

Fig. 2.—Representation of the variation of the ratio $\{k(h_6)/k(d_x)\}_0$ as a function of x (after Rabinovitch and Setser, ref. 10).

to H migration in all cases), the computational results cannot be exact, but undoubtedly give the correct magnitudes. The rise shown in Fig. 2 between $x = 5$ and $x = 6$ corresponds to a primary effect due to the gross alteration in the collisional activation reaction coordinate attendant upon the *complete* replacement of H atoms by D atoms. Although information on primary intermolecular isotope effects can be obtained^{11,12} at the higher pressures from the measurements of the

- (11) (a) R. E. Weston, *J. Chem. Phys.*, **23**, 988 (1955); **26**, 975 (1957);
 (b) R. H. Lindquist and G. K. Rollefson, *ibid.*, **24**, 725 (1956).
 (12) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).

total rates of isomerization for the cases, $1 \leq x \leq 5$, the change in the nature of the reaction coordinate precludes the possibility of finding similar information from such measurements at the low pressure limit; detailed knowledge of the proportions of the various possible isotopic products would be necessary, in addition, in order to decipher the intramolecular rate ratios.

Weston^{11a} has studied the variation with pressure of the isotope effect for cyclopropane-cyclopropane- t_1 at 775°K. He found that the primary isotopic rate ratio per bond, k_H/k_T , had a high pressure value of 3.7, under the approximation of no secondary isotope effects; the *total* observed isotopic ratio was reported as declining to the limiting classical statistical low pressure value, unity, at 0.4 mm.

This observed unity ratio also appears to have been identified¹³ as the limiting primary isotope value corresponding to $p = 0$. However, it should be noted that the limiting low pressure regime actually lies well below 0.4 mm. (*cf.* Fig. 1 and ref. 14). Also the experimental method of Weston did not isolate primary and secondary intermolecular kinetic isotope effects from each other, and, if it were carried to the true low pressure region, the technique could provide a measure of intermolecular secondary effects only.

A curve similar to Fig. 2 but of more exaggerated shape applies to tritiated compounds, and the ratio $[k(h_6)/k(t_1)]_0$ should be even more substantially less than one (and order of magnitude 0.55); also, $E_0(h_6) - E_0(t_1) = \Delta E_0$ probably is unmeasurably different from zero, when $p = 0$. The lowest pressure measurement of Weston at 0.4 mm. is substantially affected by the present quantum statistical secondary intermolecular effects.

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 (14) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A217**, 563 (1953).

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., LINDEN, NEW JERSEY]

Catalysis over Supported Metals. I. Kinetics of Ethane Hydrogenolysis over Nickel Surfaces of Known Area

BY D. J. C. YATES, W. F. TAYLOR, AND J. H. SINFELT

RECEIVED JANUARY 28, 1964

A method of determining the specific catalytic activity of a supported metal, *i.e.*, the activity per unit area of the metal, has been demonstrated for a Ni-on-SiO₂ catalyst used in the hydrogenolysis of ethane. The method involves hydrogen chemisorption measurements of the metal surface area, coupled with reaction rate determinations obtained at low conversions in a flow reactor. Samples of the catalyst were heated in air at various temperatures prior to reduction of the nickel. After reduction at a standard set of conditions, these samples had nickel surface areas which varied over a threefold range. It was observed that the rate of hydrogenolysis of ethane was proportional to the nickel surface area; *i.e.*, the specific catalytic activity of the nickel was essentially unchanged by heating in air prior to reduction. Furthermore, the apparent activation energy and reaction orders were also unchanged.

I. Introduction

Supported metal catalysts are of great technical interest. However, as pointed out by Bond,¹ very little information has been reported on the specific catalytic activities of supported metals, *i.e.*, the activity per unit surface area of the dispersed metal. A major part of the difficulty in determining the specific catalytic activity of supported metals, until

recent years, has been the unavailability of direct methods for determining the surface area of the metal itself, as distinguished from the total surface area which is readily determined by the B.E.T. method.²

Electron microscopy, for example, is rendered useless for this purpose because of the obscuring effect of the support. The only practical method appears to be to find a gas which will adsorb on the metal and not

(1) G. C. Bond, "Catalysis by Metals," Academic Press, Inc., New York, N. Y., 1962, p. 239.

(2) S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

on the support, as in many cases the area of the support is much greater than that of the metal. In general, this usually means that a gas has to be used which will chemisorb on the metal.

