trock et al. (2) and Sikes (1) also could not get positive results by their methods below this level. Even in the closed can test (2), where as much as 1500 g meal were used, no flashes were obtained below 0.04% hexane.

If the apparatus is air tight and the fluctuations in room temp are ± 0.5C, the results are reproducible. Calibration curves will have to be drawn for each solvent at the prevailing room temp for purposes of comparison and quantitative determination. The method seems to have sufficient merit to be considered for plant control purposes.

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Raney Nickel Catalyst of Improved Stability and Reactivity in the Hydrogenation of Triglycerides[1]

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Abstract

The degree of activity of Raney nickel catalysts in the hydrogenation of triglycerides has been found to vary considerably with and to depend upon unknown factors in the original alloy. Highly active preparations of Raney nickel rapidly lost their activity when stored in absolute ethanol due to the formation of acetaldehyde. Loss of activity was associated with the amount of residual aluminum in the catalyst. The nickel was found to dissolve to some extent in the acetaldehyde-ethanol solution. Catalysts deactivated by acetaldehyde could be reactivated to a greater degree of activity than that possessed originally by treating with acetic acid. The activity of the original Raney nickel catalyst was preserved to a greater extent by storage in dioxane instead of ethanol.

Introduction

IN THE COURSE of an investigation directed toward reducing the isomerization of unsaturated fatty acid groups during the hydrogenation of vegetable oils, it became evident that low-temp hydrogenation (below 100C) offered the most promise of attaining the desired objective. Since the nickel catalysts usually employed in the commercial hydrogenation of vegetable oils are not active below 100C, Raney nickel catalysts (2,3), which are prepared from a nickel-aluminum alloy and which are active below 100C, were selected. Most of the investigations were conducted with a specially-prepared Raney nickel designated by the developers as W-5 (2). It reportedly is a more active form than that obtained in the ordinary preparation. However, a W-5 catalyst loses its high activity after about a week's storage in absolute ethanol.

It was discovered that the rapid loss in activity of a W-5 type catalyst during storage in ethanol is caused by the formation of acetaldehyde. The substitution of dioxane for ethanol as the storage medium greatly prolonged the active life of the catalyst. Attempts to reactivate the acetaldehyde "poisoned" catalyst resulted in the development of a method of regenerating the catalyst in a form more active and stable than that originally present. This paper is a report of the details of the work on improving the stability and reactivity of Raney nickel catalyst.

Experimental

Three different lots of Raney alloy from two commercial sources were used. All of the alloys were of the same general composition. Semi-quantitative spectrophotometric analyses indicated that all contained small amounts of copper, iron, cobalt, and silicon; each particular trace metal was found to be present at ca. the same level of concn in all alloys.

The alloys were activated by a low-temp procedure based on that of Adkins and Billica (2). Sixty g of the alloy was added in one-half hour to a solution of 80 g sodium hydroxide in 300 ml water at a temp of 10–20C. Digestion was continued for 1 hr at a temp below 50C. The digested alloy was washed 5 times with approximately 500 ml water each time, the wash water being removed by decantation. The catalyst was then transferred to a medium-grade, fritted-glass funnel (350-ml capacity) and washed continuously by filtering 12 l water through it. After the water washing the catalyst was washed successively with 450 ml portions 95% ethanol and absolute ethanol. Each portion was divided into at least three smaller ones, and the catalyst was filtered practically to dryness between each addition. A dioxane wash, when used, immediately followed and was performed in the same manner as the alcohol washes. The catalyst was stored in the material last used for washing it. Catalyst prepared by this method will be referred to as W-5 type or low-temp digestion catalyst throughout this report.

