Two Catalysts for Selective Oxidation of Contaminant Gases

One oxidizes halocarbons and ammonia; the other oxidizes ammonia.

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Two catalysts for the selective oxidation of trace amounts of contaminant gases in air have been developed for use aboard the International Space Station. These catalysts might also be useful for reducing concentrations of fumes in terrestrial industrial facilities — especially facilities that use halocarbons as solvents, refrigerant liquids, and foaming agents, as well as facilities that generate or utilize ammonia.

The first catalyst is of the supported-precious-metal type. This catalyst is highly active for the oxidation of halocarbons, hydrocarbons, and oxygenates at low concentrations in air. This catalyst is more active for the oxidation of hydrocarbons and halocarbons than are competing catalysts developed in recent years. This catalyst completely converts these airborne contaminant gases to carbon dioxide, water, and mineral acids that can be easily removed from the air, and does not make any chlorine gas in the process. The catalyst is thermally stable and is not poisoned by chlorine or fluorine atoms produced on its surface during the destruction of a halocarbon. In addition, the catalyst can selectively oxidize ammonia to nitrogen at a temperature between 200 and 260 °C, without making nitrogen oxides, which are toxic. The temperature of 260 °C is higher than the operational temperature of any other precious-metal catalyst that can selectively oxidize ammonia.

The purpose of the platinum in this catalyst is to oxidize hydrocarbons and to ensure that the oxidation of halocarbons goes to completion. However, the platinum exhibits little or no activity for initiating the destruction of halocarbons. Instead, the attack on the halocarbons is initiated by the support. The support also provides a high surface area for exposure of the platinum. Moreover, the support resists deactivation or destruction by halogens released during the destruction of halocarbons.

The second catalyst is of the supported-metal-oxide type. This catalyst can selectively oxidize ammonia to nitrogen at temperatures up to 400 °C, without producing nitrogen oxides. This catalyst converts ammonia completely to nitrogen, even when the concentration of ammonia is very low. No other catalyst is known to oxidize ammonia selectively at such a high temperature and low concentration. Both the metal oxide and the support contribute to the activity and selectivity of this catalyst.

This work was done by Ali Kashani of TDA Research for Johnson Space Center. For further information, contact the JSC Innovation Partnerships Office at (281) 483-3809. MSC-23054-1

Nanoscale Metal Oxide Semiconductors for Gas Sensing

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A report describes the fabrication and testing of nanoscale metal oxide semiconductors (MOXs) for gas and chemical sensing. This document examines the relationship between processing approaches and resulting sensor behavior. This is a core question related to a range of applications of nanotechnology and a number of different synthesis methods are discussed: thermal evaporation-condensation (TEC), controlled oxidation, and electrospinning. Advantages and limitations of each technique are listed, providing a processing overview to developers of nanotechnology-based systems.

The results of a significant amount of testing and comparison are also described. A comparison is made between SnO₂, ZnO, and TiO₂ single-crystal nanowires and SnO₂ polycrystalline nanofibers for gas sensing. The TEC-synthesized single-crystal nanowires offer uniform crystal surfaces, resistance to sintering, and their synthesis may be done apart from the substrate. The TEC-produced nanowire response is very low, even at the operating temperature of 200 °C. In contrast, the electrospun polycrystalline nanofiber response is
high, suggesting that junction potentials are superior to a continuous surface depletion layer as a transduction mechanism for chemisorption. Using a catalyst deposited upon the surface in the form of nanoparticles yields dramatic gains in sensitivity for both nanostructured, one-dimensional forms.

For the nanowire materials, the response magnitude and response rate uniformly increase with increasing operating temperature. Such changes are interpreted in terms of accelerated surface diffusional processes, yielding greater access to chemisorbed oxygen species and faster dissociative chemisorption, respectively. Regardless of operating temperature, sensitivity of the nanofibers is a factor of 10 to 100 greater than that of nanowires with the same catalyst for the same test condition. In summary, nanostructure appears critical to governing the reactivity, as measured by electrical resistance of these SnO2 nano-materials towards reducing gases. With regard to the sensitivity of the different nascent nanostructures, the electrosyn spun nanofibers appear preferable.

**Lightweight, Ultra-High-Temperature, CMC-Lined Carbon/ Carbon Structures**

This refractory composite material is applicable to defense vehicles, combustion chambers, rocket nozzles, hot gas generators, and valves using both liquid and solid propellants.

John H. Glenn Research Center, Cleveland, Ohio

Carbon/ carbon (C/C) is an established engineering material used extensively in aerospace. The beneficial properties of C/C include high strength, low density, and toughness. Its shortcoming is its limited usability at temperatures higher than the oxidation temperature of carbon — approximately 400 °C. Ceramic matrix composites (CMCs) are used instead, but carry a weight penalty. Combining a thin laminate of CMC to a bulk structure of C/C retains all of the benefits of C/C with the high temperature oxidizing environment usability of CMCs.

Ultramet demonstrated the feasibility of combining the light weight of C/C composites with the oxidation resistance of zirconium carbide (ZrC) and zirconium-silicon carbide (Zr-Si-C) CMCs in a unique system composed of a C/C primary structure with an integral CMC liner with temperature capability up to 4,200 °F (≈2,315 °C). The system effectively bridged the gap in weight and performance between coated C/C and bulk CMCs. Fabrication was demonstrated through an innovative variant of Ultramet's rapid, pressureless melt infiltration processing technology. The fully developed material system has strength that is comparable with that of C/C, lower density than Cf/SiC, and ultra-high-temperature oxidation stability. Application of the reinforced ceramic casing to a predominantly C/C structure creates a highly innovative material with the potential to achieve the long-sought goal of long-term, cyclic high-temperature use of C/C in an oxidizing environment. The C/C substructure provided most of the mechanical integrity, and the CMC strengths achieved appeared to be sufficient to allow the CMC to perform its primary function of protecting the C/C.

Nozzle extension components were fabricated and successfully hot-fire tested. Test results showed good thermochemical and thermomechanical stability of the CMC, as well as excellent interfacial bonding between the CMC liner and the underlying C/C structure. In particular, hafnium-containing CMCs on C/C were shown to perform well at temperatures exceeding 3,500 °F (≈1,925 °C).

The melt-infiltrated CMC-lined C/C composites offered a lower density than Cf/SiC. The melt-infiltrated composites offer greater use temperature than Cf/SiC because of the more refractory ceramic matrices and the C/C substructure provides greater high-temperature strength.

The progress made in this work will allow multiple high-temperature components used in oxidizing environments to take advantage of the low density and high strength of C/C combined with the high-temperature oxidation resistance of melt-infiltrated CMCs.

This work was done by Matthew J. Wright, Gautham Ramachandran, and Brian E. Williams of Ultramet for Glenn Research Center. Further information is contained in a TSP (see page 1).

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office. Attn: Steven Fedor, Mail Stop 4–8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-18492-1.