The gases which have found most favor for this work in the past have been hydrogen³⁻⁶ and carbon monoxide.⁷ For nickel, it is very difficult to use carbon monoxide because of the danger of forming nickel carbonyl, which would cause irreversible changes in the system. Thus, hydrogen was chosen in the present work; the utility of this method has been clearly shown by the thorough investigation reported by Schuit and van Reijen.⁸

However, despite the fact that a method is now available for determining the surface area of supported metals, there has been little attempt to integrate the results of such measurements with kinetic data on reactions over these catalysts. Studies of this type are clearly essential for any fundamental understanding of catalytic activity. Some progress along these lines appears to have been made by Schuit and van Reijen,⁸ who studied both the chemisorption and catalytic properties of a series of silica-supported metal catalysts. From measurements of the chemisorption of hydrogen on the various catalysts, they adjusted the measured activities to the same metal surface area. The reactions investigated included hydrogen-deuterium exchange and the hydrogenation of ethylene and benzene.

Clearly, there is a need for more data on the kinetics of reactions over supported metal catalysts of known metal surface area. Recently, we have been interested in the hydrogenolysis of saturated hydrocarbons over supported metal catalysts, and in this paper present results on the kinetics of hydrogenolysis of ethane over silica-supported nickel. This reaction has been investigated previously by Taylor and co-workers,⁹⁻¹¹ but the nickel surface areas of their catalysts were not known. In the present work, the nickel surface area of a given nickel-silica preparation was varied by heating samples in air to various temperatures prior to reduction. The nickel surface areas were determined by hydrogen chemisorption. In this way it was possible to determine the relation between catalytic activity and nickel surface area and to investigate any effect of desurfacing on kinetic parameters such as the activation energy and orders of reaction.

A serious problem in studying the kinetics of surface reactions is the deactivation of the catalyst during a series of kinetic measurements. The kinetic data on ethylene hydrogenation reported by Schuit and van Reijen⁸ were complicated by catalyst activity variations, as the authors themselves point out. An elaborate statistical analysis of the data was therefore necessary, and the utility of such data seems doubtful. In the present work the complications due to catalyst

deactivation have been largely eliminated by employing a procedure involving bracketing of all rate determinations by a rate measurement at a standard set of conditions. The rates can therefore be referred to the rate at standard conditions in making a kinetic analysis of the data. This procedure serves to correct for activity variations during an extended series of rate measurements. Furthermore, the technique employed in obtaining the rate data made it possible to measure rates directly at very low conversions, so that the majority of the data were obtained at conversions less than 0.5%. The technique approaches that of a differential reactor and has the advantage that the concentrations of reactants remain essentially constant throughout the reaction zone, thus simplifying the kinetic analysis of the data. An additional advantage of the technique is that it permits extensive kinetic measurements to be made in times that are not prohibitively long, and therefore makes it feasible to obtain detailed kinetic data on all catalysts investigated.

II. Experimental

A. Kinetic Measurements. Apparatus and Procedure.—

The reaction rate measurements were carried out in a flow system at atmospheric pressure. The reactor was a stainless steel tube approximately 1.0 cm. in diameter and 8 cm. in length. The reactor was held in a vertical position and was surrounded by a small electrical oven. The catalyst was centered with respect to the ends of the reactor, occupying a space approximately 1.5 to 4.0 cm. in length in the various runs. A fritted stainless steel disk was used to support the catalyst in the reactor, and quartz wool was packed on top of the catalyst to hold it in place. A 3-mm. axial thermowell containing an iron-constantan thermocouple extended upward through the fritted steel disk into the catalyst bed, so that the tip of the thermowell was located at the center of the catalyst bed. The reaction gases were passed downflow through the catalyst bed, and the products were analyzed by a chromatographic unit coupled directly to the outlet of the reactor. The chromatographic column was 2 m. in length and 0.6 cm. in diameter. The column was packed with 100 mesh silica gel and was operated at 40°. Helium was used as a carrier gas, and a thermal conductivity detector was used with the column.

