Activity and Stability of Sulfuric Acid Decomposition Catalysts for Thermochemical Water Splitting Cycles

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ABSTRACT

Thermochemical cycles produce hydrogen through a series of chemical reactions where the net result is the production of hydrogen and oxygen from water at much lower temperatures than from direct thermal decomposition. The sulfur-based family of thermochemical cycles appears to have significant technical viability for producing hydrogen. The sulfur-based cycles employ a high-temperature catalytic sulfuric acid decomposition reaction step. The reaction produces oxygen and generates SO_2, which is used in other reaction steps of the cycle. The reaction takes place from 750 to 900 °C, or higher, and is facilitated by a heterogeneous catalyst.

In this work, we explored the activity and stability of supported platinum catalysts for the decomposition of sulfuric acid. Supports studied were TiO_2 and α-Al_2O_3 with platinum loadings of 0.1 and 1.0 wt%. Tests were conducted at 800 and 850 °C for typical reaction times of 24 hours. The Pt/TiO_2 catalysts appeared to have the greatest stability and platinum loadings of 1 wt% provided the highest product yields. Although relatively stable, the Pt/TiO_2 catalyst did not display long term stability and preliminary results suggest that the catalyst is not stable at temperatures at and above 850 °C.

INTRODUCTION

Thermochemical cycles produce hydrogen through a series of chemical reactions where the net result is the production of hydrogen and oxygen from water at much lower temperatures than from direct thermal decomposition. All chemicals within the cycle are fully recycled and the heat to drive the reactions, which tend to be endothermic, must be provided by a primary energy source. When the primary energy driver is nuclear or solar heat, hydrogen can be generated without producing green-house gasses, and can provide independence from our dwindling supplies of fossil fuels.

The sulfur-based family of thermochemical cycles appears to have significant technical viability for producing hydrogen [1]. All of the sulfur-based thermochemical cycles, including the Sulfur-Iodine cycle [2], the Hybrid Sulfur cycle [3], and the Sulfur-Bromine Hybrid cycle [4], incorporate the sulfuric acid decomposition reaction as the high temperature step in their cycles. This reaction decomposes sulfuric acid to oxygen, steam, and sulfur dioxide. The production of oxygen represents half of the water splitting reaction and is a product from the cycle. The generated steam and SO_2 are recycled to the processes and are used in the other reaction steps to complete the water splitting reaction to produce hydrogen.

The sulfuric acid decomposition reaction takes place at temperatures between 750 and 900 °C, or higher, and is catalyzed by a heterogeneous metal oxide or precious metal catalyst. This reaction is the highest temperature unit operation in the thermochemical hydrogen production process and dictates the temperature requirements of the primary energy source. Due to thermodynamic limits, high temperatures for the sulfuric acid reaction are necessary to achieve high levels of chemical conversion, and hence energy efficiency.

The sulfuric acid decomposition reaction takes place in two steps, a non-catalytic thermal decomposition of the acid to form gaseous SO_3 and H_2O at temperatures above 350 °C, followed by a catalytic decomposition of the SO_3 to produce the SO_2 and O_2 products. At feasible operating temperatures, between 750 and 900 °C, the reduction of SO_3 does not take place without a catalyst.

Catalysts for sulfuric acid decomposition were explored during the 1970s and 1980s [5-10]. Activities of over 30 catalysts have been reported. However, the majority of these studies examined catalyst behavior under ideal conditions, including very dilute acid solutions, excess catalyst, low space velocities and short experimental times [5-9]. Those studies found that there were few highly active catalysts. Most metal oxides had low activity due to the formation of sulfates on the catalysts [6-9]. The formation of sulfates was more significant at lower reaction temperatures and was predicted to be problematic as reaction pressure increased to anticipated operating values [8,9]. In addition, catalysts were found to fail due to formation of volatile acid salts [7], support poisoning [7], and catalyst attrition [10]. Although a few catalysts appeared promising under ideal conditions, primarily platinum supported on porous metal oxides, their long-term stability had not been reported. Catalyst stability is an important consideration since the decomposition reaction environment is extremely harsh where catalysts are exposed to conditions of high-temperatures and aggressive chemicals, including high-temperature steam, oxygen, SO_3, and SO_2.

