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Hydrogen Gas Getters: Susceptibility to Poisoning

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Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The objective of this project was to obtain fundamental information on the chemical mechanism of the catalytic reaction of hydrogen with one commonly used hydrogen getter, DEB. Experiments with these materials showed that the method of exposure affects the nature of the reaction products. The results of this work contributed to the development of a mechanistic model of the reaction.

Background and Research Objectives

The focus of this Laboratory Directed Research and Development (LDRD) project was on acquiring fundamental information regarding the chemical mechanism and kinetics of the reaction of hydrogen with the getter DEB. DEB is a di-alkyne compound wherein two alkyne linkages connect three phenyl rings (1,4-bis (phenylethynyl)benzene). It is formulated as mixture of 75% DEB and 25% catalyst (5% Pd on carbon). The objective was to gain insight into the molecular mechanism by which hydrogen reacts with DEB.

Importance to LANL's Science and Technology Base and National R&D Needs

About 40% (~9,000) of the ~23,000 transuranic (TRU) waste drums at Los Alamos National Laboratory (LANL) are presently unshippable because conservative calculations suggest that the hydrogen concentration may exceed the lower explosive limit for hydrogen. This situation extends across nearly all DOE sites holding and generating TRU waste.

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The incorporation of a hydrogen getter such as DEB into the waste drums (or the TRUPACT II shipping containers) could substantially mitigate the explosion risk. The result would be to increase the number of drums that qualify for transportation to the Waste Isolation Pilot Plant (WIPP) without having to resort to expensive re-packaging or waste treatment technologies.

However, before this approach can be implemented, key technical questions must be answered. Foremost among these is the question of whether the presence of other chemical vapors and gases in the drum might "poison" the catalytic reaction between hydrogen and DEB.

Scientific Approach and Accomplishments

In order to understand the results of the poisoning experiments, we felt that it would be valuable to have a better understanding of the molecular mechanism of the reaction between hydrogen and the DEB getter.

Two key issues were addressed:

1) Do the hydrogen atoms catalytically added across the unsaturated triple bonds stay localized on those carbon atoms or do they become delocalized across the phenyl ring structure?

Nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) studies of DEB that had been reacted with deuterium indicated that the deuterium atoms remained localized on the sites of the alkyne linkages. This is an important result because it eliminates from consideration those more complex mechanisms involving dynamic hydrogen exchange among all sites on the molecule.

2) What is the nature of the intermediate species formed during the reaction?

Gas chromatography/mass spectroscopy (GC/MS) analyses of DEB exposed to sub-stoichiometric amounts of hydrogen in a slow, controlled fashion indicate that while small amounts of the alkene analogs are present, the majority of the reaction product is the fully saturated alkane analog. However, when DEB is instantaneously exposed to an excess of hydrogen, the analysis of the reaction products show a broader mix of unreacted alkyne, cis- and trans- forms of the alkene form, perhaps even meta- and ortho-substituted compounds, as well as completely saturated alkanes.

As a result of this work, we now have an improved conceptual model of the reaction mechanism.

Under conditions where hydrogen is slowly passed over an excess of getter held at constant temperature, hydrogen molecules are in continuous dynamic exchange with the surface of the catalyst material. When on the catalyst surface, a fraction of the sorbed

hydrogen molecules migrate to a Pd cluster where they become disassociated into hydrogen atoms resident on the surface of the Pd cluster. An electron-rich DEB molecule in close proximity to a Pd cluster can react with hydrogen atoms until completely saturated. Diffusion of DEB molecules and/or hydrogen atoms along the catalyst surface or along chains of unsaturated DEB molecules keeps the reaction proceeding from the di-alkyne form, through the alkene forms, and on to the alkane form until hydrogen atom transport paths are broken by the formation of fully saturated alkanes. As this happens, the overall reaction rate slows and finally stops. When performed in this manner, the getter can react with over 90% of its stoichiometric capacity for hydrogen.

Under conditions where an excess of hydrogen is rapidly added to the getter material without temperature control, the reaction rates are accelerated and accompanied by a rapid rise in temperature due to the exothermic nature of the reaction. This tends to more readily and rapidly disrupt the orderly, sequential saturation of DEB from alkyne, through the alkene forms and on to the alkane form. Hence we observed a broad mix of unreacted DEB, the alkene forms as well as the alkane form when conducting experiments of this nature.