The reactant gases, ethane and hydrogen, were passed over the catalyst in the presence of helium diluent. Gas flow rates were measured using orifice-type flow meters with manometers. A total gas flow rate of 1 l./min. was used throughout. The run procedure consisted of passing the reactant gases over the catalyst for a period of 3 min., at which time a sample of the product was taken for chromatographic analysis. The ethane was then cut out and hydrogen flow was continued for a period of 10 min. at the reaction temperature prior to another run. In this way, it was possible to minimize variation in catalyst activity from period to period. In each run 0.2 g. of catalyst was diluted with 0.5 g. of ground Vycor beads of the same particle size as the catalysts. In beginning a run, hydrogen was passed over the catalyst at a rate of 500 cc./min. for 30 min. at room temperature and for 2 hr. at 100° prior to heating to 370°. The reduction of the catalyst was then carried out overnight at 370° at a hydrogen flow rate of 50 cc./min., corresponding to a hydrogen space velocity of 250 cc./min./g. of catalyst. In the hydrogen chemisorption measurements to be described subsequently, the hydrogen space velocity was maintained at 500 cc./min./g. of catalyst during reduction. Supplementary experiments indicate that such a variation would have a negligible effect on the resulting catalyst activity or nickel surface area.

Materials.—The ethane used in this work was obtained from the Matheson Co. A chromatographic analysis of the ethane showed no detectable impurities. It is estimated that an impurity, e.g., methane, would have been detected by the chromatographic analysis if it were present at a concentration above 0.01 wt. %. High purity hydrogen was obtained from the Linde Co., and was further purified by passing it through a Deoxo unit containing palladium catalyst to remove traces of oxygen as water, prior to passage through a molecular sieve dryer.

(3) G. C. A. Schuit and N. H. de Boer, *Rec. trav. chim.*, **70**, 1067 (1951).

(4) G. K. Borekov and A. P. Karnaukhov, *Zh. Fiz. Khim.*, **26**, 1814 (1952).

(5) L. Spenadel and M. Boudart, *J. Phys. Chem.*, **64**, 204 (1960).

(6) S. F. Adler and J. J. Keavney, *ibid.*, **64**, 208 (1960).

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(8) G. C. A. Schuit and I. L. van Reijen, *Advan. Catalysis*, **10**, 242 (1958).

(9) K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Am. Chem. Soc.*, **58**, 1795 (1936).

(10) C. Kemball and H. S. Taylor, *ibid.*, **70**, 345 (1948).

(11) A. Cimino, M. Boudart, and H. S. Taylor, *J. Phys. Chem.*, **58**, 796 (1954).

The catalysts employed in this work were prepared in the following manner. Catalyst 1 was prepared by impregnating 25 g. of a high purity form of silica (Cabosil), obtained from the Cabot Corp., Boston, Mass., with 13.8 g. of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in sufficient deionized water to just wet the silica. The catalyst was then dried overnight at 105° . The dried catalyst was placed in a 1.125-in. i.d. die and pressed at 8000 p.s.i.g. The resulting wafers were broken up with a razor blade and screened to -45 to $+60$ mesh. Catalyst 2 was prepared by heating a sample of catalyst 1 in air for 4 hr. at 760° . Catalyst 3 was prepared by heating a sample of catalyst 1 in air for 4 hr. at 650° . Catalyst 4 was a replicate of preparation 1.

B. Chemisorption Measurements. Apparatus and Materials.—A conventional glass vacuum system was used, with a mechanical backing pump, an 80 l./sec. oil diffusion pump, and a trap cooled with either solid carbon dioxide or liquid nitrogen. The ultimate dynamic vacuum reached by the system was about 10^{-7} torr and was measured by an Alpert-type ionization gauge.

The cell used was made of Pyrex and had two stopcocks to permit the hydrogen to flow through the sample. Capillary tubing was used where possible and the portion of the cell containing the sample charge (about 1 g.) was 0.8 cm. in diameter and 5.0 cm. long. In some cases, similar cells have been made of fused silica for work at temperatures above 500° .

Hydrogen of 99.984% purity was purchased from the Linde Co., Linden, N. J. Traces of oxygen were removed from it by a Deoxo purifier, obtained from Englehard Industries, Inc., Newark, N. J. The water formed in the Deoxo unit was removed by a trap cooled with solid carbon dioxide. The helium used in calibrating the cells was obtained from the Bureau of Mines, Amarillo, Texas, and had a purity of 99.98% or better. It was dried by passage through a trap cooled by liquid nitrogen before use.

Procedure.—The sample was glass-blown into the cell. The cell was weighed before and after putting in the sample so that corrections could be made for water and oxides of nitrogen driven off during the reduction and subsequent evacuation.

