

tion of the history of the preparation. It is suggested that the mode of heating is critical, and the variability commonly observed with catalysts prepared by the older procedure may be accounted for by variations in the heating process.

The temperature of 520° is not critical, since catalysts prepared at 500° and at 540° were almost as active as those prepared at 520°. Decreased activities are obtained with temperatures in excess of 540°.

Whereas specific data are given for maleic acid, a corresponding degree of reproducibility was obtained with gossypol, and pertinent data relating to the hydrogenation of this toxic pigment will be reported elsewhere.

Reagents Used.—The ethyl alcohol was distilled from an alkaline suspension of colloidal silver oxide. The maleic acid, C.P. grade, was removed from the manufacturers container and recrystallized three times from diethyl ether. The hydrogen was a commercial grade of electrolytic hydrogen. The chloroplatinic acid was C.P. grade, and it was taken directly from the manufacturers container. The sodium nitrate was reagent grade.

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Carbonyl Nickel Films as Hydrogenation Catalysts

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Thin nickel films produced by the thermal decomposition of nickel carbonyl on Pyrex glass have been found to be active hydrogenation catalysts. Films of nominal thickness of 0.1 μ were satisfactory catalysts for the reaction of hydrogen with propylene. Small quantities of carbonyl nickel catalysts were readily prepared using a static decomposition method. A continuous flow method was found suitable for obtaining large amounts of catalyst. Several series of experiments were carried out with catalysts formed on Pyrex wool at 150°, employing about 90 mg. of nickel, as well as thin films (*ca.* 4 mg.) deposited directly on the walls of a Pyrex vessel. For equimolar mixtures of hydrogen and propylene at 37 and 80°, the rate of the reaction could be expressed accurately by the equation: $-dp/dt = kp^2/(1 + Kp)^2$, where p is the partial pressure of either reactant. This suggests that the operative mechanism is competitive adsorption of both reactants with no interference from product. It was not found possible to produce surfaces of reproducible catalytic activity. The films were quite susceptible to poisoning.

Introduction

Although nickel carbonyl has been used as a catalyst for various reactions,² the catalytic behavior of pure nickel produced from the thermal decomposition of nickel carbonyl does not appear to have been investigated. This report is concerned with the direct use of carbonyl nickel films as catalysts for kinetic investigations. A brief study of the hydrogenation of propylene was undertaken to ascertain the suitability of such catalysts for controlled kinetic experiments. Previous investigations have employed evaporated nickel films,^{3a} nickel filaments activated by oxidation and reduction,^{3b} bulk nickel from the decomposition of nickel carbonate with subsequent reduction,⁴ and Raney nickel.⁵ Except for the evaporation technique, these methods lead to uncertainty in the initial condition of the surface, particularly with regard to dissolved and adsorbed hydrogen. It is thought that the preparation of a pure nickel film from nickel carbonyl combines many desirable features of the evaporation technique with relative simplicity of procedure. It is certain that the surface may be obtained initially free of hydrogen, which may be of value in studies involving isotopes

of hydrogen. The total surface area and crystalline state should depend upon the decomposition temperature, the initial pressure of nickel carbonyl, the area of the hot wall at which decomposition occurs, and the out-gassing conditions. These may possibly be controlled more easily than the many variables involved in some of the other preparatory methods.

Experimental

Materials.—Nickel carbonyl (International Nickel Co.) prepared by the Mond process and subsequently distilled, is stated to contain <0.004% Fe, other metals and sulfur absent. The liquid was out-gassed at -78° directly before use.

Propylene (Phillips "Pure" Grade) was purified by bulb-to-bulb distillation. Mass spectrometric analysis showed 1.3% propane, with no other impurity.

Electrolytic tank hydrogen was purified by diffusion through a heated palladium tube.

Apparatus.—The experiments were carried out in a Pyrex high vacuum system, consisting of a conventional gas purification and storage arrangement, a gas mixing and Toepler transfer system for introduction of hydrogen and propylene into the reaction chamber, and several different nickel carbonyl decomposition vessels. A capillary mercury manometer was used to follow the hydrogenation reactions. In order to minimize the introduction of mercury vapor by diffusion, the cell was never connected with the manometer while under vacuum. Reactant gases were passed through a packed tin trap before admitting to the cell.

