

Operating characteristics for two precious metal monolithic water gas shift catalysts for hydrogen generation

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Introduction

Hydrogen production is achieved on a large scale through steam methane reforming, followed by the water gas shift and final gas clean-up by either pressure-swing absorption (PSA) or methanation reaction [1]. In the small scale production of hydrogen for fuel cell applications, hydrogen filling stations or industrial hydrogen use, new catalyst technology and process engineering solutions have been developed for these “scaled down” hydrogen plants.

Precious metal monolithic catalysts are often the catalysts of choice because of beneficial properties in these applications. These include fast start-up and fast response to transients, stability to start-stop conditions and water condensation and possibly the tolerance of the catalysts to poisons like sulfur.

Many of these desired properties are known from automotive exhaust purification (i.e. TWC catalysts) but cannot be taken for granted under the very different operating conditions and catalyst compositions used in fuel processing. Here we present data on two precious metal water gas shift catalysts with very different composition and resulting characteristics. The catalysts differ in their preferred operating window, sulfur sensitivity, methanation rate as well as start-stop stability.

Materials and Methods

Pt-Na and Pt-Re containing- catalysts were prepared according to proprietary methods. Both catalysts have precious metal contents of 7-8 g/liter monolith and are supported on cordierite monolith substrates with 62 cells/cm². In general, washcoat powder is coated onto the monolith substrate until the desired loading is achieved. Alternatively, the washcoat powder was measured separately, with “monolith equivalent” space velocities being reported.

The catalysts were measured in tubular quartz reactors by being heated in nitrogen gas to ~110-150 °C to avoid water condensation. Reformate gas containing 9.8% CO, 7.7% CO₂, 52.5% H₂ and 30% H₂O (14% CO in dry gas) was then admitted and the temperature ramped as described in the figures.

Results and Discussion

Significant differences between Pt-Re and Pt-Na catalysts are seen in several areas of operation of the catalysts in hydrogen generation applications.[2] One such difference is seen if the catalysts are exposed to reformate streams containing various amounts of H₂S. The activity of a base metal promoted Pt-Re catalyst is shown in the left panel of figure 1. The activity decreases (CO outlet concentration increases) sharply when sulfur H₂S is contained in

the feed gas. The amount of activity remaining after prolonged exposure is less than 10% of the original even for H₂S concentrations as low as 0.1 ppm. The activity (characterized as the temperature of 50% CO conversion T₅₀) of a Pt-Na catalyst is shown on the right side. The catalyst initially loses activity (increasing T₅₀) as a result of thermal aging. With increasing sulfur content, little activity is lost. After the sulfur is removed from the reformate, the original activity is re-gained.

The difference in composition between the two samples obviously results in a stark difference in sensitivity to sulfur, leading to different requirements for the reformate. Other differences include the thermal stability and methanation rate of the catalysts. These differences have to be determined and can lead to catalyst recommendations tailored to strengths and weaknesses of each catalyst.

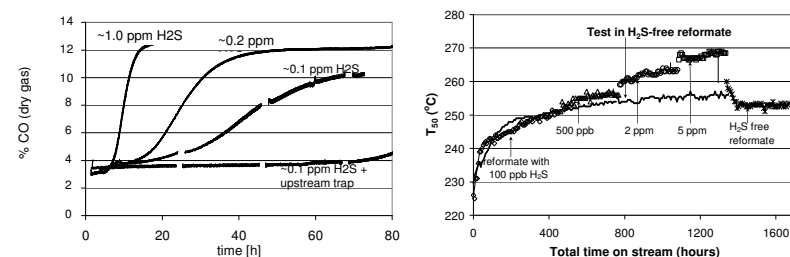


Figure 1. Water gas shift activity of Pt-Re (left) and Pt-Na catalyst (right) in the presence of H₂S. Left panel: conditions are T_{inlet} = 350 °C isothermal and VHSV=30,000h⁻¹; right panel: VHSV = 30,000 h⁻¹ and T_{inlet}=350 °C; T(50) was measured by running a temperature ramp from 200-350 °C at 3 °C/min.

Significance

The operating parameters of WGS catalysts in hydrogen generating applications have to be determined individually and cannot be assumed to be universal, even though materials may be similar. Our experience shows that a careful inspection of the operating conditions is necessary to make the correct catalyst recommendation.

References

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2. Farrauto, R. J.; Liu, Y.; Ruettinger, W.; Ilinich, O.; Shore, L.; Giroux, T., Catal. Rev. **2007**, 49, (2), accepted for publication.