Monitoring the Preparation Process of NiO/Al₂O₃ Catalysts

Xinjie Zhang¹, Yong Wang¹, Kuiyang Jiang², Jianli Hu¹, Xiaohong Li¹, Todd A Werpy³

¹Pacific Northwest National Laboratory, P. O. Box 999/MS K8-93, Richland, WA 99352
²Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, NY, 12180

Introduction

To highly disperse metals, metal oxides or salts on supports is a usual requirement for the preparation of most catalysts, absorbents and sensors etc. Highly dispersed functional centers on the supports not only lead to high activities but also high selectivities. Impregnation is a typical method for the preparation of these materials. Commonly, the precursors are dissolved in solvents, dried and calcined to form the final functional materials. The preparation processes are critical to the properties of the final functional materials. While the specific surface areas of the supports are generally considered in these preparation processes, the support pore volumes are often neglected. We here report the support pore volume plays an important role on the formation of highly dispersed functional centers by monitoring the preparation process of NiO/Al₂O₃ catalysts, which is a new promising low temperature catalyst for oxidative dehydrogenation of ethane to ethylene¹.

Results and Discussion

Alumina support has a specific surface area of 164m²/g and a pore volume of 0.286ml/g. The NiO/Al₂O₃ catalysts are prepared by impregnation of aqueous solution of Ni(NO₃)₂·6H₂O with Al₂O₃. The amounts of Ni(NO₃)₂·6H₂O used are designed to get 5, 10, 15, 20, 25 and 30wt% NiO on Al₂O₃. The resultant slurries are dried at 110ºC for 12 hours and designated as xNA110, where x is the weight percent of NiO. xNA110s are calcined at 450ºC for 10 hours and designated as xNA450.

DSC of xNA110s show there are absorption peaks from 20 to 260ºC because of the loss of H₂O, and the absorption peaks ranged from 260 to 400ºC are the decomposition of Ni(NO₃)₂·6H₂O. Pure Ni(NO₃)₂·6H₂O loses 4 H₂O when heated to 110ºC². XRD characterizations of xNA110s show that for 5NA110, 10NA110 and 15NA110, there are no obvious crystal Ni(NO₃)₂·nH₂O species on the supports. 20NA110 shows small peaks of Ni(NO₃)₂·2H₂O, and 25NA110 shows large peaks of Ni(NO₃)₂·2H₂O, while on 30NA110, peaks attributed to crystal Ni(NO₃)₂·2H₂O and Ni(NO₃)₂·4H₂O both show up.

XRD of xNA450 show that there are no obvious crystal NiO peaks on 5NA450, 10NA450 and 15NA450. The peaks of crystal NiO appear on 20NA450, 25NA450 and 30NA450, and the particle sizes of crystal NiO increase from 14.5 to 43.5nm. The result demonstrates that the amorphous Ni(NO₃)₂·nH₂O on the support converts to highly dispersed NiO, and the crystal Ni(NO₃)₂·nH₂O decomposes to crystal NiO.
The differences between 15NA110 and 20NA110, as well as 15NA450 and 20NA450 are analyzed by combination of BET and XRD characterizations presented in the figure here. As the increases of the Ni salt amounts, the pore volumes of xNA110s decrease. For 20NA110, 25NA110 and 30NA110, the pore volume is towards zero, which indicates the Ni salts prefer to stay in the support pores. It can be anticipated that when the support pore volume is big enough to hold Ni(NO$_3$)$_2$·nH$_2$O (n=1~4), they prefer to stay in the support pore and form amorphous Ni(NO$_3$)$_2$·nH$_2$O species and become highly dispersed NiO after calcination; and when the support pore is full by holding these Ni(NO$_3$)$_2$·nH$_2$O, excessive amounts have to stay outside of the pore, form crystal Ni(NO$_3$)$_2$·nH$_2$O and finally become crystal NiO. The figure here also shows that NiO particle size increases as the NiO loading increases. The intersection of these two curves corresponds to 16.5wt% NiO on support. This is the important point where “Support Pore Volume Confinement” takes effect.

As we state above, the pore volume of Al$_2$O$_3$ support is 0.286ml/g. From the TGA of xNA110, we know Ni(NO$_3$)$_2$·nH$_2$O (n=1~4) presents on the xNA110. Let us take the average, Ni(NO$_3$)$_2$·2.5H$_2$O. The density of Ni(NO$_3$)$_2$·2.5H$_2$O is supposed to be similar with pure Ni(NO$_3$)$_2$·6H$_2$O, which is 2.05g/ml, so the pores of 1g support can hold 0.586g Ni(NO$_3$)$_2$·2.5H$_2$O. This amount can be converted to 0.201g NiO, which corresponds to 16.7wt% NiO on the catalyst.

In order to verify our assumption, the 30NA450 catalyst was prepared by totally eliminating the SPVC effect through 5 impregnation-drying-calcination cycles. The final catalyst (30NA450-5T) has very small crystal NiO, ~ 6.0nm (while on 30NA450, 43.5nm). TEM confirms XRD result. This catalyst can improve the highest ethylene yield from 38.6% to 43.0% in the oxidative dehydrogenation of ethane.

"Support Pore Volume Confinement (SPVC)" defines the upper limit of the amount of highly dispersed species. SPVC is a simple, basic but important principle to the preparation of many functional materials. Only the species that can well wet the support may approach this limit. For those that cannot well wet the support, the amount of highly dispersed species should be smaller than that defined by SPVC. "Support Pore Volume Confinement" is especially useful when using high special surface area support, such as mesoporous zeolites and carbon nanotubes.

References