of hydrogenation, other than the fact that in general those containing an exocyclic double bond undergo hydrogenation more readily than do those where all of the unsaturation is in the ring. Whether or not the terpene is monocyclic or bicyclic appears to be unimportant since there is no apparent difference in the rates of hydrogenation of the *p*-menthadienes, dipentene and terpinolene, when compared with the pinenes and camphene which are bicyclic terpenes.

It is interesting to note that the *p*-menthadienes undergo hydrogenation on either platinum or nickel more readily than do the *p*-menthenes, since it has already been shown that cyclohexene adds hydrogen much more quickly than does either the conjugated or unconjugated cyclohexadiene.[7] In this connection it would be interesting to study one of the *p*-menthadienes which has both double bonds in the ring.

As would be expected, the rates of hydrogenation of dipentene and the optically active *d*-limonene are identical in all cases.

Acknowledgment.—The authors are indebted to the Hercules Powder Company for a fellowship which made this research possible.

Summary

Dipentene, *d*-limonene, terpinolene, α- and β-pinenes and camphene have been hydrogenated over Adams platinum or Raney nickel catalyst, and the results subjected to kinetic analysis. It has been shown that carvomenthene is an intermediate in the hydrogenation of dipentene or *d*-limonene, while terpinolene yields a mixture of 3-*p*-menthene and another *p*-menthene (perhaps 2-*p*-menthene) as intermediates. The factors influencing the rates of hydrogenation of these terpenes have been discussed.

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[7] Smith and Meriwether, THIS JOURNAL, **71**, 413 (1949).

[CONTRIBUTION NO. 64 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Preparation and Aging of Raney Nickel Catalysts

BY HILTON A. SMITH, WILLIAM C. BEDOIT, JR., AND JOHN F. FUZEK

Several different methods for the preparation of Raney nickel catalyst from the standard alloy have been described. Mozingo[1] describes a preparation from the nickel–aluminum alloy according to which the aluminum is dissolved in sodium hydroxide leaving the active catalyst. It is stated that the temperature during the reaction should not rise above 25°. The catalyst is then digested on a hot-plate for twelve hours, and washed by decantation. Pavlic and Adkins[2] have indicated a revision of this method, according to which the alloy is treated with caustic at 50°, and washing is accomplished by a continuous process. The catalyst is claimed to be much more active than that prepared by the method of Mozingo. In a still more recent paper, Adkins and Billica[3] described a further modification in which the washing process was carried out under about 1.5 atmospheres hydrogen pressure. This catalyst (designated as W-6) is described as the most active catalyst known to the authors.

In connection with Mozingo's preparation, it is stated that the catalyst may lose much of its activity if it is kept too long. The purpose of the research reported here was to study the activity of various Raney nickel catalysts, considering both their method of preparation and the length of time which they had been kept.

Experimental

Raney nickel catalyst was prepared by the methods of Mozingo,[1] Pavlic and Adkins[2] and Adkins and Billica.[3] Special care was taken to follow the directions explicitly as given by the authors. In addition, several modifications were introduced. The alloy was taken from a single drum of commercial product furnished by Mr. Raney of the Gilman Paint and Varnish Company, Chattanooga, Tennessee.[4]

The activity of the catalyst was determined by measuring the rate of hydrogenation of freshly distilled *d*-limonene at a hydrogen pressure of 1000 p. s. i. by the method previously described.[5] The latter material was prepared by fractionation under carbon dioxide of Eastman Kodak Co. technical grade product. In addition, the surface areas of a number of these preparations were measured by the adsorption of palmitic acid from benzene solution as previously described.[6]

Experimental Calculations and Results

The rate of hydrogenation of the *d*-limonene has been shown to follow the equation

$$\log p_0/p = k't/2.303\ V$$

where p is the hydrogen pressure at any time, t, p_0 is the initial pressure, V is the volume of hydrogen gas in the system, *i.e.*, the total void which is constant for any system, and k' is the reaction rate constant.[5] (By dividing the value of k' by the weight of catalyst employed rate constants (k) referred to one gram of catalyst

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[1] Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[2] Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

[3] Adkins and Billica, *ibid.*, **70**, 695 (1948).

[4] According to Mr. Raney, this alloy had the following analysis: Ni, 51.06; Al, 48.19; Si, Fe, and Cu combined, 0.75. It was further stated that these latter three elements have percentages approximately as follows: Fe. 0.5; Si, 0.15; and Cu, 0.1.

[5] Smith, Fuzek and Meriwether, *ibid.*, **71**, 3765 (1949).

[6] Smith and Fuzek, *ibid.*, **68**, 229 (1946).

