Hydrogen Pulsing as a Measure of Chemical Activity of ASC Whetlerite

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Introduction

ASC whetlerite is a high surface area (650 m^2/g) charcoal that has been impregnated with copper, chromium, and silver salts. Whetlerite has proven effective in air purification, having a large adsorption capacity for many toxic vapors. In addition, it will destroy many low molecular weight toxic gases (e.g., CNCl). It is unclear whether whetlerite acts catalytically, as a reactant, or a combination of both. In any case, it is known that as the Cr^{+6}/Cr^{+3} ratio drops so does the chemical activity of the ASC whetlerite. The objective of the current investigation was to determine a nondestructive method by which both the loss in ASC whetlerite chemical activity could be quantified and the deactivation process elucidated.

Experimental

All experiments were performed in a Sigma I gas chromatograph (Figure 1). A nitrogen carrier gas was fed dry or, if desired, saturated with water. The water content of the stream was determined using hygrometers. ASC whetlerite was packed into 20 cm x 0.508 cm stainless steel tubes which were then placed in the chromatograph oven. A van-Deemter analysis indicated a carrier gas flowrate of between 10-20 ml/min (NTP) should be optimum. A value of 10 ml/min (NTP) was generally used. The ASC whetlerite was analyzed by both magnetic susceptibility measurements and wet-chemistry techniques for change in copper and chromium oxidation states. When using the wet-chemistry analysis, atomic adsorption spectrophotometry was used to quantify the amounts of Cr^{+6}, Cr^{+3}, Cu^{+2}, and $Cu^{+1,0}$ in extracted solutions of ASC whetlerite.

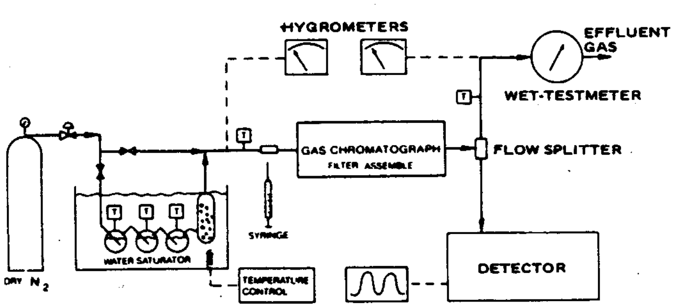

Figure 1. Schematic of test apparatus.

Results and Discussion

The experimental results can be divided into two categories. An initial set of experiments was performed to try and simulate the deactivation process. These experiments were primarily performed to see if one could artificially and systematically change the copper and/or chromium oxidation state. Figures 2 and 3 represent typical experiments. In Figure 2 the Cr^{+6}/Cr^{+3} ratio is

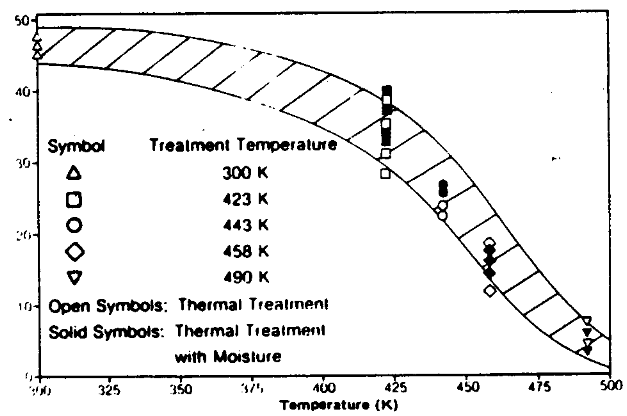

Figure 2. Effect of thermal treatment on Cr^{+6}/Cr^{+3}.

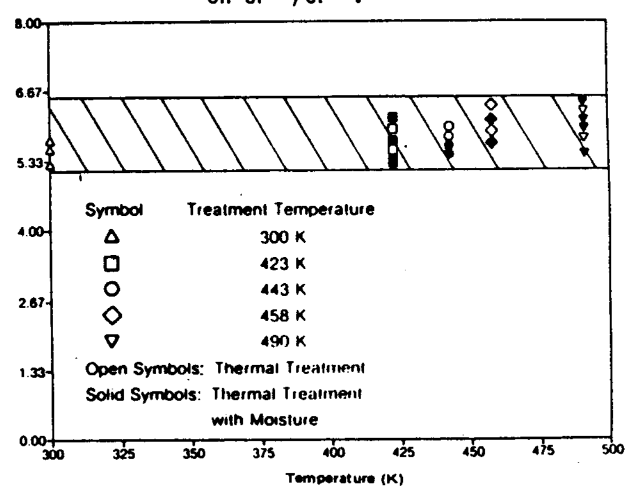

Figure 3. Effect of thermal treatment on $Cu^{+2}/Cu^{+1,0}$ ratio.

