A Model of Reduced Kinetics for Alkane Oxidation Using Constituents and Species for N-Heptane

When certain variables are judiciously combined, a self-similarity appears, allowing for a compact chemistry reduction mechanism that predicts ignition time.

NASA's Jet Propulsion Laboratory, Pasadena, California

The reduction of elementary or skeletal oxidation kinetics to a subgroup of tractable reactions for inclusion in turbulent combustion codes has been the subject of numerous studies. The skeletal mechanism is obtained from the elementary mechanism by removing from it reactions that are considered negligible for the intent of the specific study considered. As of now, there are many chemical reduction methodologies.

A methodology for deriving a reduced kinetic mechanism for alkane oxidation is described and applied to n-heptane. The model is based on partitioning the species of the skeletal kinetic mechanism into lights, defined as those having a carbon number smaller than 3, and heavies, which are the complement of the species ensemble. For modeling purposes, the heavy species are mathematically decomposed into constituents, which are similar but not identical to groups in the group additivity theory.

From analysis of the LLNL (Lawrence Livermore National Laboratory) skeletal mechanism in conjunction with CHEMKIN II, it is shown that a similarity variable can be formed such that the appropriately non-dimensionalized global constituent molar density exhibits a self-similar behavior over a very wide range of equivalence ratios, initial pressures and initial temperatures that is of interest for predicting n-heptane oxidation. Furthermore, the oxygen and water molar densities are shown to display a quasi-linear behavior with respect to the similarity variable. The light species ensemble is partitioned into quasi-steady and unsteady species. The reduced model is based on concepts consistent with those of Large Eddy Simulation (LES) in which functional forms are used to replace the small scales eliminated through filtering of the governing equations; in LES, these small scales are unimportant as far as the overwhelming part of dynamic energy is concerned.

Here, the scales thought unimportant for recovering the thermodynamic energy are removed. The concept is tested by using tabular information from the LLNL skeletal mechanism in conjunction with CHEMKIN II utilized as surrogate ideal functions replacing the necessary functional forms. The test reveals that the similarity concept is indeed justified and that the combustion temperature is well predicted, but that the ignition time is over-predicted, a fact traced to neglecting a detailed description of the processes leading to the heavies chemical decomposition. To palliate this deficiency, functional modeling is incorporated into this conceptual reduction in addition to the modeling the evolution of the global constituent molar density, the enthalpy evolution of the heavies, the contribution to the reaction rate of the unsteady lights from other light species and from the heavies, the molar density evolution of oxygen and water, and the mole fractions of the quasi-steady light species.

The model is compact in that there are only nine species-related progress variables. Results are presented showing the performance of the model for predicting the temperature and species evolution. The model reproduces the ignition time over a wide range of equivalence ratios, initial pressure, and initial temperature.

This work was done by Kenneth G. Harstad and Josette Bellan of Caltech for NASA's Jet Propulsion Laboratory. For more information, contact iaoffice@jpl.nasa.gov. NPO-47383

Thermally Conductive Tape Based on Carbon Nanotube Arrays

This material can be used for thermal management of microelectronic packages and electronic systems.

Goddard Space Flight Center, Greenbelt, Maryland

To increase contact conductance between two mating surfaces, a conductive "tape" has been developed by growing dense arrays of carbon nanotubes (CNTs, graphite layers folded into cylinders) on both sides of a thermally conductive metallic foil. When the two mating surfaces are brought into contact with the conductive tape in between, the CNT arrays will adhere to the mating surface. The van der Waals force between the contacting tubes and the mating surface provides adhesion between the two mating surfaces. Even though the thermal contact conductance of a single tube-to-tube contact is small, the tremendous amount of CNTs on the surface leads to a very large overall contact conductance.

Interface contact thermal resistance rises from the microroughness and the macroscopic non-planar quality of mating surfaces. When two surfaces come into contact with each other, the actual contact area may be much less than the total area of the surfaces. The real area of contact depends on the load, the surface roughness, and the elastic and inelastic properties of the surface. This issue is even more important at cryogenic temperatures, where materials become hard and brittle and vacuum is

used, which prevents any gas conduction through the interstitial region.

A typical approach to increase thermal contact conductance is to use thermally conducting epoxies or greases, which are not always compatible with vacuum conditions. In addition, the thermal conductivities of these compounds are often relatively low. The CNTs used in this approach can be metallic or semiconducting, depending on the folding angle and diameter. The electrical resistivity of multiwalled carbon nanotubes (MWCNTs) has been reported. MWCNTs can pass a current density and remain stable at high temperatures in air. The thermal conductivity of a MWCNT at room temperature is measured to be approximately 3,000 W/m-K, which is much larger than that of diamond. At room temperature, the thermal conductance of a 0.3 cm^2 array of CNTs was measured to be as high as 10 W/K. The high thermal conductivity and the nanoscale size make CNTs ideal as thermal interface materials.

The CNT-based thermal tape can be used for the thermal management of microelectronic packages and electronic systems. It also can be integrated with current device technology and packaging. The material would allow for an efficient method to manage excess heat generation without requiring any additional power. Lastly, the CNT tape can be used to enhance thermal contact conductance across two mating surfaces on some NASA missions.

This work was done by Ali Kashani of Atlas Scientific for Goddard Space Flight Center. For further information, contact the Goddard Innovative Partnerships Office at (301) 286-5810. GSC-15607-1

Two Catalysts for Selective Oxidation of Contaminant Gases

One oxidizes halocarbons and ammonia; the other oxidizes ammonia.

Lyndon B. Johnson Space Center, Houston, Texas

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 John D. Wright 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

John H. Glenn Research Center, Cleveland, Ohio

A report describes the fabrication and testing of nanoscale metal oxide semiconductors (MOSs) 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 SnO_2, ZnO, and TiO_2 single-crystal nanowires and SnO_2 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