Since the Pt based catalysts were previously reported as the most promising, this effort focused on platinum/metal oxide supported materials and examined their catalytic activity and stability. Previously, we reported on catalysts comprised of low weight fractions of platinum supported on high, medium, and low surface area supports [11]. Platinum loadings were between 0.1 and 0.2 weight percent. Supports explored were γ-Al_2O_3, ZrO_2, and TiO_2 with surface areas of 180, 51 and 2 m^2/g, respectively. In that work, it was found that initial conversions increased with support surface area, but only the low surface area catalyst was stable over short duration testing. The higher surface area supports lost activity primarily due to support structure collapse in the aggressive reaction environment.

In this contribution, we continue the exploration of platinum catalysts. Low surface area supports were studied since they appeared likely to be stable at reaction conditions. Platinum loadings explored were 0.1 and 1.0 wt%. Supports studied were TiO_2 and α-Al_2O_3. Both supports are considered to be stable at high temperatures and to be acid resistant. Tests were conducted at 800 and 850 °C for typical reaction times of 24 hours.

EXPERIMENTAL METHODS

A high-temperature continuous flow catalyst test system was used to examine the catalytic reaction in flowing, concentrated sulfuric acid at atmospheric pressure. The system was built of Teflon tubing and glass and employs a high-temperature quartz reactor. The system includes two top loading balances for sulfuric acid feed and collection mass balance, a pulse-free peristaltic feed pump, a mass flow controlled reference gas stream, and a gas chromatograph (GC) for product quantification.

In the test system, concentrated sulfuric is pumped into a heated zone where the acid vaporizes and decomposes to SO_3 and steam. Generated vapors flow over a bed of catalyst for the reduction of SO_3 to produce SO_2 and oxygen. Any unreacted SO_3 exiting the reactor recombines with H_2O to form sulfuric acid which is condensed and collected. The remaining gasses combine with a reference gas stream which together flow through a GC sample valve and are then vented to a hood. The system is protected from overpressure via two pressure relief valves, one prior to the entrance of the reactor and a second in the product collection section.

Product concentrations of SO_2 and O_2 are determined approximately every 20 minutes by GC analysis of the reactor effluent gas. Product rates were determined from measured concentrations and known reference gas mass flow rate.

Reaction took place in a single piece, high-temperature quartz reactor housed inside a Lindberg Blue M tube furnace. The inlet section, where preheat, vaporization, and SO_3 generation takes place, has an inside diameter of 4 mm, an outside diameter of 6 mm, and had approximately 30 cm of tube in the heated furnace. The SO_3 decomposition section, with approximately 30 cm in the heated zone, had an inside diameter of 10 mm and an outside diameter of 12 mm. The initial 10 to 12 cm of the decomposition section was packed with den stones which aided temperature stabilization. The catalyst sample was packed inside the decomposition section starting at about 15 cm downstream of the inlet section and was held in place with plugs of quartz wool. Gas temperatures exiting the catalyst bed were measured using a type K thermocouple that was sheathed inside a quartz tube that was sealed from the reaction environment.

Catalyst testing focused on platinum on low surface area supports. Platinum loadings explored were 0.1 and 1.0 wt%. Supports studied were TiO_2 and α-Al_2O_3. Tests were conducted at 800 and 850 °C for typical reaction times of 24 hours. Both catalysts were tested as 2 to 4 mm pellets and were reduced in hydrogen prior to testing. Liquid sulfuric acid at 95 to 96 wt% was pumped into the catalytic reactor at 52 g/hr. One gram of catalyst was loaded into the reactor resulting in a weight hour space velocity (WHSV) of 52 hr^{-1}. Catalyst activity was monitored with time on stream (TOS) and catalyst properties were examined *ex situ* following the reaction study.