The sample was then heated and evacuated until 100° was reached. After evacuating at this temperature for 1 hr., the hydrogen was passed through the sample at a flow rate of 500 cm^3/min . The temperature was then slowly raised to 370° , while maintaining the above flow. The sample was then reduced overnight at 370° and 500 cm^3/min . The hydrogen was then cut off and the sample was evacuated at 370° for 1 hr. At the end of this time, pressures in the region of 10^{-6} torr were obtained. The sample cell was then isolated from the pumps, and cooled to 20° . The hydrogen isotherm was then run, usually four or five points being obtained with the highest pressure used being about 30 cm. The isotherm was then plotted, and the amount adsorbed at a pressure of 10 cm. was taken as the monolayer point.

The metal area was calculated on the basis that each nickel atom in the surface adsorbs one hydrogen atom. Assuming that equal areas of the (100), (110), and (111) planes of nickel are presented,¹² one finds that each hydrogen atom occupies 6.5 \AA^2 . This procedure has been shown to be valid by O'Neill,¹³ who studied reduced nickel powders, where the total area obtained by physical adsorption of argon agreed very well with the hydrogen area measured as described above.

Earlier workers⁸ considered that to ensure complete coverage of the surface with hydrogen, it is necessary to cool the sample down, in 10 cm. of hydrogen, from 400 to -78° . As the above procedure takes 6 days⁸ we found our present procedure much more practical as we had a considerable number of samples to run.

III. Results

Samples of the catalysts were reduced *in situ* in the H_2 chemisorption equipment under conditions of temperature identical with those employed in the kinetic reactor. The nickel surface areas were then measured by hydrogen isotherms and are given in Table I. The nickel areas of catalyst 1 and its replicate, catalyst 4, agree within 3% of each other, showing that the nickel areas are reproducible, and that the catalyst preparation procedure is reproducible. It can

be seen that sintering the catalyst in air reduced the nickel area by a factor of about three.

TABLE I
SUMMARY OF NICKEL SURFACE AREAS AND KINETIC
PARAMETERS FOR ETHANE HYDROGENOLYSIS

	Catalyst			
	1	2	3	4
Nickel surface area, m^2/g . of catalyst	13.6	4.37	5.26	13.3
Apparent activation energy, kcal./mole	40.6	38.3	39.0	39.5
n , reaction order, C_2H_6	1.0	0.9	1.0	1.0
m , reaction order, H_2	-2.2	-2.0	-1.9	-2.1
Specific activity at 191° , ^a $\times 10^6$	15.5	10.2	11.2	12.3

^a Moles of C_2H_6 converted/ m^2 of nickel/hr. at $p_{\text{E}} = 0.030$ atm. and $p_{\text{H}} = 0.20$ atm.

The reaction of ethane and hydrogen over the supported nickel catalysts took place readily at temperatures above 180° to yield methane. In studying the kinetics of the hydrogenolysis reaction, the approach taken was to measure the rates of reaction at low conversion levels. The degree of conversion in the present work ranged from 0.1% to about 7%, most of the data having been obtained at conversion levels below 0.3%. Consequently, the partial pressures of the reactants (ethane and hydrogen) do not vary much through the reaction zone, and the system approaches that of a differential reactor. The reaction rates per gram of catalyst were determined from the relation

$$r = \frac{F}{W} x$$

where F represents the feed rate of ethane to the reactor in moles/hr., W represents the weight in grams of the catalyst charged to the reactor, and x represents the fraction of ethane converted to methane.

In an actual run to determine reaction rates, the catalyst was first prerduced with flowing hydrogen, after which the reactor was cooled in flowing hydrogen to a convenient reaction temperature. At a standard set of conditions of hydrogen and ethane partial pressures, p_{H} and p_{E} , respectively, the activity of the freshly reduced catalyst was determined. Following this, the activity was measured at a series of temperatures in a rising temperature sequence. The data for the four catalysts are shown in the Arrhenius plots in Fig. 1. From the slopes of these plots, the apparent activation energies of the ethane hydrogenolysis reaction were determined and are given in Table I. The maximum difference between apparent activation energies is less than 6% of the average value and is felt to be within the range of experimental accuracy.

After determining the effect of temperature on rates over the freshly reduced catalyst, the temperature was lowered to an intermediate value in the range studied, and a series of measurements was made to determine the effects of the partial pressures of hydrogen and ethane on the rates. Since it had been observed from preliminary experiments that a series of such measurements over an extended period of time resulted in some loss of activity, it was decided to bracket all the rate measurements with measurements at a standard set of conditions. In this way it was possible to detect

(12) D. F. Klemperer and F. S. Stone, *Proc. Roy. Soc. (London)*, **A243**, 375 (1958).

