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NOTES

The Promoting Effect of Chromium on a Sprayed-Nickel Catalyst

The promoting effect of chromium oxides on nickel hydrogenation catalysts has been reported for various supported and unsupported catalysts prepared from compounds of nickel and chromium such as carbonates and formates (*5, 6, 10, 11*). Recently nickel films produced in this laboratory by standard vacuum procedures using Ni-Cr alloy wires were shown to possess enhanced hydrogenation activity compared to that exhibited by pure nickel films (*10*). In extending this work over a range of chromium concentrations one is restricted by the limited number of alloy wires commonly marketed. We chose, therefore, a more flexible technique of catalyst preparation using a powder-metal spray gun. Waterman and deKok (*12*) prepared metal catalysts such as a nickel-chromium catalyst using a spray gun and alloy wire. The resulting powder was activated by hypochlorous acid treatment and hydrogen reduction. By using instead a gun designed for powder feed we were able to vary with ease the chromium content of the finished catalyst over a significant range. The nature of the resulting catalyst samples was studied using X-ray and electron diffraction, and differential thermal analysis. Hydrogen adsorption was used as a measure of activity as suggested by Locke and Rase (*7*). The technique of catalyst preparation here described is evaluated as a tool for catalytic research.

Experimental Work

Nickel and chromium powders (99+% purity, 100 mesh) were weighed and physically mixed to make a number of samples with varying chromium contents. These mixtures of pure metals were sprayed through a flame atomizing pistol into a large beaker of water used to condense and collect the finely divided particles. The pistol assembly was manufactured by Schori Process Corp. of Port Washington, New York. It contains inlets and control valves for hydrogen and oxygen as flame gases, an aspirator for creating suction to transport metal powders into the flame, and a special spray nozzle for producing the flame and injecting the metal powders into the flame. Metal powders may be fed to the pistol assembly through a rubber hose from a conically-shaped hopper.

The various fused metal mixtures were then oxidized by placing 10 g of powder into a beaker of 150 ml of sodium hypochlorite (5 wt % solution) and 75 ml of 0.1 *N* HCl at 50°C and maintaining vigorous stirring until the rapid and visible reaction had subsided. The oxidized particles were washed well with distilled water at 60°C in a suction funnel and placed into an oven to dry for 2 hr at 110°C. Samples of this unreduced catalyst were prepared by crushing the dried mass and sieving out the −50 to +100 mesh particles.

Chemical analyses of the various oxidized mixtures (unreduced catalyst) were performed by dissolving the solid particles and analyzing for nickel and chromium composition by polarograph. It was necessary to partially dissolve the catalyst solids in dilute nitric acid and then fuse the remaining residue with sodium carbonate.

Thermograms of the unreduced catalyst containing 3.698 Cr atoms with 100 Ni atoms were obtained using a controlled atmosphere differential thermal analyzer (R. L. Stone Co. Model DTA-DS-2) with an alumina reference. Hydrogen, nitrogen, and air atmospheres were employed (see Fig. 1). DTA cycling studies with hydrogen were carried out on the catalysts containing various percentages of chromium. These were reduced in a hydrogen atmosphere for 30 min at 260°C while in the

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* Present address: Fish Engineering Corp., Houston, Texas.

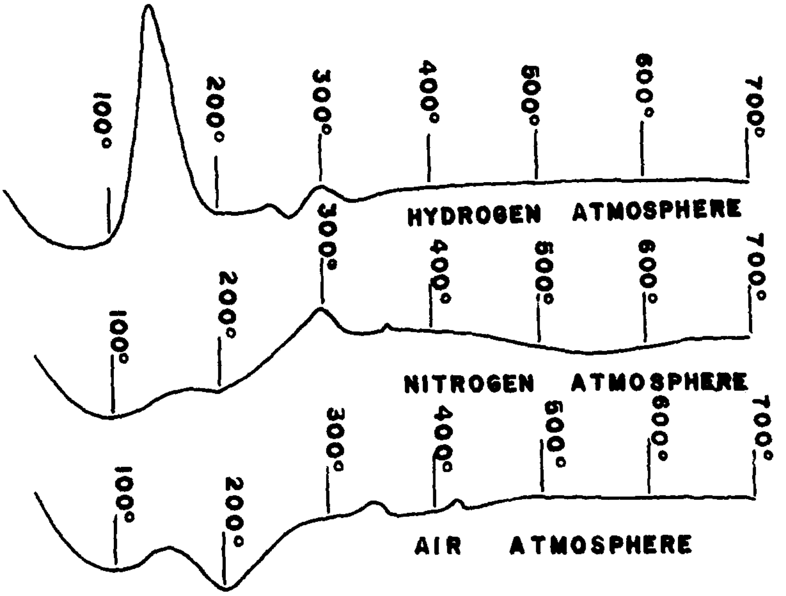

FIG. 1. Straight DTA of catalyst in different atmospheres.

