THE PREPARATION AND TESTING OF NICKEL CATALYSTS FOR HYDROGENATION*

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In the course of an investigation of the hydrogenation of organic compounds over nickel and other base metal catalysts it seemed desirable to compare the relative merits of different catalysts. It was then necessary to consider what characteristics of the catalyst should be used as a basis for comparison. A catalyst for hydrogenation may have merit in a number of different ways, for example, catalyst X may be better than catalyst Y in that (I) it is possible to hydrogenate at a lower temperature or (2), pressure than with catalyst Y; or (3), less of X than of Y may be required to give a certain effect; or (4), catalyst X may cause a more rapid rate of absorption of hydrogen under a given set of conditions than does catalyst Y; or (5), a given amount of X may cause complete hydrogenation of a given weight of material in less time than does the same amount of Y; or (6) less of some undesired reaction may occur with X than with Y.

The more important variables that determine the numerical values which may be assigned to these characteristics are even more numerous than the characteristics which they modify. The rate of hydrogenation over a nickel catalyst may vary with (1) the acceptor of hydrogen, (2) the impurities in the latter, (3) the temperature during hydrogenation, (4) the pressure of hydrogen, (5) the amount and (6) kind of solvent, (7) the amount of catalyst, (8) the ratio of catalyst to hydrogen acceptor, (9) the time and (10) the temperature involved in all stages of the hydrogenation experiment, (11) the thoroughness of the mixing of the hydrogen acceptor, catalyst, and hydrogen. The last of these factors is made up of at least two components, one of these being the rate or thoroughness of mechanical agitation of the reactants, and the other the ease of dispersion of the catalyst in the reaction medium.

It will appear that not only the *numerical* but also the *relative* values of the characteristics of the various catalysts are dependent upon the acceptor of hydrogen, temperature, pressure, and the other variables referred to above, which are actually used in the testing of the catalysts. It is one of the primary purposes of this paper to exhibit experimental evidence that general and sound conclusions as to the relative activities of nickel catalysts, for example, may not be reached as the result of following what may be termed a conventional method of scientific work. By this is meant the method in which each factor is in turn varied while the other factors are held constant, followed by the tacit assumption that if there are for example three variables X, Y, and Z, the effect of varying X and Y *simultaneously* may be concluded from a knowledge of the effect of varying X and Y separately.

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For example, it will be shown that the relative merits of two catalysts are not the same for two different acceptors of hydrogen, nor for different characteristics of the catalyst, and therefore, it may be suspected that even the relative merits are not independent of the other variables, such as temperature, ratio of catalyst to acceptor, etc. which have been listed above. It has been shown in a previous paper¹ that the effect of variation in the pressure of hydrogen was rather specific for the compound undergoing hydrogenation, and it may be suspected that it differs with other variables such as the catalyst.

One may well be appalled at the amount of work involved in acquiring sufficient data to justify drawing positive conclusions on a reaction which involves six or more measurable characteristics and perhaps twice as many variables. This is especially true if the effect of simultaneous variability may not be predicted from a knowledge of the effect of the variation of one factor at a time. It is not the intention of the authors to attempt any such systematic survey but rather in the future to give especial consideration to those factors which determine the ratio of competitive or simultaneous reactions over nickel catalysts.

Preparation and Method of Treating Catalysts

In the experimental work described in this paper numerical values have been assigned to four of the characteristics of eight nickel catalysts for the hydrogenation of acetone, resorcinol, toluene, and benzyl alcohol. The temperature and the amount and ratio of catalyst to acceptor used for the hydrogenations were chosen because they gave a reasonably rapid rate of hydrogenation. The pressure of hydrogen (100 atmospheres) used is quite effective and is one that may be used without expensive equipment.¹ The rate of shaking of the reactants (41 cycles per minute) was one that has appeared to give a good suspension of the catalysts. The units for heating the bomb were of such a capacity that the contents of the bomb could be heated to 125° in 30 minutes and to 175° in 55 minutes.