Two methods of catalyst preparation were employed. For large amounts, a known quantity of nickel carbonyl was allowed to flow through a heated tube packed with Pyrex wool; for small deposits, a static method was used whereby a known quantity of the gas was decomposed on the heated walls of a Pyrex vessel. After deposition of the film, the catalyst chamber was out-gassed at temperatures above 300°, and in certain cases allowed to cool in the presence of hydrogen (*ca.* 2 cm.). The details of a typical experiment of each type are presented below.

(1) Taken from M.S. thesis of L. Baker, Illinois Institute of Technology, 1951.

(2) For example, see: G. DuPont, P. Piganiol and J. Vialle, *Bull. soc. chim. France*, 529 (1948).

(3) (a) O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc. (London)*, **A177**, 62 (1940); (b) O. Toyama, *Rev. Phys. Chem. Japan*, **14**, 86 (1940).

(4) E. S. Corner and R. N. Pease, *Ind. Eng. Chem., Anal. Ed.*, **17**, 564 (1945).

(5) R. Paul, *Bull. soc. chim.*, **7**, 296 (1940).

For the experiments designated CI, nickel carbonyl was rapidly pumped from a 340-cc. reservoir through a Pyrex wool packed cell of 11.6 cc., maintained at 150°. The initial and final pressures were 10.1 and 1.60 cm., respectively, corresponding to 90 mg. of nickel deposited, assuming complete decomposition. The absence of nickel at the downstream end of the heated column evidenced complete decomposition. After evacuation at 390° for several hours, an equimolar mixture of hydrogen and propylene was introduced to a pressure of about 12 cm., with the cell at 80°, and pressure vs. time data obtained. After a run, the cell was evacuated either at the ambient temperature or at 350° and a new charge of reactants introduced.

For the catalyst FI, the static method of decomposition was used. Two adjacent unpacked tubes of 11 cc. each were connected in parallel so that the decomposition could be carried out in each simultaneously. Each cell was provided with a separate manometer for isolation; kinetic runs were obtained for the individual catalysts. Nickel carbonyl was introduced to a pressure of 15.20 cm. in a total volume of 190 cc. A dewar flask containing glycerol at 150° was rapidly raised immersing the cells. The final pressure at room temperature was 19.13 cm. Thus, the calculated amount of nickel deposited on the walls of each cell was 3.9 mg.⁶ After deposition of the catalyst, the cells were evacuated at 315° and then brought to 80° for the duplicate kinetic runs. Between successive runs in the series the two catalysts were treated identically.

Results

Three different catalyst preparations on Pyrex wool substrates were made by the flow method. In experiment CI, after initially out-gassing the catalyst, the first hydrogenation proceeded to equilibrium so rapidly (*ca.* 2 min.) that no quantitative rate data were obtainable. After again out-gassing at 350° a series of successive runs were carried out at 37°, out-gassing at 37° between runs. The experimental data for runs 7, 8, 9 and 10 are shown in Fig. 1. The solid curves represent the theoretical fit to the data using the rate expression $-dp/dt = kp^2/(1 + Kp)^2$, where p is the partial pressure of either reactant, and k and K are parameters whose significance will be discussed later.

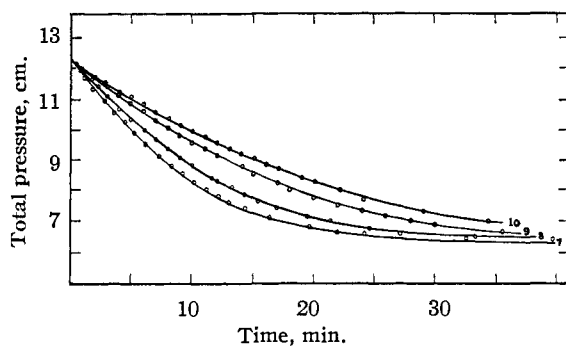


Fig. 1.—Hydrogenation runs CI-7, 8, 9 and 10; Pyrex wool packed reactor, 37°; equimolar $H_2-C_3H_6$ mixture: O, experimental points; —, theoretical curve.

For catalyst FI, prepared in the dual cell apparatus, the results of a typical experiment at 80° are shown in Fig. 2 for run FI-3(LH).

