

## Nanostructured TiO<sub>2</sub> Support Effect on Hydrothermal Stability of Platinum based Catalysts

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Platinum (Pt) based catalysts are widely used in petrochemical refinery, automotive emission control, and fuel cell applications [1]. However, large active surface area of Pt nanoparticles (NPs) catalysts tends to decrease drastically as a result of agglomeration into much larger particles at high temperature, shortening the catalyst lifetime. Therefore, Pt NPs are usually anchored on highly stable metal oxide supports to slow down the agglomeration and keep their activity [2]. TiO<sub>2</sub> is an earth-abundant and chemically stable support for Pt based catalysts [3]. The physical-chemical and catalytic properties of Pt NPs have been reported as supported on titania of different crystalline forms including anatase, rutile, and brookite. However, the precursors of TiO<sub>2</sub>, such as titania hydrates, are not well studied as supports for noble metal NPs. Meanwhile, one-dimensional (1D) metal oxide nano-arrays have been studied as supports for Pt based catalysts for various reactions [4]. The well-defined 1D structures make it possible to make rational comparison between effects of different support structures on the sintering resistance of Pt NPs.

In this work, two types of TiO<sub>2</sub> nano-array supported Pt catalysts with different initial support structures were prepared. Pt precursors (50 g/ft<sup>3</sup>) were initially dip-coated onto two types of TiO<sub>2</sub> nano-arrays, the fresh nano-arrays (50Pt-TOH), which are composed of hydrogen titanium oxide hydrate (H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O, JCPDS 47-0124), and the anatase nano-arrays (50Pt-AN), which were obtained by annealing the fresh nano-arrays. All the samples were further annealed at 500 °C for 2 h to increase the crystallinity of the Pt NPs and transit H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> to anatase. Hydrogen reduced samples (50Pt-TOH-HR and 50Pt-AN-HR) were obtained by reducing the catalysts in 4 % H<sub>2</sub>/Ar at 500 °C, and all the samples were finally hydrothermally aged at 800 °C for 50h (50Pt-TOH-HR-HTA and 50Pt-AN-HR-HTA) to compare the hydrothermal stability of the Pt NPs.

The evolution of the Pt NPs in the samples is displayed in the HAADF-STEM images in **Figure 1**. Both the as-prepared (50Pt-TOH, 50Pt-AN) and the H<sub>2</sub> reduced catalysts (50Pt-TOH-HR, 50Pt-AN-HR) showed well dispersed Pt NPs on the nano-arrays. However, for the hydrothermally aged samples, highly dispersed Pt NPs retained on the 50Pt-TOH-HR-HTA samples, while for the 50Pt-AN-HR-HTA sample, only large Pt NPs were revealed on the nano-array surfaces.

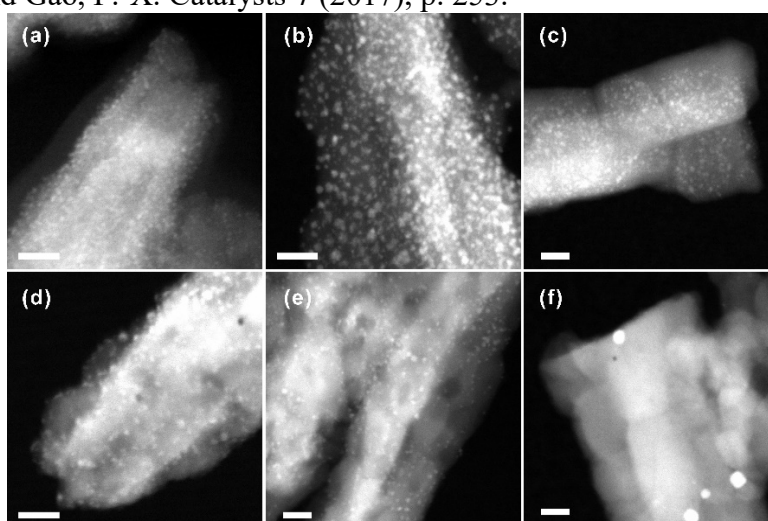
CO oxidation was employed as a probe reaction to compare the catalytic performance of these catalysts. The tests were conducted on an Agilent 490 Micro GC (0.25% CO+10% O<sub>2</sub> in N<sub>2</sub>). The light-off curves and the transition temperatures are displayed in **Figure 2**. The difference in the catalytic activities can be explained by the comparative structural observation from in **Figure 1**. Both the as-prepared and the H<sub>2</sub> reduced catalysts showed low light-off temperatures for CO oxidation due to the well dispersed Pt NPs. For the hydrothermally aged samples, 50Pt-TOH-HR-HTA still shows an excellent catalytic activity for CO oxidation with a slight increase of the T<sub>50</sub> by 20 °C, but for 50Pt-AN-HR-HTA, the catalytic activity deteriorated greatly due to the severely sintered Pt NPs. The better hydrothermal stability of the 50Pt-TOH-HR-HTA sample is supposed to originate from the greater interaction between the Pt NPs

