Regeneration of Used Nickel Catalyst

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ABSTRACT

Regeneration of used nickel catalyst from a hydrogenation plant has been achieved by converting the nickel content of slurry into NiO and $Ni(OH)_2$, and the subsequent reduction of these compounds by hydrogen gas at temperatures of 450 C and 290 C respectively. A laboratory and plant apparatus for reduction are designed. Activity of regenerated catalyst was measured in comparison with reference catalyst (G15). Pretreatment of discarded catalyst prior to reduction is described.

INTRODUCTION

Nickel catalyst used for hydrogenation of edible oils loses its activity by the attack of poisonous materials in oils and gas (1). Both oils and gas, even after considerable refining and preparation, contain trace amounts of catalyst poisions, such as sulphur compounds, sodium soap and carbon monoxide, (2,3). Therefore, nickel catalyst has a short life span, such that during the first hour of hydrogenation nearly 15% of the nickel catalyst will become deactivated (1).

The regeneration of used catalyst could be based on the classical methods of catalyst preparation. Pyrolysis of nickel formate (4), reduction of nickel salt according to the patents of Murray Ranley (5) and the dry-reduction method of Schnabel (6), using nickel salt solution absorbed on carriers such as diatomaceous earth, are among the most common methods of catalyst production. Kane and Saitwadekor (7) have used the latter technique for nickel oxide reduction by fluidization at 450-550 C using hydrogen and nitrogen gases.

In this instance the dry-reduction method was used. Because the slurry contained large amounts of impurities, such as oil, inert support materials, etc., pretreatment of the used catalyst was necessary.

EXPERIMENTAL PROCEDURE

Materials

All chemicals used were of analytical reagent grade obtained from Ventron, Alpha Products, Danvers, MA. Support for the catalyst was a filter aid hydro super-cel, obtained from the Johns Manville Product Corp., New York, NY.

Ninty-nine percent hydrogen (1% impurity due to methane), which is used for oil hardening by the Narges-e-Shiraz Vegetable Oil Plant, was used for catalyst reduction. Used catalyst samples were obtained from the above plant; the catalyst was discarded and said to be inactive. G-15 commercial catalyst which contains silica support and is supported by vegetable oil flakes (Girdler Division of Chemetron Inc., Louisville, KY) was used as the standard catalyst. Refined and bleached commercially processed cottonseed oil was obtained from the Narges-e-Shiraz Shortening Co. plant, Shiraz, Iran. All of the samples had the same saponification value, which was 195.

Apparatus

A silica tube with open ends was constructed and used in conjunction with a tube furnaced heater (Gallenkamp, England). All parts of the reactor tube connection were made leak proof by means of the Teflon strips. This was connected to gas, vapor, and sulphur absorbents (calcium chloride and lead acetate) and set up as indicated in Fig. 1, and shown diagramatically in Fig. 2.

A metallic unit was also constructed for industrial purpose reduction with a reactor diameter of 15 cm and length of 55 cm and which was rested on two stands. This was joined to two metal pipes with a diameter of 2 cm and a length of 30 cm having a valve on each side. One of the pipes was the sample inlet and the other was a gas outlet. A side pipe with a diameter of 1 cm and a length of 30 cm, which also had a valve, was joined to the sample inlet pipe for hydrogen gas inlet (Fig. 3). The inside of the reactor was partitioned with longitudinal metallic half plates for the purpose of tilting the material and exposing most of its surface area to gas for complete reduction. Gas burners provided the heat for the reaction. Agitation was produced by a handle on one end of the reaction tube. All of the connections were made leak proof by means of teflon strips, prior to initiation of the experiment. Hydrogenation of oil was carried out in a Parr hydrogenation instrument, with a one liter converter equipped with an external heating loop. Refractive index was measured with a refractometer model R.L.1, (P. Z. O. Warszawa Poland) attached to an ultrathermostat type U.T. (W. A. T. Krakow, Poland).