Resorcinol, benzyl alcohol and acetone were hydrogenated at 125° while with toluene the temperature regulator was set for 175° but due to the rapidity of the hydrogenation the temperature of the toluene in some cases rose to about 250° . Two g. of catalyst containing approximately 16 percent of nickel was used with 1 mole of acetone, 0.62 moles of resorcinol and 0.23 moles of benzyl alcohol. Three g. of catalyst was used with 0.935 moles of toluene. Thirty five ml. of anhydrous ether was used as a solvent in the hydrogenation of resorcinol.

Seven different methods for the preparation of nickel catalysts were used in this investigation. Three of these involved differences in the source of nickel. In two of these the nickel was from nickel nitrate of varying purity and in one was from nickel chloride. Three different reagents, i.e., sodium carbonate, sodium bicarbonate, and potassium hydroxide were used for the

¹ Adkins, Cramer, and Connor: J. Am. Chem. Soc., 53, 1402 (1931.).

precipitation of nickel on the kieselguhr support. Two different methods for mixing the reagents were used. One of these (Method A) involved the addition of the soluble nickel compound (on kieselguhr) to the precipitant, in the other (Method B) the reverse order was followed, i.e., the addition of the precipitant to the soluble nickel compound (on kieselguhr).

In the preparation of all catalysts the solution of the nickel salt was thoroughly incorporated into the kieselguhr by grinding the partly moistened powder in a mortar until it was of a cream-like consistency. This procedure which was originally suggested and used by Mr. Karl Folkers in this Laboratory, makes it possible to easily reproduce very active catalysts. The use of kieselguhr as a support for a nickel catalyst has been criticised because difficulty was experienced in reproducing the activity of catalysts. A similar difficulty was encountered in this Laboratory until Folkers' procedure was used. All catalysts were washed as previously described¹ except that they were suspended twice instead of once in 300 ml. of water. The concentration of the various precipitating solutions used with 100 g, of acid washed kieselguhr and 100 g. nickelous nitrate hexahydrate (or its equivalent) in 150 ml. of water were as follows:--120 g of sodium carbonate decahydrate in 100 ml. of water, 60 g. sodium bicarbonate in 260 ml. of water, 24 g. of potassium hydroxide in 100 ml. of water. Sodium bicarbonate as a precipitant was first used in this Laboratory by Mr. Ralph Connor who did so on the supposition that a basic nickel carbonate of more uniform composition could be obtained under certain conditions with this reagent than through the use of sodium carbonate.² The methods and reagents used in preparing each catalyst are indicated in Table I.

Reagents:—A "C.P." grade of nickel nitrate from the Baker and Adamson Company was used unless otherwise noted. Nickel nitrate prepared from the reaction of "C.P." grade nitric acid and pure nickel pellets from the International Nickel Company was used in the preparation of catalyst 11 Cv. The toluene b.p. 110.5-111° was C.P. grade free of sulfur. The acetone had a b.p. of 56.5 while the resorcinol was a U.S.P. grade m.p. 110°. The best grade of benzyl alcohol from the Eastman Kodak Company was further purified since rather erratic results were obtained in attempting to reduce different lots of this product. The alcohol was refluxed 12 hours with a 35 percent solution of potassium hydroxide; and then distilled through a Widmer column at 203.5-205.0°. The product was then heated for 5 hours at 100°, under 70 atmospheres of hydrogen with reduced nickel. This removed any halogen containing impurities. The nickel was prepared by the reduction of 5 g. of nickel oxide (prepared by the decomposition at 250° of nickel carbonate) for four hours at 350°. The amount of nickel so obtained was used with 150 ml of alcohol.

The products from the hydrogenation of benzyl alcohol were fractionated, toluene being collected $108-112^{\circ}$ (740 mm) and cyclohexyl carbinol 175-185 (740 mm) by far the greater part coming over $179-180^{\circ}$. Cyclohexanol and

¹ Adkins and Cramer: J. Am. Chem. Soc., 52, 4351 (1930).

² Cf. Gmelin-Kraut: 5, 108.

cyclohexanediol 1-3 from the hydrogenation of resorcinol were collected at 60-65° (10 mm) and 124-134 (10 mm) respectively, although in most cases at least oo percent distilled over a 1° range. The products from the hydrogenation of toluene and acetone were methyl cyclohexane and propanol-2, respectively, and each distilled over a 1° range.