Table I summarizes the data for the series CI-4 through CI-10 and FI-3(LH and RH).

A series of experiments was carried out with catalyst FII, prepared in exactly the same way as FI. Each of two tubes was plated at 150° with

(6) Subsequent polarographic analysis of solutions obtained by eluting the nickel from the cells with nitric acid gave 3.7 and 4.4 mg. Ni for the individual tubes.

TABLE I
KINETIC DATA FOR TYPICAL HYDROGENATIONS

Expt.	K (cm.) ⁻¹	k (cm.) ⁻¹ (min.) ⁻¹	$t_{1/2}$ (min.)
CI-4	0.833	0.717	4.8
5	.760	.526	5.6
6	.699	.404	6.4
7	.640	.326	7.2
8	.643	.265	8.6
9	.600	.181	11.7
10	.612	.156	14.0
FI-3(LH)	.342	.038	28.5
(RH)	.203	.0033	179

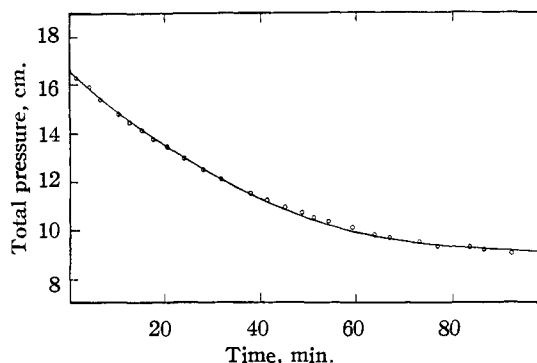


Fig. 2.—Hydrogenation run FI-3(LH); unpacked reactor, 80°; equimolar $H_2-C_3H_6$ mixture: O, experimental points; —, theoretical curve.

4.2 mg. of nickel. Hydrogenations were carried out at 0° using a 3:1 molar ratio of hydrogen to propylene. The catalyst was out-gassed at 310° and allowed to cool in a hydrogen atmosphere before each run. Data for experiments FII-6 and 7(RH) are shown in Fig. 3.

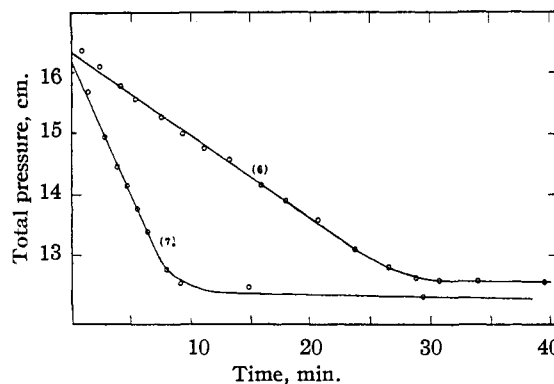


Fig. 3.—Hydrogenation runs FII-6(RH) and FII-7(RH); unpacked reactors, 0°; 3:1 molar ratio $H_2-C_3H_6$: O, experimental points.

In addition to the kinetic experiments, some of which were reported above, certain qualitative observations of the properties of the carbonyl nickel films were made. A special cell was constructed to allow observation of the catalyst surface during the deposition. This cell was made with an inner-sealed tube (1.2 × 10 cm.) through which glycerol at 150° could be pumped rapidly, with nickel being deposited on its outer surface. The cell volume was 183 cc.; the initial and final pressures were

10.6 cm. and 33.4 cm., respectively, corresponding to a total deposit of 44 mg. of nickel. At first, a brilliant mirror was formed; this suddenly became a coarse black surface, which gradually took on the gray metallic appearance of bulk nickel. The threshold of appearance of the black surface corresponded to 6 mg. of nickel (nominal surface concentration, 0.15 mg./cm.²). Table II gives the appearance and estimated surface concentrations for all catalysts.

TABLE II
CHARACTERISTICS OF CATALYST SURFACES

No.	Wt. of Ni, mg.	Nominal concentration mg./cm. ²	Nominal film thickness, microns ^c	Appearance
AII	150	"..	..	Black ^b
CI	90	"..	..	Black ^b
CII	105	"..	..	Black ^b
DII	5.0	0.090	0.10	Mirror
EI	29	.310	.35	Grey
FI	3.9	.067	.07	Mirror
FII	4.2	.070	.08	Mirror
GI	44	1.13	1.30	Grey

^a Catalyst supported on Pyrex wool. ^b Packing appeared black, walls had mirror-like appearance. ^c Nominal film thickness based on a uniform film of density 8.9 g./cc.

