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CHARACTERIZATION OF THE SURFACES OF PLATINUM/TIN OXIDE BASED CATALYSTS BY FOURIER TRANSFORM SPECTROSCOPY (FTIR)

by

Joseph T. Keiser
Assistant Professor
Chemistry Department
University of Richmond
Richmond, VA 23173

The Laser Atmospheric Wind Sounder (LAWS) Program has as one of its goals the development of a satellite based carbon dioxide laser for making wind velocity measurements. The specifications for this laser include the requirement that the laser operate at a repetition rate of 10 Hertz continuously for three years. This technology does not currently exist. Earth-based carbon dioxide lasers can operate for only a short time on a single charge of gas because the lasing action causes the CO_2 to break down to CO and O_2. Therefore, earth-based CO_2 lasers are generally operated in a "flow through" mode in which the spent gas is continually exhaused and fresh gas is continually added. For a satellite based system, however, a recirculator system is desired because it is not practical to send up extra tanks of CO_2. One of the projects in the Instrument Research Division of NASA, therefore, is to develop a catalyst which could enable a recirculating CO_2 laser to function continuously for three years.

In the development of a catalyst system there are many variables, such as the choice of the metal, the choice of the support, the weight ratio of the metal to the support, and the effect of the pretreatment conditions. Obviously, not all possible formulations can be tested for three years. In fact, it is unlikely that <u>any</u> formulation will be tested for a full three years. Therefore, an accurate model which is based on the reaction mechanism is needed.

The construction of a multistep reaction mechanism is similar to the construction of a jig saw puzzle. Different techniques each supply a piece of the puzzle and the researcher must put the pieces together. Transmission infrared spectroscopy has been shown to be very useful in supplying some of the information needed to elucidate reaction mechanisms. Some of the advantages of the infrared method are:

a) surfaces may be probed in-situ; i.e., while the gas is being passed over the surface and while the surface is being heated

b) chemical (not just atomic) information is supplied.

The main disadvantages of this approach is that infrared absorption spectroscopy is not as sensitive as the ultra high vacuum surface analytical techniques such as Auger or ESCA. Another disadvantage is that the exact assignment of the bands observed by infrared spectroscopy may be difficult.

This purpose of this work was to see what kind of information might be obtained about the NASA catalyst using infrared absorption spectroscopy. Approximately 200 infrared spectra of the prototype Pt/tin oxide catalyst and its precursor components under a variety of different conditions. The most significant observations are summarized below:

1. A number of impurity bands were observed in the catalyst starting materials. These may or may not have an effect on the catalyst activity but efforts are underway to further identify and track these species.
2. Significant amounts of water and hydroxyl groups were observed in the NASA catalyst under almost all of the conditions tested. This is particularly important to note because both of these species are included in the current version of the proposed mechanism.
3. CO chemisorbed onto platinum can be observed in-situ on the prototype NASA catalyst. The CO was observed to absorb in an an "atop" configuration and the saturation coverage was logarithmic versus the gas phase CO pressure. Also, the adsorption appeared to be an activated process since more CO adsorbed at higher temperatures. The absorbed CO could be pumped off at room temperature although sometimes this took a period of hours.
4. NASA researchers were particularly interested to see if carbonate or bicarbonate species could be detected. This is because these species are believed to be involved in the catalyst degradation mechanism. Although no direct observation of carbonate/bicarbonate was made, it was observed that when tin oxide samples which had been exposed to CO and CO_2 were heated in the presence of H_2, CO was predominantly released along with some CO_2 and water vapor.

In summary, this work has broken new ground by demonstrating the usefulness of the infrared approach for the specific catalyst of interest in the LAWS project. Currently several other NASA projects involving infrared spectroscopy have been initiated and these will be able to build on the results obtained by this project.