(13) C. E. O'Neill, Ph.D. Thesis, Columbia University, 1961.

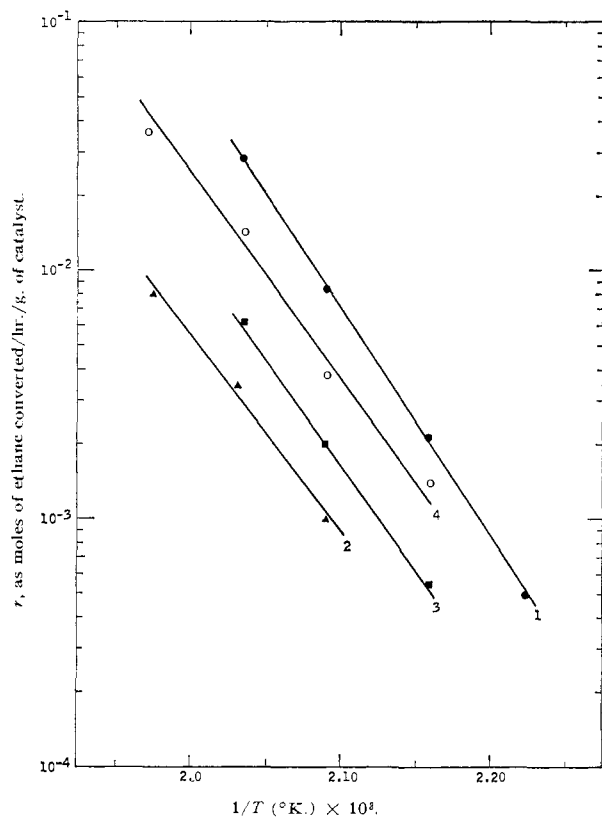


Fig. 1.—The reaction rate of ethane hydrogenolysis as a function of temperature; $p_H = 0.20$ atm., $p_E = 0.030$ atm.: catalyst 1, ●; catalyst 2, ▲; catalyst 3, ■; catalyst 4, ○.

variations in catalyst activity during the series of measurements. This procedure is illustrated in Table II and Fig. 2, which show the results of a sequence of measurements on catalyst 4. It can be seen that the activity does vary to some degree, as shown by the repeated observations at the standard conditions ($p_H = 0.20$ atm., $p_E = 0.030$ atm.). Although the activity varied somewhat during the run, the "bracketing" technique made it possible to minimize the effects of activity variations in the analysis of the kinetic data. The effect of a kinetic variable such as hydrogen or ethane partial pressure was then determined by comparing the rate at a given set of conditions with the average of the rates at the standard conditions immediately before and after the period in question. For each set of conditions the rate r relative to the rate r_0 at the standard conditions can be expressed by the ratio r/r_0 , which should be reasonably independent of moderate variations in catalyst activity. The value for r/r_0 is unity by definition at the standard conditions ($p_H = 0.20$ atm., $p_E = 0.030$ atm.). The values of the relative rates r/r_0 for all four catalysts are given in Table III as a function of ethane and hydrogen pressures.

The data show that the rate of ethane hydrogenolysis increases with increasing ethane pressure, but decreases markedly with increasing hydrogen partial pressure. The dependence of the rate on the partial pressures of ethane and hydrogen can be expressed in the form of a simple power law, $r = k p_E^n p_H^m$.¹¹ Approximate values of the exponents n and m as derived from experimental data are summarized in Table I. It can be seen that the effect of ethane and hydrogen pressure is essentially the same for all four catalysts, despite

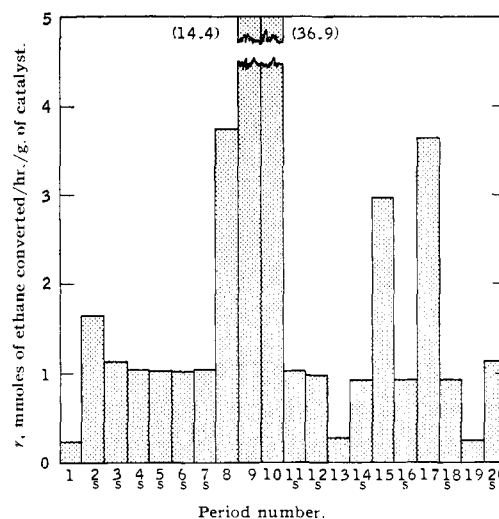


Fig. 2.—Variation of reaction rate of ethane hydrogenolysis over catalyst 4, illustrating the use of the "bracketing technique" to minimize the effect of changes in catalyst activity during the run on the measurement of the effect of reactant partial pressures; S means arbitrarily chosen standard set of conditions, $p_H = 0.200$ atm., $p_E = 0.030$ atm., temperature = 191°.