The kieselguhr used as a support for the nickel catalyst was in most cases from the Meyer Drug Company, St. Louis. However, there appeared to be no difference in activity between the catalysts on this support and those on "Filter-Cell" supplied by the Johns-Manville Company, New York.

The apparatus and method of experimentation were essentially the same as those previously described by Adkins and Cramer.

Reproducibility of Results:--The extent of variation in the data obtained in different experiments with duplicate samples of catalysts and with samples of catalysts prepared in the same way but at different times is indicated by plus and minus figures given in Tables I and II. All significant experiments were duplicated at least twice while the total number of hydrogenation experiments on which this paper is based is 145.

Comparison of Catalysts

The relative merits of catalysts may be compared in a number of different ways as noted above. Four of the characteristics of nickel catalysts will be considered in this comparison. The experimental basis for the first comparison is the time required for the adsorption of the middle 60 percent of the total amount of hydrogen absorbed. For this purpose the time for the absorption of the first and last 20 percent of hydrogen is disregarded. This comparison is thus between the activities of catalysts during the chief period of activity.

There is tabulated in Table I the time for the 60 percent of hydrogenation used as the basis for the first comparison. Limiting the comparison for the moment to the four catalysts made by the two methods through the use of sodium carbonate and sodium bicarbonate, it may be seen from the data in the table that they are all four quite active towards toluene, the differences between them being small. For acetone the bicarbonate A method catalyst (10 Cv) was distinctly inferior to the other three catalysts. The carbonate A method catalyst (8 Cv) was distinctly inferior as regards the rate of hydrogenation of benzyl alcohol and of resorcinol. The B method of preparing catalysts is better than the A method in every case for the carbonate catalysts (15 Cv) and is better than or as good as the A method in case of the bicarbonate catalysts. However, with no compound is the difference between the two methods as marked with the bicarbonate as with the carbonate catalysts.

Extending the comparisons to include the eight catalysts it may be said that potassium hydroxide may be used as a precipitant for nickel, the resulting catalyst (13 Cv) being somewhat inferior to the corresponding carbonate catalyst except for benzyl alcohol. A similar statement may be made in

TABLE I

Time in Minutes for Hydrogenations over Various Catalysts¹

Catalyst	Toluene	Acetone	Benzyi Alcohol	Resorcinol
$8 \text{ Cv} (\text{Ni}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3) \text{ A}$	7.5±1.5 (11)	12.5±3 (27)	15 ±2	430 ±75 (1250)
15 Cv (Ni(NO ₃) ₂ + Na ₂ CO ₃) B	$\begin{array}{c} 6.5 \pm 2.0 \\ (26) \end{array}$	11.5±2 (18)	8 ± 1	275 (490)
10 Cv (Ni(NO $_3$) ₂ + NaHCO $_3$) A	8.7 ±0.7 (21)	18.5±2 (56)	8.5±0.5	260 ±25 (540)
16 Cv (Ni(NO ₃) ₂ + NaHCO ₃) B	6 ± 1.0 (14)	$(34)^{13.7 \pm 2}$	8 ± 2	217 ±8 (490)
13 Cv (Ni(NO ₃) ₂ + KOH) A	9.7±0.8 (24)	16 ±1 (37)	7 ±1	350 ±13 (900)
12 Cv (NiCl ₂ + NaHCO ₃) B	7 · 5 ± 1 · 0 (20)	13.8±1 (30)	4·5 ±°	220 ±50 (425)
$11 \text{ Cv} (\text{Ni}(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3) \text{ A}$	8 ±2.0 (17)	16 ±4 (31)	I2 ±3	265 ±65 (715)
13 HC (Ni(NO ₃) ₂ + Na ₂ CO ₃) A	36 ± 18 (60)	40 ±10 (66)	19 ±2	562 ±12 (1410)

¹ The figures in parenthesis are the average times for complete hydrogenation, while the others are for the "middle 60 percent" of hydrogenation.

regard to nickel chloride as a source of nickel except that toward benzyl alcohol and resorcinol it was one of the most active catalysts used in this investigation.