The acetaldehyde, acetic acid, and ethanol were of the purest grades available. In all treatments, the quantities of catalyst and treating solution were found not to be critical; it was only necessary to have enough solution to cover the catalyst. Usually 5–10 g catalyst

TABLE I

Composition of Nickel-Aluminum Alloys

Alloy	Sieve analyses				Chemical composition	
	on 140 %	on 200 %	on 325 %	through 325 %	Al %	Ni %
1	0.2	5.9	25.6	68.2	45.4	50.6
2	0.3	9.0	22.9	67.8	47.6	49.4
3	0.0	2.0	15.5	82.5	45.9	51.0

and 50 ml solution were satisfactory. The acetaldehyde was used as a 20% solution, by volume, in absolute ethanol. In a typical treatment, freshly prepared catalyst was stirred in the acetaldehyde solution at room temp for 16 hr. The catalyst was used in a hydrogenation directly from the acetaldehyde treatment without washing. The acetic acid was used as a 20% solution, by volume, in distilled water. In an acid treatment, freshly prepared catalyst, or the acetaldehyde treated catalyst, was usually mixed with the acid solution for 5 min at 40C. After acid treatment, the catalyst was washed in the usual manner with water and ethanol. The various solvents were not removed completely from the catalyst for any of the treatments; the catalyst was simply transferred with as little solvent as possible from one solution to another.

A commercially refined, bleached, and deodorized cottonseed oil (iodine value 109.5) was used in all hydrogenations. Hydrogenations were carried out at atmospheric pressure in an essentially all-glass system previously described (1). Each hydrogenation was essentially a zero order reaction. The activity of the catalyst was gauged by the amount of hydrogen consumed by the oil in at least two 15-min intervals during the early stages of the hydrogenation. For very fast hydrogenation rates, readings were taken at 5-min intervals. The hydrogen uptake of a sample in the first 5 or 10 min of a run was not used to calculate the activity in order to allow for possible induction periods or other pecularities at the very beginning of the reaction. In the few instances when the rates of hydrogen uptake during the 15-min intervals were not the same, an average value was used. All hydrogenations were carried out at either 70C with 3% nickel or 170C with 0.5% nickel. Both original and treated catalysts were used immediately after preparation. Each series of hydrogenations using a particular preparation of original catalyst was completed within 24 hr. The amount of nickel was determined by stripping the solvent from the approximate amount of catalyst needed, accurately weighing the dried catalyst, and then adding the calculated amount of oil to give the correct concn. All operations were carried out under hydrogen. Sample sizes varied between 15 and 30 g. Activities were calculated as the ml of hydrogen adsorbed by 1 g oil in 1 min for each 1.0% of the catalyst.

One of the alloys was digested in the usual manner as described by Hilditch (3) for comparison with the W-5 type catalyst. The Hilditch catalyst will be referred to as a regular type or high-temp digestion catalyst throughout this report.

The amount of aluminum in the alloys and in the catalysts was determined by the method of Willard and Tang (4). The nickel content of the alloys was determined by precipitating with dimethylglyoxime after separating aluminum.

Results

Catalysts prepared in the same way from apparently similar alloys varied as much as fivefold in their activity. This variation was greater when the catalysts were used in low-temp hydrogenations (compare Alloys 1,2). There was no correlation among the activity of the catalysts in the high- and low-temp hydrogenations; the most active catalyst in the low-temp hydrogenations was not the most active in the high-temp hydrogenations. The regular type catalyst was considerably more active at the low temp than

TABLE II

Effect of Acetaldehyde and Acetic Acid Treatment on Relative Activities [a] of Type W-5 Raney Catalysts in the Hydrogenation of Triglycerides

Alloy	Original catalyst	Treatment		
		Acetaldehyde	Acetic acid	Acetaldehyde and acetic acid
Low-temp hydrogenation, 70C				
1	9	0	70	75
2	48	0	90	85
3	11	0	42	60
1 [b]	105	127	116	93
High-temp hydrogenation, 170C				
1	100	44	522	578
2	210	50	410	2500
3	258	88	778	800
1 [b]	78	1126	1572	3200

[a] Expressed as (ml hydrogen per g oil per min per 1% catalyst) $\times 10^3$.
[b] High temp digestion.

at the high temp. Fresh catalysts prepared from Alloy No. 1 were consistently low in activity; those prepared from Alloy No. 2 were consistently high.