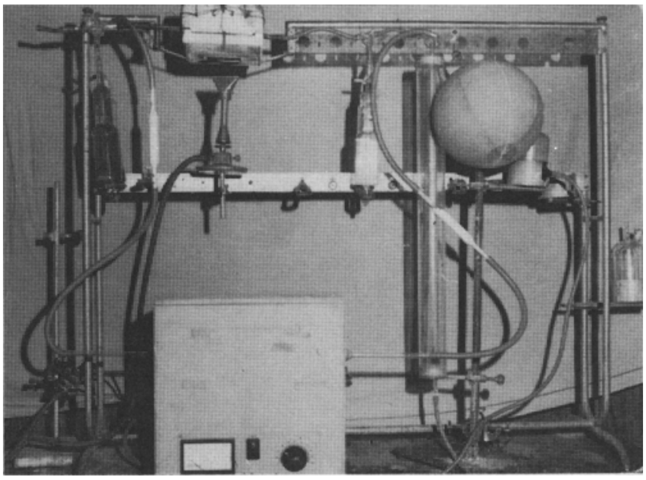

FIG. 1. Portrayal of the glass reduction unit.

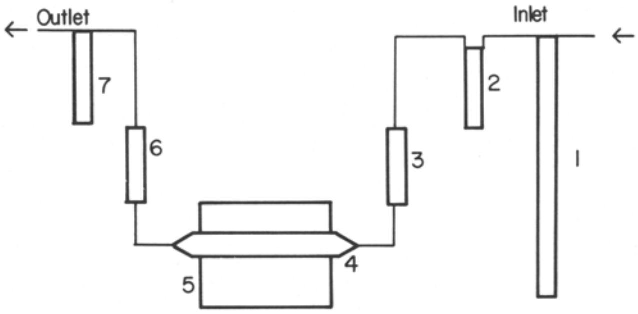

FIG. 2. Schematic diagram of the glass reduction unit. (1) Graduated hydrogen gas tube; (2) Potassium hydroxide; (3) Calcium chloride and lead acetate; (4) Sample tube; (5) Heater; (6) Calcium chloride; and (7) Confining bottle.

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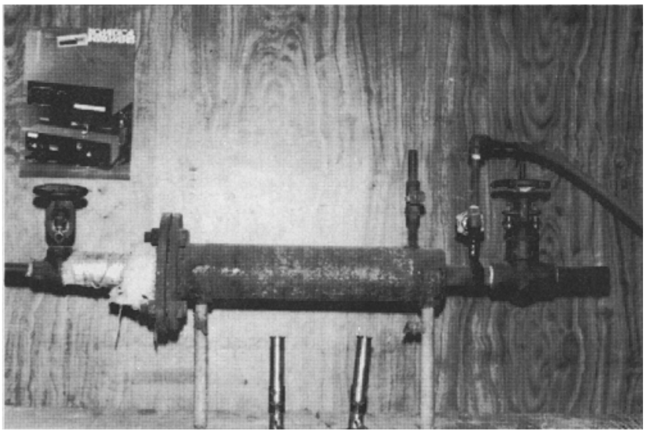

FIG. 3. Portrayal of the metallic reduction unit.

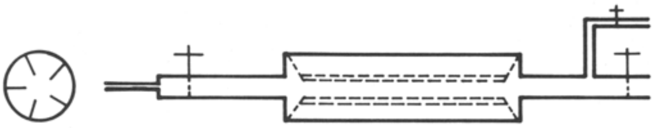

FIG. 4. Schematic diagram of the metallic reduction unit.

Sieving was done by means of available shaker and sieves (Karl Kolb Scientific Co., Germany). All weighings were made with a semimicro mettler balance. An electrical rapid asher (Type K.S.V.R. 400, Karl Kolb, West Germany) and a muffle furnace (Gallemkamp, London, England) were used for convertion of nickel nitrate to nickel oxide.

Analytical Determination

Nickel was determined gravimetrically and volumetrically using dimethylglyoxime (D.M.G.) and ethylene diamine tetra-acetate (E.D.T.A.) titration methods, respectively (8,9). Determination of iodine value (I.V.) was carried out by Wijs method according to the Association of Official Analytical Chemists Method Cd1-25 (10). Melting points were determined according to the AOCS official methods Cc1-25 (10) using the capillary tube method, and the refractive index was measured according to the A.O.A.C. method 26-006 (11).