BET surface areas were determined by krypton physisorption using an automated Quantachrome Autosorb-1C system. Fresh and spent samples were outgassed at 300 °C for 3 hours before the physisorption measurements. Prior to outgassing, the fresh catalyst samples were heated in-situ under flowing helium from room temperature to 800 °C in 2 hours to resemble the initial pretreatment conditions of the samples submitted to reaction. B.E.T. surface areas were calculated in the range of P/Po between 0.05 and 0.35.

XPS spectra were recorded using an Perkin-Elmer 5600 LS instrument fitted with a hemispeherical analyzer (HSA) operated in fixed analyzer transmission (FAT) mode. X-irradiation of the catalysis specimens used either the Mg K-alpha (1253.6 eV) or Al K-alpha (1486.6 eV) lines from a dual anode X-ray source, operated at 15 kV and a power of 300 W. The spheroid samples were fixed to the multi-sample platen using Cu-tape (SPI, West Chester, PA). The mounted specimens were introduced to an introduction chamber where they were pumped overnight to a base pressure of $< 3 \times 10^{-7}$ Torr to reduce outgassing in the main analysis chamber. The main anaylisis chamber was maintained at a base pressure of < 5 x 10^{-10} Torr.

RESULTS

The time dependent decomposition of sulfuric acid over Pt/TiO_2 catalysts to produce SO_2 is shown in Figure 1. Catalytic activity was relatively stable over 24 hours for both platinum loadings and at both temperatures. Higher temperatures and higher platinum loadings resulted in improved reaction rates. Without platinum, the TiO_2 support had little catalytic activity.

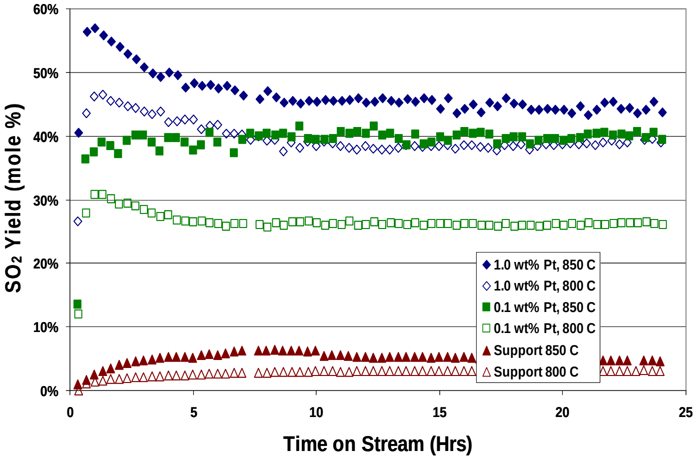

Figure 1: Production of SO_2 over Pt/TiO_2 catalysts at 800 and 850 °C.

Catalytic activity of Pt/α-Al_2O_3 catalysts is shown in Figure 2. Conversions over the alumina based catalysts were generally lower than the titania based catalyst. The alpha alumina catalyst was not as stable as the titania catalyst for the test duration of 24 hours. Similar to the Pt/TiO_2 catalysts, increased platinum content improved reaction rate. However, in contrast to Pt/TiO_2, increased temperature did not improve activity for the Pt/α-Al_2O_3 catalysts. In the absence of platinum metal, the support facilitated almost no production of SO_2.

A comparison between the reaction rate results suggests that the Pt/TiO_2 catalysts are preferred and have the potential to provide high activity and stability for long term operation. To examine this potential, a 10 day test was performed at 850 °C using the 0.1 wt% Pt/TiO_2 catalyst. The higher temperature was chosen since it would place more stress on the catalyst. The lower platinum loading was examined since it would provide a more sensitive response to the reaction environment.