The catalyst (11 Cv) prepared from nickel nitrate made in this Laboratory from C.P. nitric acid and C.P. nickel pellets was not much more active than that made from the Baker and Adamson nickel nitrate. The catalyst prepared by Cramer (13 HC), which was one of the most active of those used in his experimentation, was very distinctly inferior to the catalyst prepared by the modified method described in this paper.

The experimental basis for a second comparison of catalysts is the temperature at which the pressure of hydrogen reached a maximum and will be referred to as the "inflection temperature". This temperature is the one at which the rise in the pressure of hydrogen due to the rise in temperature of the bomb was compensated for by the absorption of hydrogen. Along with this may be considered the percentage of the compound which was hydrogenated before the temperature set for hydrogenation was reached. These two experimental observations in almost all cases parallel each other and both give an insight into the behavior of the catalyst in its youth. For toluene the inflection temperature was approximately 105° for 15 Cv, 10 Cv, and 16 Cv while for 8 Cv it was 130° . For acetone the inflection temperature was 80° for 15 Cv and above 100° for the other catalysts. For benzyl alcohol catalyst 12 Cv gave an inflection temperature of 90° while for the others the inflection temperature, with resorcinol. In the case of 15 Cv with acetone 53 percent was hydrogenated below 125° while with other catalysts the amount so hydrogenated was usually less than 30 percent. With benzyl alcohol 83 percent of the compound was hydrogenated below 125° with catalyst 12 Cv while with most of the other good catalysts only 50 to 60 percent so reduced.

The experimental basis for the third comparison is the time required for the absorption of all the hydrogen. These values are given in parenthesis in Table I. Toluene is hydrogenated so rapidly and the reaction is so exothermic that the hydrogenations did not occur under identical temperatures. However, it should be noted that catalyst 8 Cv which was quite inactive at low temperatures gave a complete hydrogenation in the shortest time (11 minutes) as compared with the bicarbonate catalyst 10 Cv which required 21 minutes and 13 HC which required 60 minutes. With acetone the bicarbonate catalysts (10 and 16 Cv) required a distinctly longer time (34 to 56 minutes) than did the carbonate catalysts (8 and 15 Cv) (18 to 27 minutes). With resorcinol catalyst 8 Cv required 1250 minutes while 15, 10, and 16 Cv need approximately 500 minutes.

The fourth basis of comparison is only applicable to benzyl alcohol and resorcinol for it involves the ratio of products formed, i.e., toluene and cyclohexyl carbinol from the former and cyclohexanol and cyclohexanediol 1-3 from the latter compound. There is recorded in Table II the percentage yield of these products over six catalysts. Only the two products mentioned above are formed from benzyl alcohol, so that the percentages of toluene and cyclohexyl carbinol add up to 100 percent. However, in the case of resorcinol there is formed over some catalysts (notably 8, 13, and 15 Cv) considerable quantities of condensation products so that the percentages of cyclohexanol and cyclohexanediol add to 78, 87, 84, 94, and 100 percent for the various catalysts.

The carbonate catalysts gave 150 to 200 percent as much cyclohexyl carbinol as did the bicarbonate catalysts. The potassium hydroxide catalyst gave the lowest yield of the alcohol. The bicarbonate catalysts gave the better yields of cyclohexanediol 1-3 from resorcinol, the B method of catalyst preparation being very much superior. The A method with the bicarbonate gave the same yield of cyclohexanol as did the B method with the bicarbonate. If A and B are interchanged in the above sentence it is still true. It is rather striking that the catalyst (16 Cv) which was least active in eliminating a hydroxyl from resorcinol was the most active (of the carbonate and bicarbonate catalysts) for the removal of the hydroxyl group in benzyl alcohol.