The acetaldehyde treatment of the fresh W-5 catalysts resulted in a complete deactivation for hydrogenation at 70C and a significant reduction in activity at 170C. However, the regular catalyst showed an increased activity when treated with acetaldehyde, particularly for hydrogenations at 170C. The acetaldehyde treatment was observed to noticeably reduce the particle size of the catalyst and increase the apparent density.

The acid treatment of the freshly prepared catalysts increased their activity in every instance. The increase for the W-5 type catalysts varied from about two- to eightfold (compare Alloys No. 1,2), and this increased activity due to acid treatment was exhibited at both low and high temp of hydrogenation. As was the case with the acetaldehyde treatment, the acid treatment of the regular type Raney catalyst gave unusual results, only a small increase in activity at the low-temp hydrogenation but a surprising, twentyfold increase at the high temp.

The acid treatment of an acetaldehyde treated or "poisoned" catalyst of the W-5 type was effective in reactivating the catalyst, generally to the same order of magnitude as the acid treatment of an active catalyst. The acetaldehyde-acid treatment of the regular type catalyst had practically no effect on activity at 70C but increased greatly the activity at 170C, when measured against that of the original catalyst. With one exception the activity of acetaldehyde-acid treated catalysts was greater than that of the original catalysts. Also, there was evidence that acetaldehyde-acid treated catalysts could retain their activity through at least three or four hydrogenations whereas the acid-treated and original catalysts could not.

Two samples of W-5 catalyst prepared from Alloy No. 3 were stored for a month and a half in a refrigerator. When used in hydrogenations at 170C, the sample stored in dioxane had a relative activity of 0.214 ml per g per min per 1.0% catalyst, while the one from alcohol had fallen to 0.054. The original activity of both samples had been 0.258.

The relative activity of a commercial type, supported nickel catalyst prepared by electrolytic reduction of nickel hydroxide was 0.000 and 1.800 ml per g per min per 1.0% catalyst for hydrogenations at 70C and 170C, respectively. These hydrogenations were conducted at nickel concn equal to those employed with the Raney catalysts.

Discussion

In general, the activity of a catalyst depended on

the particular alloy used, the temp at which the hydrogenation was carried out, and the method of preparation of the catalyst. The method of preparation greatly affected the activity, but not always in the manner expected. That a regularly prepared catalyst was considerably more active in the hydrogenation of triglycerides at a low temp than at a high temp was surprising. This increase in activity at the lower temp may be due to the effect of catalyst concn. Six times as much catalyst was used in the hydrogenations at the low temp. That the highly active W-5 type catalyst was comparatively inactive in the low-temp hydrogenation of triglycerides was also unexpected. However, this catalyst was effective in the hydrogenation of methyl esters prepared from the same type oil used in the present investigation. Because molecular size and structure are known to greatly affect hydrogenation rate, the differences encountered are not too surprising. The greater viscosity of the oil cannot be responsible for the difference in activity because the addition of solvent to the oil did not prove a remedy. Adkins and Billica (2) hydrogenated stearolic acid to elaidic acid in 2 min with a W-6 catalyst but needed 118 min to hydrogenate the elaidic acid to stearic acid.

The results reported here were obtained toward the end of an investigation involving more than 30 catalyst preparations and 130 hydrogenations. However, it is not claimed that the conditions described represent the optimum for any of the treatments.

Although the dependence of the initial activity of a catalyst on the composition of the alloy has been suggested by other investigators (5), the great variation revealed in the present work was unexpected. This variation is much greater than can be accounted for by the experimental error of the methods. The activity of catalysts prepared from the same alloy by the same procedure resulted in activities of the same order of magnitude. Since there were no significant differences detectable in the alloys, the variations in activity must be due to unknown factors in the alloys.