Procedure

100 g of the slurry (used catalyst resembling a black, soggy mass) was burned in a nickel or platinum dish until smoke no longer came out of the sample. The residue was dissolved in 250 ml of (4M) nitric acid. To expel nitrogen diozide, the solution was heated to boiling until the initial brown gas disappeared. It was then filtered to remove any undissolved substances. The filtrate, which consisted of nickel nitrate, was divided into two parts. A one part sodium hydroxide solution (1M) was added until the solution became basic (pH = 9-10) and all of the nickel nitrate was converted to nickel hydroxide precipitate. The precipitate was filtered and washed with distilled water (until the washing liquid became neutral) and dried at 100 C. The precipitate was then ground to different mesh sizes and two samples with diameters of 0.05 and 0.063 mm were prepared. The second portion of the nickel nitrate solution was transfered to a 200 ml beaker and heated at 100 C until dry. The residue was heated by means of an electrical asher up to a temperature of 400 C until the color changed from green to black. The granular black sample was ground to different mesh sizes. Two samples with diameters of 0.063 and 0.08 mm were prepared.

Reduction of nickel hydroxide. The nickel hydroxide precipitate was mixed thoroughly with 10 g of support material and placed in the opened silica glass tube (Figs. 1 & 2). The outlet end was closed with glass wool to protect the powdered sample from the flow of hydrogen gas. The tube containing the sample was put into the heater and connected to the potassium hydroxide column (the tube containing solid calcium chloride and lead acetate was placed between the sample tube and potassium hydroxide column), which was connected to the top of the graduated hydrogen gas tube. The bottom of this tube was connected to a movable reservior (leveling bottle) containing a confining liquid, 20-25% sodium chloride solution acidified with dilute hydrochloric acid and colored with methyl red (9). The outlet of the sample tube was also connected to another tube containing calcium chloride. The other end of this tube was joined to another leveling bottle containing the same confining liquid as the above movable reservior. These leveling bottles showed the decrease in hydrogen gas volume in the graduate hydrogen gas tube. The heater was adjusted to 250 C and the sample system was allowed to come to equilibrium with this temperature. Air was evacuated from the system with vacuum pump and the graduated hydrogen gas tube was filled with 100 ml of hydrogen gas. The heater was adjusted to appropriate temperatures (280, 290, and 300 C) and reduction of samples of both mesh sizes were carried out separately at each specified temperature.

The hydrogen gas was allowed to flow over the sample with aid of the start and end point leveling bottles. The hydrogen gas was circulated through the sample, with manual rotation of the tube, until the gas was used up in the system. The hydrogen gas tube was further refilled, and was run through the sample tube. Again, this practice was repeated until no hydrogen gas usage was shown in the graduated gas tube. The heater was then turned off until the system cooled to room temperature. Ten ml of hot (70-80 C) hydrogenated oil (iodine value ~ 3) was then injected into the sample tube. Hydrogen gas was evacuated from the system by means of vacuum pumps. The sample tube was disconnected from the system, and the hot oil which contained active nickel catalyst was poured into a 20 ml beaker.

Reduction of nickel oxide. In this case the above apparatus was also used. 0.05 g of tungsten powder (or active copper powder) and 10 g of support were added to the sample and mixed. The heater was adjusted to appropriate temperatures (480, 500, and 520 C) and reduction of

TABLE I

Composition of Used Catalyst

No. of samples tested	Oil content (%)	Inert matter (%)	Aluminum and traces of iron	Nickel (%)
4	49.8[a]	39.8	2.0	8.4
5	50.8	37.5	2.0	9.7
3	37.6	48.0	2.4	12.0

[a] Figures are the mean for the number of samples with close results.

TABLE II

Iodine Value Efficiency of Nickel Catalyst Prepared from Nickel Hydroxide and Nickel Oxide Reduction Methods. For Hydrogenation Conditions, Refer to the Text.

