temperature.

Materials and Methods

To synthesize model γ-Al_2O_3, we first synthesize the ammonium aluminum carbonate hydroxide (AACH) with fibrous morphology using the procedure from the previous study.[2] After calcined at 750 °C for 5 h the as-prepared AACH (labeled as A750), 0.5 wt% Pt and 0.9 wt% Sn were loaded by the incipient wetness co-impregnation method. The samples were calcined in 20% O_2/He (total 100 sccm) at 500 °C for 4 h, and then reduced in 10% H_2/He (total 60 sccm) at 590 °C for 2 h. Propane dehydrogenation tests were conducted at 590 °C using 50 mg of catalysts in a quartz flow reactor with WHSV of propane = 5.2 h^{-1} in C_3H_8:H_2:He = 1:1.25:4 (volume ratio) under atmospheric pressure. Ethanol temperature-programmed desorption (TPD) experiments for the characterization of alumina surfaces were conducted following the similar procedure in our previous report.[3] HAADF-STEM images were collected with JEOL JEM-2100F microscope operated at 200 kV.

Results and Discussion

In this work, we synthesized a γ-Al_2O_3 (A750) from ammonium aluminum carbonate hydroxide and compared it with a commercial alumina (Sasol Puralox SBA-200; P200). XRD patterns of alumina shown in figure 1(a), confirmed γ-Al_2O_3 (JCPDS no. 10-425) phase of A750 which had the same structure as commercial a γ-Al_2O_3 (P200). However, they showed very different surface properties from ethanol TPD shown in figure 1(b). Both the number of ethoxide (A750 = 1.04 vs. P200 = 1.48 sites/nm^2) and desorption temperature (T_d, A750 = 262 vs. P200 = 220.8 °C) were significantly different despite exactly the same bulk phase confirmed from XRD. PDH conducted after PtSn loaded on these two alumina showed compatible initial activity (conversion = ~50%) and selectivity (> 95%) shown in figure 1(c). However, PtSn/P200 showed significantly fast deactivation than PtSn/A750. After 20 h, PtSn/A750 showed a slight decrease in activity (conversion = 39.9%) while PtSn/P200 dropped the activity significantly (conversion = 28.4%). HAADF-STEM images (figures 1(d-g)) demonstrated the practically same PtSn cluster size distribution from fresh prepared samples on PtSn/A750 while some sintered PtSn clusters were shown on PtSn/P200 after 20h PDH test. The amount of coke after 20h reaction tests quantified by temperature programmed oxidation tests showed that about 5 times more cokes were deposited on PtSn/P200 than PtSn/A750. These results clearly demonstrated the surface properties of alumina, especially for acid strength and the number of Lewis sites on alumina surface were critically important for metal sintering and coke deposition during PDH reactions.

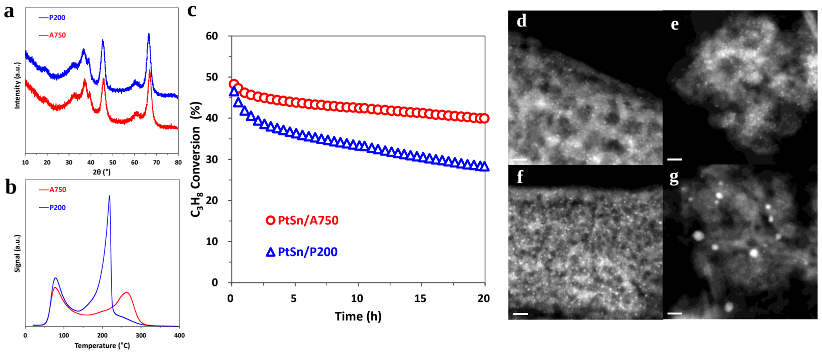

Figure 1. (a) XRD patterns and (b) ethanol TPD profiles for A750 and P200. (c) propane conversions during the PDH reaction at 590 °C for 20 h. HAADF-STEM images of the fresh (d) PtSn/A750 and (e) PtSn/P200, and of the spent (f) PtSn/A750 and (g) PtSn/P200.

Significance

In this work, we revealed that the alumina surface properties (the number and strength of acid sites) strongly influence the activity and stability of PDH catalysts based on two different γ-Al_2O_3 that have significantly different surface properties despite of the same bulk structures. This fundamental understanding will contribute to the development of alumina-based catalysts with high activity and superior stability for desired.

References

1. Sattler, J., Ruiz-Martinez, J., Santillan-Jimenez, E., Weckhuysen, B. *Chem. Rev.* 114, 10613 (2014).
2. Wang, J., Shang, K., Guo, Y., Li, W.-C. *Microporous Mexoporous Mater.* 181, 141 (19).
3. Lee, J., Jang, E. J., Kwak, J. H. *Journal of Catalysis.* 345, 135 (2017).