TABLE II

Catalyst	Benzyl Alcohol		Resorcinol		
	Toluene	Cyclohexyl Carbinol	Cyclohexanol	Cyclohexane- diol 1-3	
8 Cv (Na ₂ CO ₃) A	73 ± 3	27 ± 3	II ± 2	67 ± 3	
15 Cv (Na2CO3) B	70 ± 1	30 ± 1	$22 \pm I$	65 ±2	
13 Cv (KOH) A	90 ± 2	10 ± 2	16 ± 1	$68 \pm I$	
10 Cv (NaHCO ₃) A	82 ± 2	18±2	$20 \pm I$	$74 \pm I$	
16 Cv (NaHCO ₃) B	85 ± 2	15±2	$II \pm I$	89 ± 1	
13 HC (Na ₂ CO ₃) A	66 ± 2	34 ± 2	8 ± 1	75 ± 3	

Proportion of Products from Hydrogenation of Benzyl Alcohol and Resorcinol over Various Nickel Catalysts

It thus appears that the factors which determine the activity of a catalyst for the absorption by a hydrogen acceptor are quite different from those which determine the relative rates of what must be simultaneous and competitive reactions. For example, catalysts 15 Cv and 16 Cv gave very similar rates of hydrogenations for resorcinol while with 15 Cv the ratio of cyclohexanol to cyclohexanediol was 1 to 3 while with 16 Cv it was 1 to 8 or more. Catalyst 8 Cv and 13 HC were similar to 16 Cv in ratio (1 to 6 and 1 to 9 as compared with 1 to 8) yet the two latter catalysts were very inactive as compared to 16 Cv.

Catalysts not made by Precipitation:—The above comparison of catalysts was confined to the type in which a nickel compound was precipitated on kieselguhr, because it has seemed to us that this type of nickel catalyst was quite superior to those obtained by decomposing nickel nitrate or nickel carbonate either alone or on a support. Brown, Etzel, and Henke¹ among others decomposed nickel nitrate on kieselguhr and reduced the resulting oxide for several hours, and Bradt² reduced nickel carbonate. The following experimental evidence may be cited in justification of our preference for the "precipitated on kieselguhr" type of catalyst. Bradt obtained a 100 percent hydrogenation of p-nitrophenol within 120 minutes or less using a ratio of 1 part of nickel carbonate to 5 parts of p-nitrophenol at 125°, and 34 atmospheres pressure. A catalyst prepared in this Laboratory according to his directions brought about the complete hydrogenation of p-nitrophenol in 75 minutes. One part of our catalyst 16 Cv to 17 parts of p-nitrophenol induced 100 percent hydrogenation within 25 minutes, 90 percent of the hydrogenation occurring within 10 minutes. If the ratio of nickel to nitrophenol had been as great in this case as in the experiments of Bradt the nitro group would no doubt have been completely hydrogenated within a very few minutes. Catalyst 16 Cv brought about the complete hydrogenation of toluene and acetone in 14 and 34 minutes respectively while under identical conditions the catalyst prepared by Bradt's method did not give complete hydrogenation after 5 Nickel catalysts prepared by reducing nickel oxide, deposited by hours.

¹ Brown, Etzel, and Henke: J. Phys. Chem., 32, 633 (1928).

² Bradt: J. Phys. Chem., 34, 2711 (1930).

decomposing nickel nitrate on kieselguhr as by Brown, Etzel and Henke, were very much inferior even to those prepared by Bradt's method. It should be pointed out that almost any nickel catalyst will bring about the hydrogenation of easily reducible substances such as acetone and sulfur-free nitro compounds but that the hydrogenation of toluene and resorcinol impose a more severe test upon a catalyst.

Summary

Various bases for the comparison of nickel catalysts have been suggested and experimental evidence has been given that the relative merits of catalysts may vary with the basis of comparison, as well as with the particular compound and experimental conditions under which the comparisons are made. In particular it has been shown that for nickel catalysts there is no necessary relationship between the rate of hydrogenation and the relative rates of competitive hydrogenations. Improvements in the methods for the preparation of nickel catalysts have been described and the relative values of different precipitants for depositing nickel compounds on a carrier have been measured for the rate of hydrogenation of toluene, acetone, benzyl alcohol and resorcinol. The ratio of cyclohexyl carbinol to toluene and of cyclohexanediol 1-3to cyclohexanol produced from benzyl alcohol and resorcinol respectively has been determined for the catalysts described.

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