TABLE I

PREPARATION AND PROPERTIES OF RANEY NICKEL CATALYSTS

Temp. of reaction of alloy and caustic, °C.	Subsequent treatment	$k \times 10^4$ (l./g. × min.) for hydrogenation of *d*-limonene	Surface area, sq. meters/g.
10–25	Digested at room temperature for one hour; heated overnight on hot-plate; washed by decantation[1]	134	..
−5–+5		115	31.8
35–45		115	35.0
60 ± 2	Digested at 60–70° for one hour; heated overnight on hot-plate; washed by decantation	97	35.3
35–45	Digested at 35–40° for one hour; washed mechanically; digestion incomplete	55	27.7
35–45	Digested at room temperature for one hour; heated overnight on hot-plate; washed mechanically	106	37.5
50 ± 2	Digested at 50–60° for one hour; washed mechanically[2]	120	..
50 ± 1	Digested at 50–70° for one hour; washed mechanically	115	26.6
50 ± 2	Digested at 50–55° for one hour; washed mechanically	124	25.9
50 ± 2	Treated exactly as recommended by Adkins and Billica[3]	132	18.2

may be obtained.) It was found that slight impurities in the *d*-limonene caused variation in its rate of hydrogenation, and that a simple test could be applied to tell whether the terpene was sufficiently pure. When k' is plotted against the weight of catalyst used, a straight line passing through the origin should be obtained as long as equilibrium conditions are maintained. However, when the terpene is impure, the straight line is displaced so that it no longer passes through the origin. This is shown in Fig. 1. The deviations from linearity shown when catalyst weights greater than 0.3 g. are used are caused by inability to maintain shaking equilibrium. For this reason catalyst weights were kept below 0.3 g. Figure 2 shows a typical hydrogenation plot. It gives evidence that good results may be obtained even with the active catalysts used here.

All surface areas were calculated on the assumption that, under the conditions of adsorption of palmitic acid from benzene, the catalyst surface is covered with a unimolecular layer of palmitic acid, and that the cross section of each fatty acid molecule in the layer is 20.5 square ångström units.

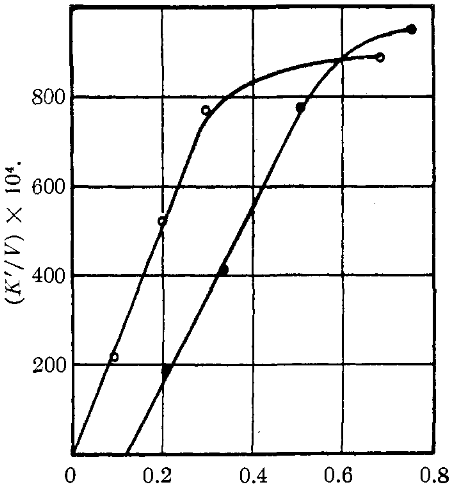

Fig. 1.—Influence of impurities on rate of hydrogenation of *d*-limonene: ○, pure sample; ●, impure sample.

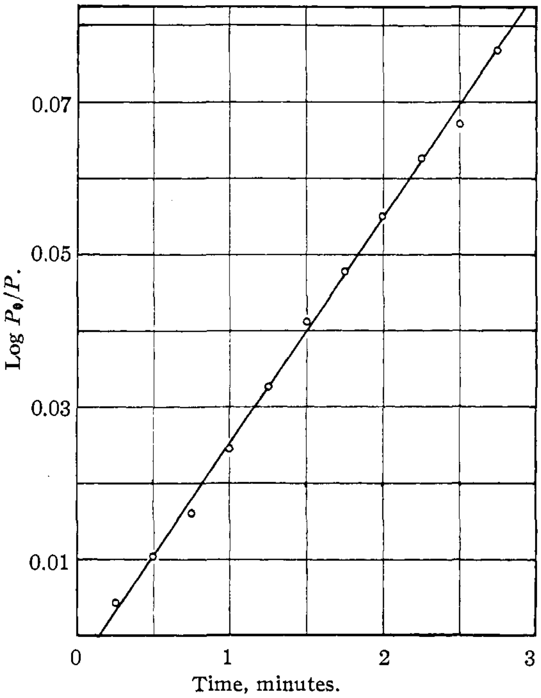

Fig. 2.—Typical hydrogenation plot for hydrogenation of *d*-limonene on an active sample of Raney nickel.

The results of both kinetic and surface measurements for a number of catalyst preparations are given in Table I. The influence of aging on the activity and surface area of such catalysts are shown in Figs. 3 and 4.