DTA. The results of these cycling studies are shown in Figs. 2, 3, and 4.

X-Ray diffraction and elemental fluorescence analysis were carried out on the unoxidized fused-metal mixtures and unreduced catalyst samples. Electron diffraction patterns of the unreduced catalyst were also obtained.

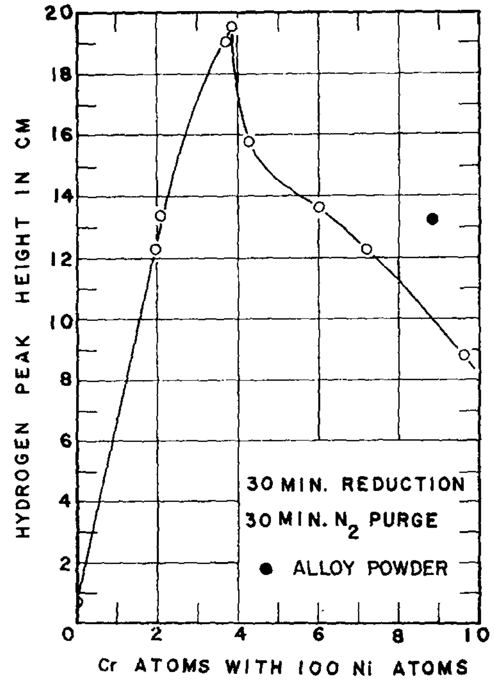

FIG. 2. Effect of chromium concentration on peak height at 260°. Moles Cr/100 moles Ni = 2.09.

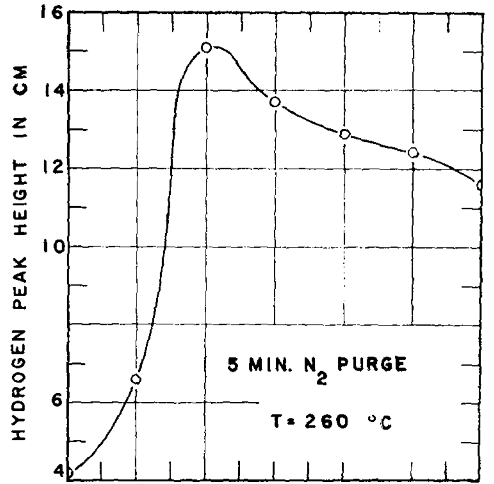

FIG. 3. Effect of reduction time on peak height. Moles Cr/100 moles Ni = 2.09.

NATURE OF THE MIXED CATALYST

Differential thermal analyses in con-

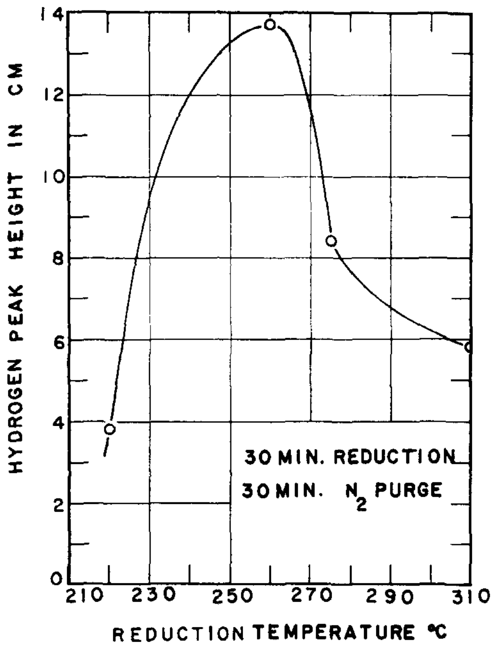

FIG. 4. Effect of reduction temperature on peak height: cycle at reduction temperature. Moles Cr/100 moles Ni = 2.09.