Results for the ten day trial are presented in Figure 3. Over the first two days of operation, SO_2 yield appeared to be stable at approximately 35%, about 5 % lower than the 24 hour stable yield shown in Figure 1, but within the expected experimental error range. After about 60 hours of operation; however, the catalyst displayed a linear loss of activity, losing about 30% of its initial activity, on a

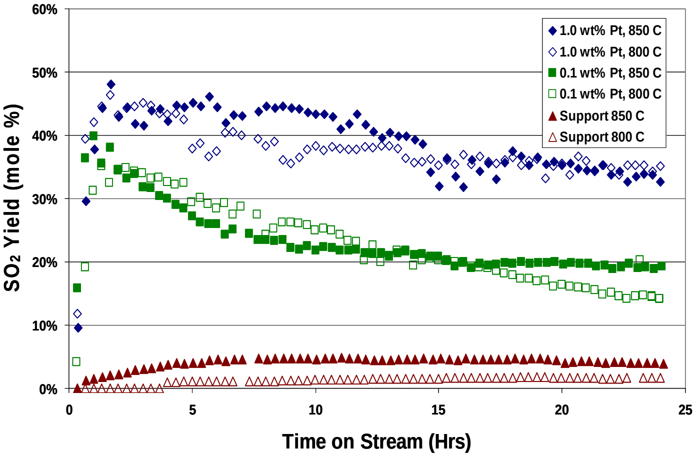

Figure 2: Production of SO_2 over Pt/αAl2O3 catalysts at 800 and 850 °C.

relative scale, over the ten day run.

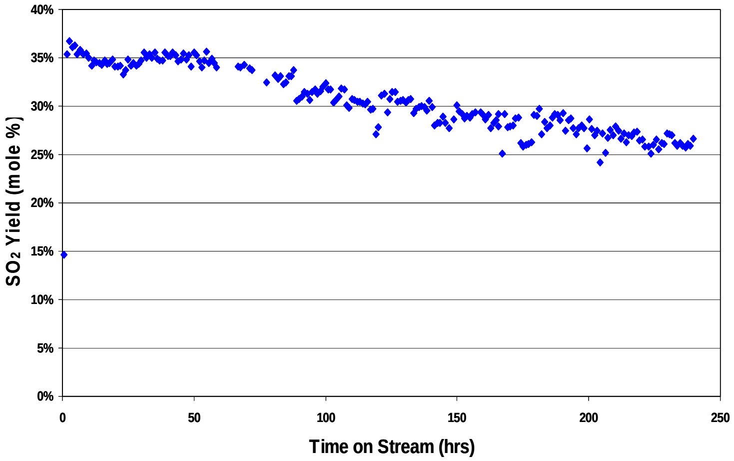

Figure 3: Production of SO_2 over 0.1wt% Pt/TiO_2 at 850 °C.

The ten day test demonstrated that this catalyst is not stable for long term use at the reaction conditions. In order to develop a stable catalyst, it is necessary to understand the processes that led to deactivation.

Several analyses of the catalyst following exposure to reaction conditions were performed in order to help develop this understanding. Elemental analyses were performed to determine spent catalyst sulfur and platinum levels. Changes in support surface area were examined by krypton physisorption. X-ray photoelectron spectroscopy (XPS) was employed to examine changes in surface composition and oxidation state of elements.

Following 24 hours of exposure to reaction conditions, platinum quantities were found to be relatively consistent with fresh levels for both supports at both platinum loadings. Thus, deactivation observed for the Pt/α-Al_2O_3 catalysts was not the result of platinum loss. However, after 240 hours of reaction, the 0.1 wt% Pt/TiO_2 catalyst appeared to have lost about 30% of its initial amount of catalytic metal. This loss of platinum correlates linearly with the observed loss in activity over the ten day experiment.

Surface area analysis by krypton physisorption was employed to measure the BET surface areas of the supported catalysts. Preliminary results suggest that both the TiO_2 and α-Al_2O_3 based catalysts lost surface area following 24 hours of exposure to reaction conditions. However, the fractional loss of initial catalyst surface was significantly less than for the high surface area Pt/γ-Al_2O_3 and Pt/ZrO_2 catalyst studied previously.