Reduction temperature of the catalyst C		IV(120)	IVE(%)
	280	79.2	27.34
$Ni(OH)_2$	290	77.3	29.08
	300	80.7	25.96
	480	81.1	25.60
NiO	500	83.6	23.30
	520	85.8	21.28

samples of both mesh sizes were carried out separately at each specified temperature.

Reduction of nickel oxide as well as nickel hydroxide was achieved in the metallic unit (Figures 3 and 4) by heating with a Meker gas burner.

Activity Measurement

To measure the activity of the regenerated catalyst, 100 g of refined commercially processed cottonseed oil with an iodine value of 109 and FFA content of 0.05% was introduced into the Parr hydrogenation equipment. Hydrogenation was carried out using 0.5 g of catalyst (containing ca. 0.1 g pure nickel) with industrially processed, pure hydrogen gas at a temperature of 185 C with an agitation rate of 400 rpm.

This experiment was performed in different batches using samples of newly regenerated catalyst as well as the commercial G-15 nickel catalyst which was used as a reference. The hydrogenated oil was filtered through a Buchner funnel and the filtered, clear oil was subjected to analytical measurements. In this evaluation, the extent of hydrogenation was measured by determination of iodine value, refractive index, and melting point. These characteristic values are directly related to the measure of activity of the catalysts.

RESULTS AND DISCUSSION

In the preliminary tests on the used catalyst, direct ashing, acid digestion, and solvent extraction of oil was tried for the destruction of organic matter and extraction of nickel from the residue (containing nickel, oil, and inert materials). It was found that dry ashing and dissolving of nickel content of the residue in nitric acid was the most successful and the most promising test for commercial use.

Following these tests, the nickel content of the used catalyst was determined using titrimetric and gravimetric procedures (8,9). The quantity of nickel found from different batches, was in the range of 8.5-12% of the bulk of the material. The results of these determinations are summarized in Table I.

Nickel oxide was produced by heating nickel nitrate. The progress of the reaction could be monitored by the change of color occuring at different temperatures as follows: Black at 400 C, grey at 500 C, grey-green at 800 C and greenish-yellow at 900 C (12).

The hydrogenation activity of regenerated nickel catalysts on cottonseed oil are summarized in Table II and III. These results were the mean value of triplicate determination of each sample at the specified temperatures.

It is evident from Table II and III that the reduction of nickel hydroxide gives more active nickel than when the catalyst was obtained from the reduction of nickel oxide. The reason for this is that all of the nickel oxide cannot be reduced to metallic nickel because of the surface coating of nickel oxide particles with reduced nickel metal (13).

The activity of reduced catalyst is dependent on the temperature at which its oxide has been treated (14), and in the present study, the oxide obtained at 400 C was used. In the process of reduction, it was observed that temperatures of 480 C for nickel oxide and 290 C for nickel hydroxide would produce a more active catalyst, and a higher temperature reduction would produce less active ones.

A study of the literature of hydrogenation makes it clear that net (nonselective) activity should be a function of crystallite size (15-18), and despite evidence to the contrary (19), it is expected that the conditions of reduction (mesh size, temperature, etc.) would have a strong modifying effect on crystallite size and reactivity.

According to J.L. Carter, et al. (16), the sintering of nickel catalyst during reduction of nickel oxide effects the crystallite size of the reduced catalyst and, therefore, it may change the specific catalytic activity (activity per unit of nickel surface area) of nickel. The reason for this is that the sintering of a fresh catalyst, where the metal is initially in a highly dispersed state, may eliminate defects in the metal crystallites which are responsible for catalytic activity. The concentration of such defects may well decrease more rapidly than the surface area during sintering, thus causing a decrease in specific catalytic activity. This is probably why an increase in reduction temperature of 480 C for nickel oxide will produce less active catalysts.

It must also be added that the agent which can modify the role of the relative effective surface and hence the activity of nickel catalysts is the support material (13).