TABLE II
TYPICAL SEQUENCE OF REACTION RATE MEASUREMENTS
ILLUSTRATING THE USE OF THE BRACKETING TECHNIQUE ON
CATALYST 4

Period number ^a	Temp., °C.	p_H , atm.	p_E , atm.
1	177	0.200	0.030
2(S)	191	.200	.030
3(S)	191	.200	.030
4(S)	191	.200	.030
5(S)	191	.200	.030
6(S)	191	.200	.030
7(S)	191	.200	.030
8	205	.200	.030
9	219	.200	.030
10	234	.200	.030
11(S)	191	.200	.030
12(S)	191	.200	.030
13	191	.200	.010
14(S)	191	.200	.030
15	191	.200	.100
16(S)	191	.200	.030
17	191	.100	.030
18(S)	191	.200	.030
19	191	.400	.030
20(S)	191	.200	.030

^a The symbol (S) refers to the standard conditions ($p_E = 0.030$ atm., $p_H = 0.20$ atm., 191°).

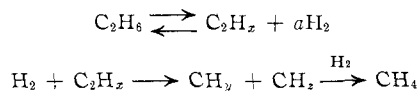
TABLE III
RELATIVE RATES OF C_2H_6 HYDROGENOLYSIS AS A FUNCTION
OF C_2H_6 AND H_2 PARTIAL PRESSURES

p_H , atm.	p_E , atm.	r/r_0^a			
		Catalyst 1 ^b	Catalyst 2 ^c	Catalyst 3 ^c	Catalyst 4 ^d
0.10	0.030	4.13	3.10	3.18	3.94
.20	.030	1.00	1.00	1.00	1.00
.40	.030	0.08	0.20	0.20	0.20
.20	.010	0.37	0.29	0.31	0.30
.20	.030	1.00	1.00	1.00	1.00
.20	.10	3.91	2.84	2.59	3.14

^a Rate relative to the rate at the standard conditions ($p_H = 0.20$ atm., $p_E = 0.030$ atm.) for the particular catalyst and temperature in question; the r/r_0 values cannot be used by themselves to compare the activities of the catalysts. ^b Determined at 177°. ^c Determined at 205°. ^d Determined at 191°.

the fact that the catalyst samples were heated in air at markedly different temperatures resulting in a threefold variation in the nickel surface area.

The general features of the kinetics of ethane hydrogenolysis over the Ni-SiO₂ catalyst employed in this study are in accord with the earlier studies of Taylor and co-workers,⁹⁻¹¹ in which the kinetics were investigated over nickel catalysts of unknown nickel area. These workers showed that the kinetics could be explained satisfactorily in terms of a mechanism involving a preliminary dehydrogenation of the ethane to an unsaturated radical on the surface, followed by attack of the surface radical by hydrogen



where a is equal to $(6 - x)/2$. On the assumption that the first step was an equilibrated one, and that the rate was limited by the rate of rupture of carbon-carbon bonds by reaction of the surface species C_2H_x with H_2 , a rate law was derived which could be put in the form

$$r = k p_E^n p_H^{(1-na)}$$

For nickel catalysts it was concluded that a value of $a = 3$ accounted best for the observed kinetics. This agrees with the present work, as can be seen by the excellent agreement between observed and calculated values of the exponent on hydrogen pressure when $a = 3$. From the experimental value of the exponent on ethane partial pressure n , the exponent $(1 - na)$ on hydrogen pressure was calculated for $a = 3$ and is compared with the experimental value m :

Catalyst	Exponent on H ₂ pressure	
	Obsd. m	Calcd. $(1 - na)$
1	-2.2	-2.0
2	-2.0	-1.7
3	-1.9	-2.0
4	-2.1	-2.0

Thus, on nickel it is concluded that the initial step in ethane hydrogenolysis involves dehydrogenation to a dicarbon fragment containing no hydrogen.