plotted versus treatment temperature. Each packed column was held at the indicated temperature for 6 hours. As indicated, whether the carrier gas was dry or wet, the Cr^{+6}/Cr^{+3} ratio decreased as the treatment temperature increased. Figure 3 is a similar plot for the $Cu^{+2}/Cu^{+1,0}$ ratio. As shown in Figure 3, for copper there was no apparent effect of treatment temperature on the copper oxidation state from that of "fresh whetlerite". These results together with a literature survey suggest that small quantities of hydrogen may be used to quantify changes in the Cr^{+6}/Cr^{+3} ratio on ASC whetlerite.

Figure 4 illustrates the results of injecting 0.1 ml (NTP) hydrogen pulses at room temperature (303 K) into pretreated (heated) ASC whetlerite packed columns. In Figure 4 the eluted areas of hydrogen are plotted versus pulse number with the pretreatment temperature as a parameter. As indicated, after the initial uptake of hydrogen, the amount of hydrogen eluted was found to reach a "steady state". Since the Cr^{+6}/Cr^{+3} ratio also changes with pretreatment temperature, it is possible to use small pulses of hydrogen to determine directly the Cr^{+6}/Cr^{+3} ratio. This idea is graphically shown in Figure 5. In Figure 5 the percentage hydrogen consumed is defined as

$$\% \text{ consumed} = \frac{A_{nr} - A_f}{A_{nr}} \times 100$$

where A_{nr} is the area obtained from a 0.1 ml hydrogen pulse passing through an empty tube and A_f is the average of the final eight pulses (i.e., after the "steady state" is reached).

Conclusion

The use of small pulses of hydrogen can be used to determine the magnitude of the Cr^{+6}/Cr^{+3} ratio on ASC whetlerite. Since a drop in this ratio is associated with increased deactivation, hydrogen can be used to probe the surface of whetlerite to determine its degree of chemical deactivation.

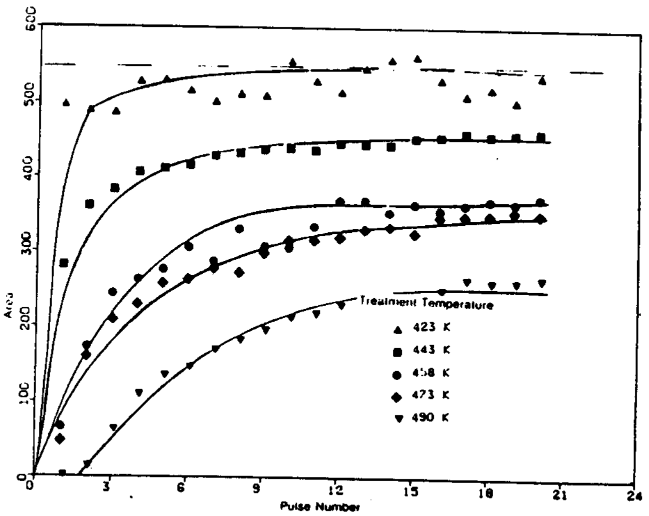

Figure 4. Gas chromatographic area response versus hydrogen pulse number.

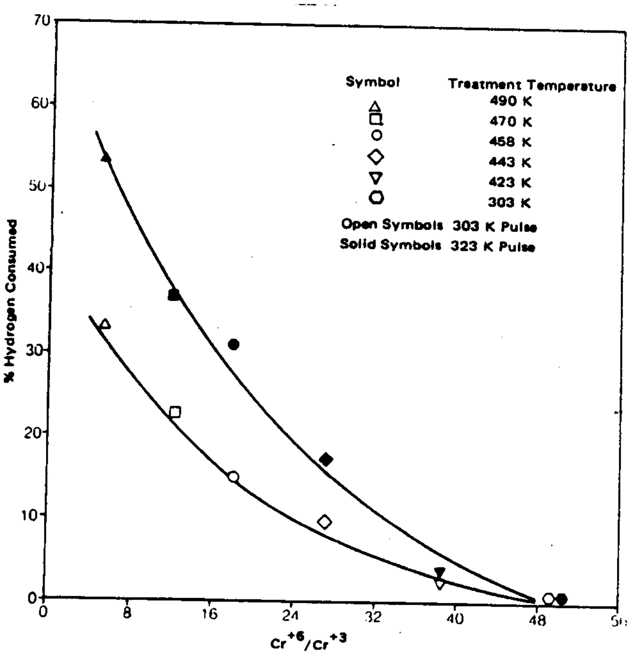

Figure 5. Percentage hydrogen consumed versus Cr^{+6}/Cr^{+3} ratio.