TABLE III

Hydrogenation of Cottonseed Oil Iodine Value of 109, with Different Catalysts (Temperature of 185 C, Starting Hydrogen Pressure of 4.5 atm, Agitation Rate of 400 rpm, Catalyst Concentration of 0.1 g Nickel, and Period of Two Hours)

Catalyst		Iodine value	Refractive index at 40 C	Relative refractive index drop	Relative refractive index drop (%)	Melting point C
Ni (commercial G-15)		76.5	1.4605	0.0105	100	38
Ni (from reduction of nickel hydroxide) at temperature of	280 C	29.2	1.4609	0.0101	96	37
	290 C	77.3	1.4606	0.0104	99	38
	300 C	80.7	1.4610	0.0100	95	37
Ni (from reduction of nickel oxide) at a temperature of	480 C	81.1	1.4611	0.0099	94	37
	500 C	83.5	1.4613	0.0097	92	36
	520 C	85.8	1.4615	0.0095	90	35

This role and function of a promoter is structural, which means that it permits the development of larger numbers of active centers on the catalyst surface. In this study, the only supporting material for catalyst reduction was filter aid hydro super cel.

The activity of regenerated catalysts was measured by using them in the hydrogenation of fatty acids and triglycerides. The measure of activity was determined as a simple lowering of iodine value after a fixed period of hydrogenation time. The values were calculated by using the following expressions:

$$IVE = \frac{IV(0) - IV(120)}{IV(0)}$$

where IVE is iodine value efficiency, IV(0) is the initial iodine value, and IV(120) is the iodine value after 120 min of hydrogenation at 185 C, with initial hydrogen gas pressure of 4.5 atm, agitation rate of 400 rpm, and catalyst concentration of 0.1 g pure nickel. These data for both nickel hydroxide and nickel oxide reduction methods are summarized (Table II).

The data in Table II refer to the hydrogenation of 100 g of cottonseed oil with an initial iodine value of 109 for a period of 120 min.

The IVE for hydrogenation of cottonseed oil with G-15 nickel catalyst by the same hydrogenation conditions was 30. By comparison of IVE's of regenerated catalysts with this IVE, it was obvious that the best and the most active regenerated catalyst was that obtained from the reduction of nickel hydroxide at 290 C as compared with respect to the reference catalyst (G-15).

The data in Table III regarding the refractive index lowering, and the increase in the melting points, could also be used as a measure of hydrogenation progress or the activity of the catalysts. However, conclusions made on melting points should always be treated with some reservation due to variation of this physical property owing to polymorphism of triglyceride molecules (20,21).

The relative refractive index drops are, therefore, calculated from the following equation (21):

$$\text{Relative refractive index drop} = \frac{\text{Refractive index drop with samples}}{\text{Refractive index drop with standard}} \times 100$$

and is given (Table III) for comparison. The refractive index of refined, unhydrogenated cottonseed oil was 1.4710. Data on relative refractive index drop confirms our previous conclusion that in the case of regenerated catalysts, the one prepared by nickel hydroxide reduction method at 290 C is superior in activity than when the starting material is nickel oxide. Based on conclusions drawn from iodine value efficiency and relative refractive index drop, the measure of activity for the catalysts could be classified in decreasing order (where A represents the activity of the catalyst) as follows: ^{A}Ni (G-15) $>^{A}$Ni from $Ni(OH)_2$ at 290 C $>^{A}$Ni from $Ni(OH)_2$ at 280 C $>^{A}$Ni from $Ni(OH)_2$ at 300 C $>^{A}$Ni from NiO at 480 C $>^{A}$Ni from NiO at 500 C $>^{A}$Ni from NiO at 520 C.

Finally, the active life and durability of regenerated catalyst were tested in comparison with the reference catalyst after ten runs of hydrogenation on each sample. It was observed that the decrease in activity was similar and in proportion with that of the reference catalyst.

The industrial reduction unit is designed so that such a unit could, in fact, be used in connection with hydrogen gas reformers where hot, dry gas could be monitored to the reduction bed for production of metallic nickel.

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[Received March 13, 1978]