Platinum Group Metal Catalysts for Hydrogen Production via the Sulfur Based Thermochemical Water Splitting Cycles

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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 [1]. All chemicals within the cycle are recycled and the heat to drive the reactions must be provided by a primary energy source.

Among the high number of thermochemical water-splitting cycles proposed in the literature, the sulfur-based cycles, including the Sulfur-Iodine and the Hybrid Sulfur cycles [2] have generated considerable interest. The sulfur based cycles employ the sulfuric acid decomposition reaction to produce oxygen and generate SO_2 for recycle to the other reactions in the cycle.

Although platinum supported on titania has been identified as a highly active sulfuric acid decomposition catalyst [3], deactivation appears to be problematic [4]. In this presentation we will discuss the effect of adding higher melting point platinum group metals (PGMs) to improve catalyst stability.

Materials and Methods

Activity measurements were performed on 1% platinum supported on titania (rutile) catalysts prepared with the addition of either zero, or 0.3% Ru, Rh, or Ir. The experimental setup consisted of a high-temperature, continuous-flow testing system built of Teflon tubing, glass, and quartz. The catalyst sample was loaded in a quartz tube reactor and reduced with hydrogen at 473 K for 2 h. The temperature was increased to 1123 K and then concentrated sulfuric acid was pumped into the system where the acid vaporized, thermally decomposed to SO_3 and H_2O, and the SO_3 reduced to SO_2 and O_2 over the catalyst bed. The unreacted SO_3 recombined with H_2O in the colder sections downstream of the reactor and was collected as a solution. The gaseous SO_2 and O_2 products were analyzed by gas chromatography. Spent catalyst samples were recovered and submitted to post-operation analyses including scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), elemental analysis, and diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS).

Results and Discussion

In the absence of an added PGM, Pt/TiO_2 deactivated in the reaction environment, displaying an order of magnitude loss in SO_2 production rate during one week of continuous operation. Analysis by electron microscopy determined that platinum sites sinterized as seen in Figure 1. DRIFTS analysis of chemisorbed carbon monoxide revealed that the platinum also became oxidized with time on stream (Figure 2).

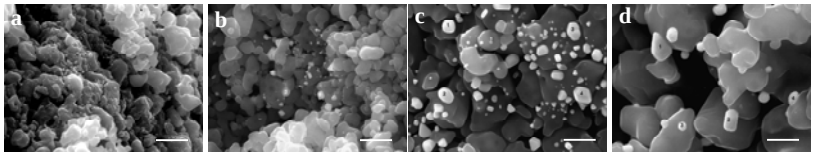

Figure 1. SEM images of Pt/TiO_2 after exposure to the reaction environment for a) 0 hrs, b) 24 hrs, c) 66 hrs, and d) 548 hrs. Scale bars equals 1 µm. Numbered regions identified as Pt [4].

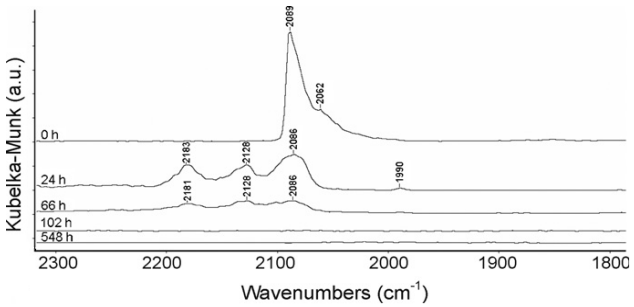

Figure 2. DRIFTS spectra of adsorbed CO for reaction times of: 0 h, 24 h, 66 h, 102 h, and 548 hrs [4].

When either Ru, Rh, or Ir was added to the 1% $PtTiO_2$ catalyst, deactivation rates decreased by a factor of three and reaction rates at the end of one week testing were improved by up to four fold. Month-long testing and post-operation sample analyses are currently in progress.

Significance

The production of hydrogen via water splitting cycles where the primary energy driver is nuclear or solar heat can reduce greenhouse gas emissions and provide independence from our dwindling supplies of fossil fuels. For the sulfur based thermochemical cycles to be viable, a highly active, stable sulfuric acid decomposition catalyst must be developed.

References

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