The effect of the nickel surface area of the various catalyst samples on the rate of ethane hydrogenolysis can be seen in Fig. 3. The rate of hydrogenolysis at 191° and standard ethane and hydrogen partial pressures ($p_E = 0.030$ atm., $p_H = 0.20$ atm.) over the freshly reduced samples is plotted as a function of the nickel surface area. The data show that the rate of hydrogenolysis is approximately proportional to the nickel surface area. The line in Fig. 3 is drawn to pass through the origin, although it is possible that it could intersect the horizontal axis at a nickel area slightly greater than zero; *i.e.*, the rate of hydrogenolysis could be virtually zero below some critical nickel surface area, say 1 m.²/g. of catalyst. Nevertheless, it is clear that in the range of nickel surface areas which are of interest catalytically the rate is approximately proportional to the nickel surface area. This means that the specific activity of the catalyst, defined as the rate of ethane hydrogenolysis per unit area of nickel surface, remains essentially constant when the nickel surface area is reduced threefold by heating the nickel oxide in air at elevated temperatures prior to reduction.

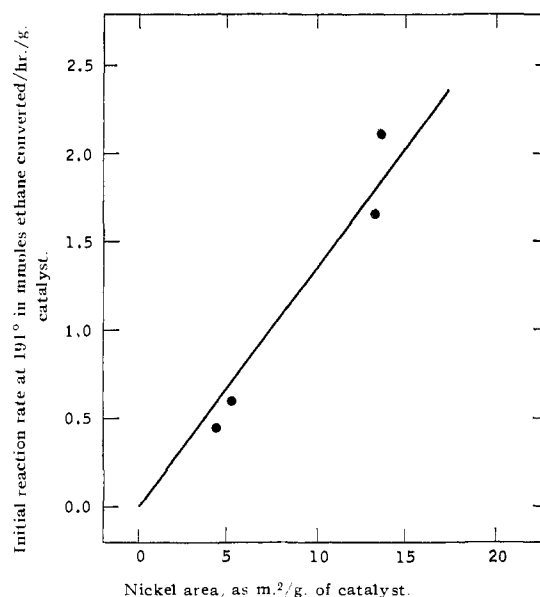


Fig. 3.—Effect of nickel surface area on the rate of hydrogenolysis of ethane over freshly reduced catalysts at 191°; H₂ pressure = 0.20 atm., C₂H₆ pressure = 0.030 atm.

Values of the specific catalytic activities of the various catalyst samples, expressed as moles of ethane converted/hr./m.² of nickel, are summarized in Table I. While there is some variation in the specific activities of the individual samples, the variation is not large compared to the threefold variation in both rates and nickel surface areas. The average value of the specific activity for all the catalyst samples at 191°, $p_E = 0.030$ atm., and $p_H = 0.20$ atm., is 12.3×10^{-5} mole/hr./m.² of Ni.

IV. Discussion

The main feature of the present work is the demonstration of a method for obtaining data on the specific catalytic activity of a supported metal, in which H₂ chemisorption measurements of the metal surface area are integrated with reaction kinetic data. The application of such a method in systematic studies of catalysis over supported metals forms a vital part of any study directed toward a fundamental understanding of their catalytic properties. For example, it is clearly necessary to refer rates to measured metal surface areas in comparing the intrinsic catalytic activities of a series of supported metals when it is desired to relate the activity to some fundamental property of the metal. Otherwise, differences in activity could be (and undoubtedly have been) confounded by differences in dispersion of the metal on the support. Furthermore, information on specific catalytic activity would also be important in determining the nature of promoter action, *e.g.*, in differentiating between electronic effects and surface stabilization effects.

In the present work the measurement of nickel surface areas by hydrogen chemisorption has made it clear that the decrease in catalytic activity due to heating the catalyst in air prior to reduction can be explained by a corresponding decrease in nickel surface area. Thus, the specific catalytic activity of the supported nickel for ethane hydrogenolysis is essentially unchanged by such treatment.

It is striking that the specific activity of the nickel, the activation energy, and the orders of reaction are

very little affected by the severe thermal pretreatments of the catalyst which were employed. Since there is little *a priori* reason to expect this, the results are of particular interest. The importance of applying a method such as that described in this paper to study

the factors influencing the catalytic activities of supported metals cannot be overemphasized.

Acknowledgment.—The authors gratefully acknowledge the contributions of Messrs. R. C. Parker and E. M. Kelley in the performance of the experiments.

