

Platinum Group Metal Catalysts for Sulfur-Based Thermochemical Water Splitting Cycles

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ABSTRACT

Thermochemical cycles can be used to split water through a series of chemical reactions where the net result is the production of hydrogen and oxygen at much lower temperatures than direct thermal decomposition. The sulfur-based family of thermochemical cycles appears promising for producing hydrogen from water. These cycles employ a high-temperature sulfuric acid decomposition reaction step. The reaction produces oxygen and generates SO₂, which is used in other reaction steps of the cycles. The reaction takes place from 750 to 900°C, or higher, and is facilitated by heterogeneous catalysts. The high-temperature, harsh chemical reaction conditions present a significantly challenging environment for catalytic materials. Current catalyst stability studies performed at the Idaho National Laboratory (INL) have found that the most active catalysts for the acid decomposition reaction, platinum supported on porous metal oxides, are not stable at the desired reaction temperatures. In this work we explore the effect of other platinum group metals, including Pd, Rh, and Ru, on the stability of precious metal catalysts.

SULFURIC ACID DECOMPOSITION CATALYST STUDIES

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 highest temperature step. 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 SO₂ 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 reduction of the SO_3 to SO_2 with O_2 as a by-products. 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, the INL 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 $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 , and TiO_2 with surface areas of 180, 51 and $2\text{ m}^2/\text{g}$, 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. Additional studies examined platinum supported on SiO_2 and $\alpha\text{-Al}_2\text{O}_3$. Of the supports examined, it was found that the TiO_2 support provided the most stable platform for the platinum catalyst [12].

Further studies of the Pt/ TiO_2 catalyst found that although the catalyst was relatively stable for 24 hours under reaction conditions at 850°C and a weight hourly space velocity (WHSV) of 50 g acid/g cat./hr, explorations run for 10 and 23 days demonstrated that the catalysts deactivated due to platinum sintering, oxidation, and volatilization.

In this work we explore the effect of other platinum group metals, including Pd, Rh, and Ru, on the stability of precious metal catalysts supported on TiO_2 . Accelerated aging tests were conducted at 850°C for typical reaction times of 7 days at WHSVs up to 2000 hr^{-1} .

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 acid 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.

Catalyst testing focused on metals supported on TiO_2 in the rutile phase. Tests were conducted at and 850°C for typical reaction times of 168 hours (7 days). Liquid sulfuric acid at 95 to 96 wt% was pumped into the catalytic reactor at 24 g/hr. As little as 12 mg of catalyst was loaded into the reactor resulting in a weight hour space velocity (WHSV) of up to 2000 hr^{-1} . Catalyst activity was monitored with time on stream (TOS) and catalyst properties were examined *ex situ* following the reaction study.

The time dependent decomposition of sulfuric acid over a 1%Pt/ TiO_2 catalyst to produce SO_2 is shown in Figure 1. Reaction conditions for this test were 850°C and a WHSV of approximately 2000 hr^{-1} . Catalytic activity declined rapidly over the course of the experiment. SO_2 yield declined by an order of magnitude from an initial production rate of 7.3 mol/hr/g cat. to less than 0.6 mol/hr/g cat. Examination of the 1% Pt/ TiO_2 catalyst run under similar reaction conditions suggests that the primary deactivation process observed here is sintering of the active metal. Due to this rapid deactivation, future studies will be performed to ascertain the activity and stability of Pd, Pt/Pd, Pt/Rh, and Pt/Ru catalysts.

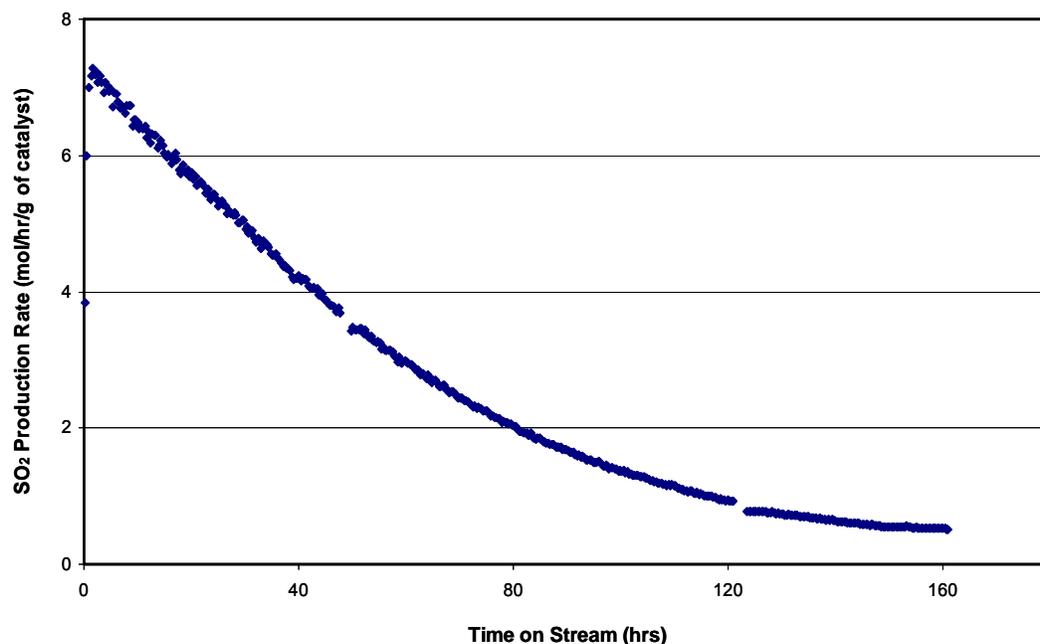


Figure 1: Transient SO_2 production rate over a 1% Pt/ TiO_2 catalyst at 850°C and a WHSV of 2000 hr^{-1} .

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