It has been conclusively proven that acetaldehyde is the material responsible for the loss in activity of W-5 catalysts stored in ethanol. Refrigerated samples of W-5 catalyst stored in ethanol for more than a year gave off an odor of acetaldehyde when opened. The acetaldehyde is probably formed by the dehydrogenation of ethanol by the catalyst (6). It is also known that acetone is a poison or deactivator for Raney catalysts (7). Our tests with acetaldehyde in ethanol solution verified what was suggested by these facts. Conclusive proof was given by the stability of the catalysts when stored in dioxane. Probably other solvents that do not contain a carbonyl group, and will not form a carbonyl group when in contact with the catalyst, would be as effective as dioxane as a storage medium. Long chain alcohols have been suggested for storing Raney nickel catalysts (8).

The action of the acetaldehyde on the catalyst is not well understood. The simplest explanation would have the acetaldehyde adsorbed on the surface of the catalyst to deactivate it. Such adsorption would account for the apparent decrease in the adsorption of palmitic acid on the surface of an aged W-5 catalyst (5). However, both nickel and aluminum were found in the filtrate from the acetaldehyde treatment of the catalyst. Dissolution of the adsorbent is not generally associated with adsorption. Evaporation of the acetaldehyde solution resulted in a residue of greenish

crystals typical of nickel compounds. Although these crystals were found to act as a catalyst and slowly hydrogenated cottonseed oil at 200C, with little change in appearance (indicating very little nickel formed), they were not investigated further. Also, the mode of operation of the acetaldehyde is related to the aluminum content of the catalyst. Apparently a certain minimum amount of aluminum must be present before the acetaldehyde treatment will deactivate the catalyst. The amount of aluminum necessary for deactivation appears to be between 4 and 12%. Catalyst prepared by low-temp digestion and containing 11.2% residual aluminum is deactivated by acetaldehyde quite easily; a high-temp digestion catalyst containing 4.2% residual aluminum is not deactivated by acetaldehyde and will, in fact, resist deactivation even when treated for three or four days.

Both organic and inorganic acids have been used to promote the activity of Raney catalysts during hydrogenation. The acids were usually added to the hydrogenation mixture (9). An acid, whether added before or during hydrogenation, probably cleans the catalyst thereby exposing a fresh surface for reaction. The relative activity of an acid treated surface was fairly constant in our experiments regardless of the alloy used, thus lending credence to the idea of a uniformly clean surface. The drop in the activity of an acid treated catalyst during the hydrogenation of a sample, noticed in some of the low-temp runs, was probably due to adsorption of fatty acids and other impurities present in the triglycerides. Smith and Fuzek (10) have reported that fatty acids with from 10–22 carbon atoms are adsorbed on a Raney nickel catalyst. Acetic acid was probably not adsorbed on the catalyst since it was stipulated that for adsorption to take place the acid should not react with the catalyst. Why an acetaldehyde-acid treated catalyst is more stable, that is, may be used for numerous hydrogenations without loss of activity, is not clear.

Acid treatment of either a fresh or acetaldehyde poisoned catalyst results in an increase of catalytic activity to a more or less uniform level, regardless of the starting alloy. This was particularly noticeable in the low-temp hydrogenations. Beacuse the increase in activity in these same runs varied manyfold, large increases in activity after a particular treatment may be interpreted as being due to poor activity in the preparation of the original catalyst. Now acid treatment of an acetaldehyde poisoned catalyst used in high-temp hydrogenations sometimes resulted in a tremendous increase in activity. Therefore, assuming the same situation exists as in the low-temp runs, it may be hoped that proper adjustment of the reaction variables for the acetaldehyde and acid treatments, particularly in combination, could result in uniformly high activities and stabilities in Raney nickel catalysts.

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