An X-ray diffraction pattern was obtained for a layer of nickel stripped from cell GI. The pattern showed all the lines⁷ for the Ni lattice with no other lines present. Their spotty structure suggested a crystallite size of 1–10 microns.

Discussion

The kinetics of hydrogenation of propylene on carbonyl nickel are most easily interpreted on the basis of a "competitive adsorption" mechanism. The postulate of competitive adsorption of reactants with no interference due to products leads to the rate expression $-dP_1/dt = k'b_1P_1b_2P_2/(1 + b_1P_1 + b_2P_2)^2$ where k' is the specific rate constant, while b_1 and b_2 are adsorption coefficients for the reactants 1 and 2 whose partial pressures are P_1 and P_2 , respectively. Eyring⁸ and co-workers concluded that this mechanism gives results in best agreement with available data for the catalytic hydrogenation of ethylene. For equimolar initial concentrations a simple method of integration may be employed. Defining $p = P_1 = P_2$, $k = k'b_1b_2$, and $K = b_1 + b_2$, the rate equation becomes $-dp/dt = kp^2/(1 + Kp)^2$. Integrating from $p = (1/2)P^0$ at $t = 0$ to $p =$

$P - (1/2)P^0$ at time t , where P^0 is the total (observed) initial pressure, and P is the total pressure at time t , one obtains the result

$$K^2(P^0 - P) + 2K \ln [P^0/(2P - P^0)] + \frac{4(P^0 - P)/P^0(2P - P^0)}{4(P^0 - P)/P^0(2P - P^0)} = kt$$

From the experimental plot of P vs. t , P^0 was determined by a small extrapolation to zero time. Two experimental points from the run were used to evaluate the parameters K and k by solving two quadratic equations simultaneously, and a "theoretical curve" drawn. It may be seen from Figs. 1 and 2 that this rate equation represents the kinetic data quite accurately.

Unfortunately, the experimental results do not entirely preclude the possibility of the alternative mechanism of "non-competitive adsorption" of reactants. Here $-dP_1/dt = K'b_1P_1b_2P_2/(1 + b_1P_1)(1 + b_2P_2)$; this reduces for the equimolar case to the form $-dp/dt = kp^2/(1 + \alpha p + \beta p^2)$, where k , α and β are obvious combinations of K' , b_1 and b_2 . This equation requires three experimental points to test its validity; because of the power of any three-parameter fit, this does not seem a definitive test.

The hydrogen-rich experiments at 0° all showed a marked zero-order behavior. Two of these curves are shown in Fig. 3. A precisely zero-order rate cannot be *explicitly* obtained from the competitive adsorption mechanism; for the non-competitive case if both adsorption coefficients are large, zero-order is obtained. Eyring has shown, however, that the competitive mechanism may give rise to curves which *appear* zero-order initially. The accuracy of our zero-order data is not sufficient to accept or reject the competitive mechanism on this account.

The marked downward trend in the two parameters k and K in series CI (shown in Table I) suggests that progressively more surface was occupied by a catalyst poison of unknown identity.⁹

The results of this investigation indicate that carbonyl nickel films may be used as hydrogenation catalysts, which may be prepared readily in the quantity desired. Since the surface is initially free of hydrogen, it would appear well suited for investigations concerned with addition, isomerization and exchange reactions of hydrocarbons using deuterium or tritium.

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(7) A. S. T. M., X-Ray Diffraction Data Cards.

(8) H. Eyring, R. Parlin, M. Wallenstein, B. Zwolinski, Office of Naval Research, Technical Report No. IV, Project No. NR-057-192, University of Utah, 9/15/50. Certain aspects of the mechanism of catalytic hydrogenation are presented in *Disc. Far. Soc.*, No. 8, 1950.

(9) Mass spectrometer analysis of the reaction products for several experiments revealed no abnormal materials. In one preliminary experiment, however, a trace of methylacetylene or propadiene was found.