junction with X-ray and electron diffraction studies indicate that the unreduced catalyst is a hydrated higher nickel oxide with trace quantities of chromium dioxide on the surface. The nickel in the higher oxide is tervalent, and the compound has a probable empirical formula of $Ni_2O_3\cdot 2H_2O$. Cairnes and Ott (*3*) studied higher oxides of nickel and showed that they are not true hydrates but contain hydroxyl groups and only have the empirical formula of hydrates. These higher oxides are known to be reduced by hydrogen around 100° into nickel oxide and water according to the following equation (*2*, *4*):

$$(Ni_2O_3\cdot 2H_2O)\cdot H_2O + H_2 = 2NiO + 4H_2O$$

Differential thermal analyses shown in Fig. 1 indicate a large exothermic peak in the range of this proposed reaction. Beginning at 105° and ending at 185°C. The second and third exotherms shown on the figure for the hydrogen atmosphere are attributed to the reduction of NiO to nickel since pure nickel oxide gave similar peaks in hydrogen and yet did not exhibit the peak at 105° to 185°C. After 30 min of reduction time the material remaining was found to be pyrophoric upon exposure to air. The long endotherm in nitrogen may be attributed to desorption of oxygen.

X-ray fluorescence analysis showed nickel and chromium peaks in the unreduced catalyst, but chromium was not detected in the X-ray patterns. Thus, chromium is probably not alloyed with the nickel but located on the surface of the nickel. Accordingly, electron diffraction observations were made and the "*d*" spacings were identified with chromium dioxide. Since it is known that chromium dioxide cannot be reduced in hydrogen under the conditions of the test, it was assumed that the reduced catalyst would also contain chromium dioxide on the surface of the nickel.

The effects of reduction time and temperature on activity were studied and curves similar to those that were observed with supported-nickel catalysts were obtained (*7*). Figures 3 and 4 indicate sharp optima for both reduction time and temperature. The sharp decrease in activity below 240° is consistent with the DTA observations which showed that reduction is not rapid below 240°. The low activities at temperatures above 280°C correspond to the description of oxygen.

Some qualitative studies were made on the poisoning of the nickel-chromium catalysts with sulfur dioxide. Although the hydrogen adsorption peaks declined after poisoning with sulfur dioxide, purging, and reactivating with hydrogen; the deactivation did not appear as great as that observed by Locke with supported nickel catalyst (*7*).

CHROMIUM PROMOTING EFFECT

Figure 2 presents the effect of chromium on hydrogen adsorption activity expressed as peak height observed with the DTA upon admission of hydrogen to a reduced and nitrogen purged sample. This curve exhibits interesting similarities with those observed by Armstrong and Hilditch (*1*) for nickel catalysts used in cotton-seed oil reduction. These catalysts were promoted with Al_2O_3 and Fe_2O_3 which, like chromium oxides, are difficult to reduce. They observed maxima at approximately the same ratios of foreign ion to nickel as were observed in this study.

Although in the realm of catalytic experimentation restraint upon the urge to speculate is necessary, one cannot resist a brief hypothesis. Experimental evidence from many laboratories suggests that some small amount of oxygen must be incorporated in the reduced nickel lattice for maximum and sustained hydrogenation and hydrogen adsorption activity (*8*, *9*). An oxide such as CrO_2 can incorporate excess oxygen in its lattice and also take up oxygen on its surface. It may be hypothesized, therefore, that CrO_2 present as interstitial impurities in the nickel lattice may alter the nickel-oxygen configuration so as to remove vicinal oxygen from the nickel. The optimum amount of CrO_2 would then be some function of the optimum amount of oxygen required in the nickel lattice for maximum activity.

The solid point on Fig. 2 which lies above the curve was obtained using an alloy powder prepared by spraying an alloy wire. This powder was in turn sprayed through the powder gun and activated as were the other samples. Its slightly higher activity may be attributed to the more intimate contacting of chromium and nickel made possible by an alloy. There was no other noticeable difference and no reason to believe that the sample produced from the alloy was not a heterogeneous mixture of CrO_2 and Ni similar to the other samples.

VALUE OF PREPARATION TECHNIQUE

The technique here described for preparing metallic catalysts is most convenient provided a suitable means of activating the catalyst can be found. In this study the activation step served mainly to produce a more finely divided and porous material. Means for accomplishing the same result with other catalyst preparations should not be difficult to develop. Other than the problem of activating the samples, the method is unusually simple to apply and has great flexibility. In addition to varying metal composition it is also possible to spray nonmetallic materials including oxide semiconductors and even well-known catalyst supports. Good reproducibility in successive batches of catalysts is possible when each batch is subjected to some elutriation or screening process so that a constant mesh size of catalyst is used for each test. In many ways this affords an advantage over preparing catalysts on supports by the usual chemical means since the control of the size of the agglomerates of active material is more positive by the sprayed-metal technique combined with screening or elutriation.

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DONALD N. FLETCHER
HOWARD F. RASE

Department of Chemical Engineering,
University of Texas,
Austin, Texas

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