

## Na Promoted Pt/TiO<sub>2</sub>: a Novel Single Stage Water Gas Shift Catalyst

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### Introduction

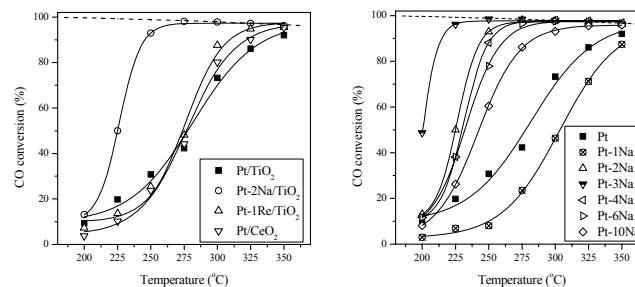
The water gas shift (WGS) reaction is a crucial step to remove CO and produce additional H<sub>2</sub> from synthesis gas obtained from reforming of hydrocarbon or oxygenated hydrocarbon fuels. Because the industrial Cu based catalyst is pyrophoric and needs a very careful activation process, it cannot easily meet the requirements for onboard hydrogen production for polymer electrolyte fuel cells. Therefore, noble metal based catalysts, especially Pt based catalysts, have received much attention for this application. Extensive studies have focused on the highly active Pt/CeO<sub>2</sub> catalyst for the reaction mechanisms: associate mechanism or redox (regenerate) mechanism [1,2]. In both reaction mechanisms, CO is adsorbed on Pt particles and H<sub>2</sub>O is activated on the support. Thus both the supported metal and support play important roles in the activity and stability of the catalyst for WGS. However, deactivation of the Pt/CeO<sub>2</sub> catalyst under working conditions (both long time on stream at certain temperatures and shutdown-startup cycles) is usually observed. Deactivation due to over-reduction of the CeO<sub>2</sub> support, surface carbonate (stable up to 430 °C) and/or formate formation as well as Pt sintering have been suggested [3,4]. Note that both over-reduction of CeO<sub>2</sub> and the consequent formation of surface carbonate (and possibly cerium (III) hydrocarbonate [5]) are related to the intrinsic properties of the high reducibility of nano-sized CeO<sub>2</sub> particles in the presence of noble metal. This presents a difficult problem because it is determined by the support properties. Some efforts have been made to overcome this problem: addition of small amounts of O<sub>2</sub> to the feed to inhibit the formation of surface carbonate [5] and addition of ZrO<sub>2</sub> to CeO<sub>2</sub> to improve the support properties. Some less reducible supports, such as TiO<sub>2</sub> and ZrO<sub>2</sub>, are possible alternatives to CeO<sub>2</sub>. Recently, addition of alkali metals to Pt/ZrO<sub>2</sub> and Pt/CeO<sub>2</sub> that were prepared by a sequential impregnation method, has been reported to improve the activity for WGS. In this work, we showed that Pt/TiO<sub>2</sub> catalyst activity and stability for WGS can be improved significantly by Na addition, which was prepared by a co-impregnation method. It is shown that the Alkali promoted TiO<sub>2</sub> catalyst is a promising single stage WGS catalyst.

### Materials and Methods

The Na promoted Pt/TiO<sub>2</sub> catalysts were prepared by a co-impregnation method using H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O (Aldrich) and NaNO<sub>3</sub> (Aldrich) with TiO<sub>2</sub> (Degussa P25). The Pt loading is fixed at 1 wt%, the Na loading was varied from 1 to 10 wt%. The samples were dried at 110 °C for 12 h and calcined at 400 °C for 4 h. The well studied catalysts Pt/CeO<sub>2</sub> [6] and 1 wt%Pt-1 wt%Re/TiO<sub>2</sub> [7] were prepared and included for comparison. The catalytic performance was tested in a quartz reactor after reduction at 300 °C for 1 h. The feed gas composition is 70% H<sub>2</sub> and 30% CO (dry basis) with a H<sub>2</sub>O:CO ratio of 5:1. The GHSV is 1.5×10<sup>4</sup> cm<sup>3</sup>/g-h.

### Results and Discussion

Pt/TiO<sub>2</sub> shows a similar activity as the Pt/CeO<sub>2</sub> catalyst. Addition of Re to Pt/TiO<sub>2</sub> improves the high temperature WGS activity (>275 °C) and also improves the stability of Pt/TiO<sub>2</sub> catalyst. A significant improvement was achieved when Na was added to the Pt/TiO<sub>2</sub> catalyst, with the best activity achieved with a Na loading of 3%. Stability tests showed Pt-3Na/TiO<sub>2</sub> was stable in operation at high conversion conditions, with concomitant CO<sub>2</sub> product accumulation. TEM results show that Na addition inhibits Pt sintering.



**Figure 1.** Effect of support and promoter on the WGS activity (left) and effect of Na loading on the Pt/TiO<sub>2</sub> activity for WGS (right).

### Significance

A significant improvement in activity and stability was achieved by addition of Na with using a simple co-impregnation method. This catalyst is capable of reducing CO from 30 to 0.5% (dry) at a very high space velocity 3×10<sup>4</sup> cm<sup>3</sup>/g-h. This system is a promising single stage WGS catalyst.

### References

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