XPS analyses of the supported platinum catalysts were carried out to understand the effect of high-temperature and the reaction environment on surface composition and oxidation states of platinum and sulfur. For both supports and both platinum loadings, fresh catalyst surface platinum levels were higher than bulk levels indicating that Pt was concentrated on the pellet outer surface. Platinum on the samples exposed only to high temperatures was present as Pt^0 species and displayed an increased degree of sintering with higher temperatures. TiO_2 supports without Pt that were contacted with sulfuric acid environments at high temperature showed the presence of sulfur-containing (i.e., SO_3 and/or $SO_4^=$) species on the surface. The surface S/Ti ratios were around 0.22. Samples of 0.1% Pt on TiO_2 submitted to sulfuric acid reaction environments showed negligible amount of surface Pt, all of which was in an oxidized state. The surface S/Ti ratios ranged between 0.5 and 1.0 and increased with reaction temperature. Samples of 1% Pt/TiO_2 did show Pt species on their surface although the concentration was lower than on the heat-treated only samples. Although most Pt on the surface was revealed as Pt^0, the presence of oxidized Pt could not be ruled out completely. Sulfur on 1% Pt/TiO_2 samples was mostly present as SO_3-like species and surface S/Ti ratios were about 0.6.

Alumina supports that did not contain platinum but that did contact sulfuric acid reaction environments showed the presence of sulfate-like species mostly on the outer surface. The concentration of sulfur species on the surface increased with reaction temperature and the S/Al ratio was 0.13 or lower. Samples of 0.1% Pt/Al_2O_3 submitted to reaction conditions showed an absence of surface Pt on light colored spots and oxidized Pt (Pt^{2+}) on darker spots. These dark spots also showed increased concentration of S as either SO_3 or $SO_4^=$ species. S/Al ratios were slightly higher than on the blank samples without Pt. Samples of 1% Pt/Al_2O_3 submitted to reaction conditions showed very small amount of surface Pt, which was present as Pt^{2+}. Deeper catalyst layers also showed oxidized Pt. Sulfur as both SO_3 or $SO_4^=$ species was concentrated on the outer surface and surface S/Al ratios reached values as high as 4.9.

For all supported samples, sulfur containing species concentrated on the outer surface. Catalysts contacting the reaction environment that contained platinum had increased amounts of sulfur oxide species than support materials. For both the TiO_2 and Al_2O_3 supported catalysts, high-temperatures caused sintering of the catalytically active metal. Sintering reduces the amount of surface metal available to catalyze the reaction. More importantly, however, exposure to the sulfuric acid decomposition reaction caused a significant reduction in the amount of surface platinum. Both supports containing 0.1 % Pt had almost no measurable platinum following 24 hours of reaction at either temperature. The catalysts containing 1 % Pt did exhibit measurable levels after reaction. Platinum was present in higher concentrations on titania and existing in the metallic state.

In addition to post reaction catalyst property analysis, a few preliminary high temperature experiments were performed with the Pt/TiO_2 catalysts. At 900 °C, both the 0.1 and 1.0 wt% platinum catalysts lost activity rapidly. Additionally, preliminary experiments were conducted at 850 °C with crushed Pt/TiO_2 catalysts. Due to the endothermic nature of the reaction and inter-particle heat-transfer limitation, the overall temperature in the powdered catalyst will be higher than for the catalyst pellet. The powdered catalyst was also observed to deactivate significantly. Although additional work is still required, these preliminary studies suggest that the Pt/TiO_2 catalysts are not stable for high temperature operation, but may well be suited for reaction temperatures lower than 850 °C.

CONCLUSION

The Pt/TiO_2 catalysts appeared to have the greatest stability and platinum loadings of 1 wt% provided the highest product yields. Although relatively stable, the Pt/TiO_2 catalyst did not display long term stability and preliminary results suggest that the catalyst is not stable at temperatures at and above 850 °C. This catalyst may be appropriate for the sulfuric acid decomposition reaction where temperatures are limited to 800 °C. Future efforts should explore methods to provide high temperature stabilization of the platinum on this support and explore other catalysts with the potential to be stable at high temperatures.

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