Discussion

A study of Table I shows that neither the method of reaction of the alloy with the sodium hydroxide solution, the time or temperature of the

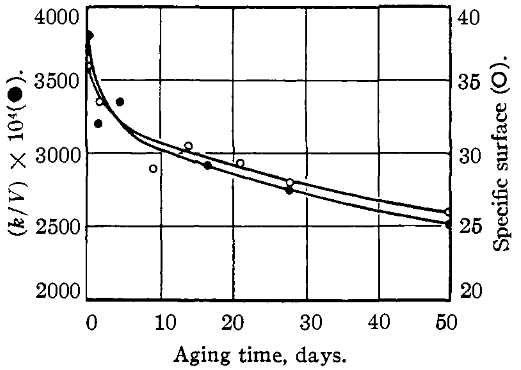

Fig. 3.—Influence of aging on surface area and catalytic activity of Raney nickel.

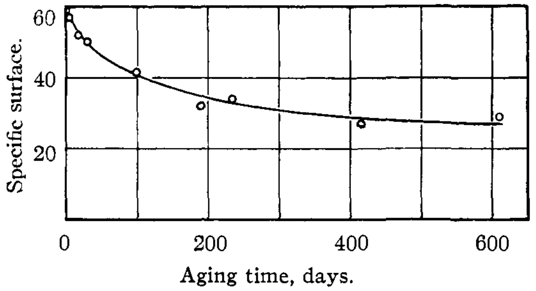

Fig. 4.—Influence of aging on surface area of Raney nickel. (These data were obtained in the course of work done under a fellowship from the Hercules Powder Company.)

digestion beyond a minimum of one hour at 50°, or the method of washing of the catalyst have any very noticeable effect on the activity of the nickel produced as measured by the rate of hydrogenation of *d*-limonene. On the other hand, differences in the original alloy may result in considerable differences in activity of the catalyst. Thus in some earlier work using different alloy rate constants much lower than those reported here were found.[6]

There seems to be no correlation whatever between surface area and initial catalyst activity. The catalyst used in connection with Fig. 4 was made from a different alloy, and had an initial activity only about 1% as great as that used for Fig. 3, although its specific surface was more than 50% greater. However, as Fig. 3 shows, there does seem to be a direct correlation between the decrease in catalytic activity and the decrease in surface area as the catalyst ages.

An examination of Figs. 3 and 4 indicates that the catalyst activity and the specific surface both decrease rather rapidly at first, but much more slowly over longer periods of time.

It has been previously shown that the activity of Raney nickel catalyst as measured by the rate of hydrogenation of *d*-limonene may be greatly affected by the presence of a small amount of additive such as palmitic acid.[7] The activity of a rather poor catalyst is increased and that of a rather good catalyst is decreased to a common value. Furthermore, the increase or decrease is proportional to the amount of fatty acid used until enough is present to cover the nickel surface, after which increasing amounts have little further effect. The catalysts prepared in connection with the work reported here were more active than those made from early samples of alloy. Therefore, a study of the influence of palmitic acid on this catalyst was undertaken. Figure 5 shows that the activity of the catalyst decreases with increasing amounts of fatty acid till it reaches about the same activity as that previously obtained, after which further addition of acid has little effect. The dotted lines in the figure are taken from earlier work[7] for comparison purposes.

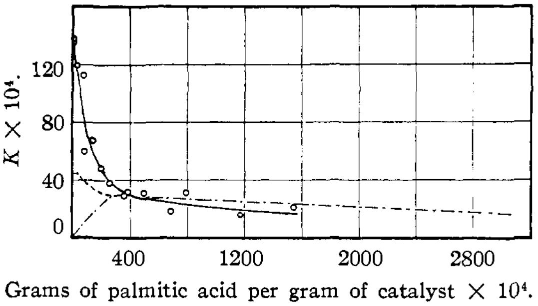

Fig. 5.—Hydrogenation of *d*-limonene on Raney nickel in the presence of palmitic acid: dotted lines represent behavior of less active catalyst samples; *cf.* Smith and Fuzek, ref. 7.

Acknowledgment.—The authors are indebted to the Office of Naval Research for financial support which made this research possible.

Summary

A study has been made of the activity of Raney nickel catalyst as affected by its method of preparation from the alloy and its age. It has been shown that different temperatures of solution of the alloy, different temperatures and times of digestion, and different methods of washing have little effect on catalytic activity as measured by the rate of hydrogenation of *d*-limonene. It has been further shown that, while the original specific surface of a catalyst has little influence on its initial activity, the change in surface with time is closely paralleled by the change in catalytic activity.

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[7] Smith and Fuzek, unpublished results.