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Study Made of Raney Nickel Technology

The term "Raney nickel" refers to a form of nickel obtained by leaching the aluminum from a nickel-aluminum alloy by reaction with sodium hydroxide. The resulting finely divided nickel powder contains large amounts of bound hydrogen, presumably in the chemisorbed state. It was considered likely that the pyrophoric properties of Raney nickel were due to the presence of this chemisorbed layer of hydrogen, the evolution of the latter being primarily responsible for the gradual loss in activity observed when Raney nickel is stored under an inert atmosphere.

Raney nickel has long been known to be a very active catalyst for many applications. It has been utilized almost exclusively, however, in the field of organic chemistry for a variety of purposes, such as hydrogenation of esters, desulfuration of thiazoles, etc. It is likely that this close association with specialized organic reactions has tended to obscure the fact that Raney nickel (and modifications thereof) is a very promising catalyst for inorganic reactions in which a source of active hydrogen is required. In particular, it appears that past applications of this material have not been concerned with its properties as a source of hydrogen atoms at cryogenic temperatures. In the form in which it is usually described in the literature, Raney nickel is stored under an inert carrier, such as ethanol, until use. Raney nickel stored, in this manner has a limited active life, generally a few weeks at most. Since it became evident that it was necessary to develop new techniques for handling and storing dried Raney nickel powders, and to verify the mechanism of the H_2/O_2 ignitions obtained from Raney nickel powders, a study was initiated. The results of the study are summarized below.

Improved Storage Life of Raney Nickel Due to Storage Under Gaseous Hydrogen

The literature references on Raney nickel checked during the study referred to storage of the Raney nickel only under carriers such as alcohols, hydrocarbons, or water. It was well known that Raney nickel stored under these conditions slowly loses its activity. The period of usefulness varied from a few days to, at most, a few weeks. As a result of the knowledge gained during the study about the ignition mechanism, it was decided that storage of the dry Raney nickel powder under gaseous hydrogen would yield virtually indefinite shelf life, as well as provide a much more useful form of the nickel for the required application. This supposition was verified experimentally as follows: A number of samples of Raney nickel stored under methanol were evacuated to dryness. Ambient hydrogen gas was admitted to each sample to about one atmosphere. Each sample was then sealed, and seven of these samples were opened after various times, up to a period of 159 days. Qualitatively, each sample was intensely pyrophoric upon exposure to ambient air, with no detectable effect of storage time. Some of these samples, including that stored for 159 days, were used to obtain cryogenic H_2/O_2 ignitions.

In addition, one stored sample was exposed to ambient air after 1 year, 7 days of storage. The sample was intensely pyrophoric, with no detectable difference from the other samples opened earlier.

Elucidation of Ignition Mechanism of Raney Nickel

It was demonstrated during the study that the mechanism of the H_2/O_2 ignitions obtained from Raney nickel is entirely catalytic in nature, and is

(continued overleaf)

due to chemisorbed hydrogen atoms on the surface of the nickel powder. It was shown that the pyrophoricity of Raney nickel is a secondary process, resulting from the heat release associated with the primary catalytic ignition reaction.

This information was gained as a result of tests in which hydrogen was alternately desorbed (by heating under vacuum) and re-adsorbed. The Raney nickel powder from which the hydrogen was desorbed showed no activity for H_2/O_2 ignition. Re-adsorption of hydrogen, with no change in particle size or configuration, restored activity for H_2/O_2 ignition.

It has long been known that a large amount of bound hydrogen is associated with Raney nickel. There appeared to be considerable difference of opinion in the literature, however, as to whether this represented adsorbed hydrogen (surface phenomenon) or dissolved hydrogen (bulk phenomenon), and the relative magnitude of each. Dissolved hydrogen would not be expected to render the nickel catalytically active for rapid H_2/O_2 ignitions. Moreover, there was speculation in the literature that the pyrophoricity of Raney nickel was due solely to its fine state of subdivision, and was not related to the presence of the bound hydrogen.

Reactivation of Reacted Raney Nickel Powder

It was demonstrated during the study that the activity of reacted, oxidized Raney nickel could be restored. This was accomplished by subjecting the reacted Raney nickel (now in the form of nickel oxide) to a hydrogen reduction process. This consisted of heating the nickel oxide powder to about $300^\circ C$, and admitting hydrogen gas to approximately 760-mm pressure. The hydrogen pressure was permitted to drop (due to the reaction with nickel oxide to form nickel and water) to some suitable lower pressure (such as 500 mm), at which time the sample was evacuated for about one hour. This process was repeated until there was no further evidence of water formation. The reduced nickel powders were then desorbed for a period of one to a few days at about $300^\circ C$ and one micron pressure. The temperature was then lowered to ambient (still under vacuum). At this time ambient hydrogen gas was admitted to about one atmosphere. This exposure was continued until there was no further evidence of significant uptake of hydrogen. The resulting material was again active for H_2/O_2 ignition, as evidenced by its pyrophoricity. The degree of pyrophoricity was, however, qualitatively milder than that observed with previously unreacted Raney nickel samples.

Entrainment of Dry Raney Nickel Powder in a Stream of Reactant Hydrogen Gas

Raney nickel powder was introduced into the ignition zone by entrainment in a stream of hydrogen gas. Since the nickel powders were stored under an atmosphere of hydrogen gas, this technique had the significance that a given charge of Raney nickel, suitably protected by check valves or similar devices, could be used to obtain multiple ignitions. This was accomplished by entraining a relatively small amount of the nickel powder in a brief surge of hydrogen gas. During the study, this surge was due to the total hydrogen flow to the injector. This was possible, since the study was concerned solely with the ignition process, rather than with steady-state combustion. It appears, however, that a similar technique could be used for prolonged combustion. This would be accomplished by diverting a small hydrogen bleed stream through the catalyst fluidizer during the ignition process. Following ignition in the combustion chamber (or antechamber), flow through the catalyst fluidizer would be shut off until a new ignition was desired.

This general technique would appear to be amenable to entirely different types of reaction (i.e., the Fischer-Tropsch series of reactions) in which a stream of hydrogen gas is to be catalytically reacted with a second gas stream. It would appear to be possible to retain the nickel powders after the reaction, and subject them to a regeneration process. This would create the potential of a steady-state commercial process utilizing the great catalytic ability of Raney nickel, without the drawbacks associated with the conventional storage techniques of this material.

Note:

Additional details are contained in: *Feasibility Studies of Oxygen/Hydrogen Powdered Metal Ignition*, by W. B. Lee, Final Report, No. 25, 179, The Marquadt Corporation, September 1965. Copies of this report are available from

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