and the  $\text{H}_2\text{Ti}_2\text{O}_5$  surfaces with lower crystallinity compared with the crystalline anatase surfaces. The sintering resistance of the Pt NPs is therefore enhanced by the potentially better anchoring effect from the  $\text{H}_2\text{Ti}_2\text{O}_5$  support.

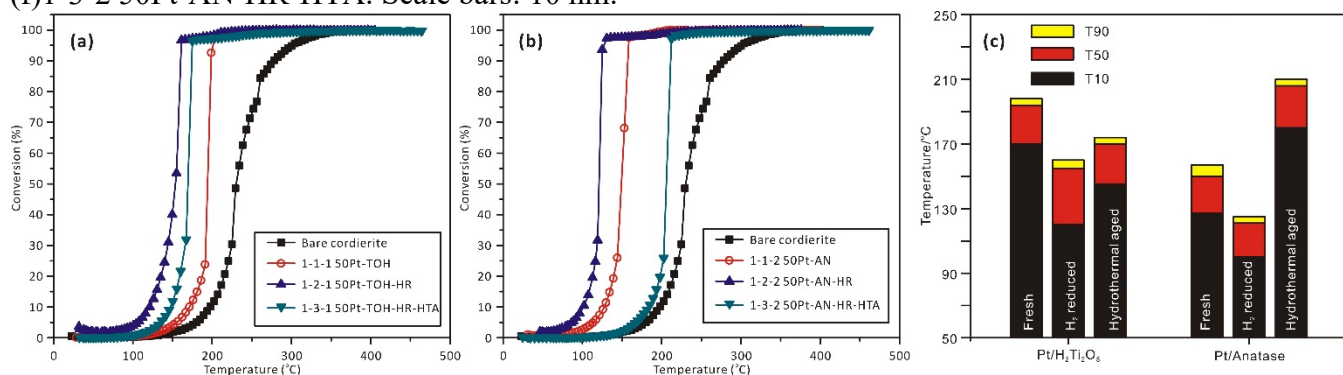
In summary, by loading the Pt NPs on two types of  $\text{TiO}_2$  nano-arrays, the promotional effects of the support structures on the hydrothermal stability of the  $\text{TiO}_2$  nano-array supported Pt catalysts were studied in this work. According to the microstructural evolution of the Pt NPs and the catalytic activity for CO oxidation of the sample before and after hydrothermal aging, the hydrogen titanium oxide hydrate nano-arrays showed better sintering resistance on the Pt NPs than the crystalline anatase nano-arrays. Considering the wide application of  $\text{TiO}_2$  supported Pt catalysts, this new finding may provide a new pathway to design highly stable Pt based catalysts for different gas phase reactions.

#### References:

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**Figure 1.** HAADF STEM images of the  $\text{TiO}_2$  nano-array supported Pt catalysts: (a) 1-1-1 50Pt-TOH, (b) 1-2-1 50Pt-TOH-HR, (c) 1-3-1 50Pt-TOH-HR-HTA, (d) 1-1-2 50Pt-AN, (e) 1-2-2 50Pt-AN-HR, (f) 1-3-2 50Pt-AN-HR-HTA. Scale bars: 10 nm.



**Figure 2.** Light-off curves for CO oxidation of  $\text{TiO}_2$  nano-array supported Pt catalysts (a) 50Pt-TOH series and (b) 50Pt-AN series. (c) Summary of the transition temperatures of all the samples.