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The Acetylacetonate Anion. Molecular Orbital Calculations in the Huckel and Self-Consistent Field Approximations¹

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RECEIVED FEBRUARY 7, 1964

Huckel and self-consistent field calculations of the acetylacetonate ion π -electron structure have been made. In contrast to the marked sensitivity of the Hückel results to the parameter choice, the s.c.f. results are relatively independent of these quantities. The effects of metal ion charge and penetration integrals largely cancel out, and a simplified s.c.f. treatment is adequate for the calculation of transition energies and intensities.

Introduction

In the interpretation of the spectra of metal complexes, it is often useful to distinguish electronic transitions largely localized within the ligands from those involving charge transfer between the metal ion and ligands. The spectra of metal complexes in which the acetylacetonate ion is the ligand have been studied in detail,^{2,3} and attempts to distinguish ligand-localized from charge-transfer transitions have been made.³⁻⁶ Such an analysis generally proceeds by first examining the spectrum of the free ligand and then considering the perturbing effect of the metal ion on the ligand states. The electronic structure of the acetylacetonate anion has been calculated by two semiempirical procedures—the Huckel^{3,4} and self-consistent field (s.c.f.) methods.⁶

The success of the Hückel method in the interpretation of the spectra of alternant hydrocarbons coupled with the computational simplicity of this scheme has led to its extensive applications to π -electron systems. The widespread availability of digital computers has now minimized the computational advantages of the Hückel method. In this paper, the electronic structures of the acetylacetonate ion as determined by the Hückel method and a computationally simple version of the s.c.f. method are compared in order to determine the relative merits of each technique.

The determination of the electronic structures of metal acetylacetonates with two and three ligands should be based on a knowledge of the single ligand structure. In this study, the first step in the treatment of the more general problem, the acetylacetonate ion (as in alkali metal complexes), is considered.

Hückel Calculations.⁷—In the Hückel method, the normalized molecular orbitals are of the LCAO form

$$\phi_i = \sum_p c_{ip} \chi_p \quad (1)$$

- (1) Supported by the United States Atomic Energy Commission.
 (2) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).
 (3) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).
 (4) J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97, 102 (1963).
 (5) T. S. Piper and R. I. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962).
 (6) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963).
 (7) For a comprehensive survey of this method see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

where the summation index p extends over all the atoms in the π -electron framework or "core." Neglecting overlap, the coefficients, c_{ip} , and orbital energies, ϵ_i , are determined by diagonalizing the \mathbf{H} matrix, with elements defined as

$$H_{pq} = \int \chi_p H^{\text{eff}} \chi_q d\tau$$

The Coulomb integrals, $H_{pp} \equiv \alpha_p$, and the resonance integrals, $H_{pq} \equiv \beta_{pq}$ (these are assumed to be zero unless p and q refer to neighboring atoms), are assigned semiempirically, and the \mathbf{H} matrix may be diagonalized with a digital computer using a program in which the c_{ip} and ϵ_i are evaluated.

In the simple Hückel method, electron repulsion is not incorporated explicitly, but is included to some extent by the choice of α_p and β_{pq} parameters. This procedure has been fairly successful in treating the spectra of alternant hydrocarbons, but serious ambiguities arise when heteroatoms are included in the π -electron system.^{8,9} The α_p parameters must then be adjusted for the differential electronegativity of the atoms and the β_{pq} altered for the varying bond lengths. The uncertainties inherent in this approach can be seen by reference to Table I where the results of the three Hückel calculations are summarized. The numbering system is shown in Fig. 1. In calculation Ia,

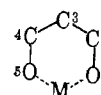


Figure 1.

parameters rather similar to those suggested by Streitwieser⁷ were employed. The effect of the metal ion in increasing the electronegativity of the oxygen atoms was intentionally overestimated in calculation Ib, while in calculation Ic another "reasonable" choice of parameters was employed.¹⁰ The six π -electrons fill the three lowest orbitals, ϕ_1 – ϕ_3 , and in all three cases the lowest energy transition is assigned as $\phi_3 \rightarrow \phi_4$. The assignment of the next higher transition is doubtful, however. Not only are the transition energies

- (8) M. J. S. Dewar, *Rev. Mod. Phys.*, **35**, 586 (1963).
 (9) G. Del Re and R. G. Parr, *ibid.*, **35**, 604 (1963).
 (10) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961), and private communication.