Activity and Properties of Nickel Catalysts in the Hydrogenolysis of Propane

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A series of nickel-alumina catalysts was made by heating samples of a coprecipitated catalyst between 340° and 1160°. The catalyst contained alkali metal. The catalysts were examined by means of physical adsorption, hydrogen chemisorption, X-ray line-broadening, and electron microscopy. The nickel oxide/nickel system sintered more easily at low temperatures than the alumina. Three types of nickel crystallites were found in reduced catalysts.

The reaction between propane and hydrogen was studied in the temperature range 200° to 350° and the activity of most catalysts was directly proportional to metal surface area. The apparent activation energy was approximately 50 kcal/mole except on a highly sintered catalyst which gave a value of 35 kcal/mole. Reduction of the hydrogen partial pressure reduced the apparent activation energy.

At low conversions the reaction on most catalysts could be described by the empirical equation, rate $= k(\text{propane})^n(\text{hydrogen})^{-m}$, where n and m had approximate values of 1 and 2, respectively. One can obtain equations of this type by assuming cleavage of the carbon–carbon bond to be the slow step. This assumption leads to the conclusion that alkali metal reduced the degree of hydrocarbon dissociation on the catalyst surface. However, the evidence for desorption control was slightly more convincing.

Removal of alkali metal gave increased specific activity; possible reasons for this effect are discussed.

INTRODUCTION

The activity of a metal catalyst depends on many factors, such as the method of preparation, the pretreatment, and the reaction conditions. Often catalytic studies concentrate either on the catalytic activity or on the catalyst itself and, with a few exceptions, it is only in the past decade that the two approaches have been combined in attempts to relate activity of industrial catalysts to their physical and chemical properties. Schuit and van Reijen (1) used chemisorption of hydrogen and carbon monoxide to measure the metal surface area in a variety of catalysts and showed that the activity of the catalyst could be related to the metal surface area. Supported platinum catalysts have been widely studied by use of chemisorption, X-ray line-broadening and electron microscopy techniques (2–11) and for some reactions the metal surface area was found to be related to catalytic activity (12, 13).

Despite their industrial importance, nickel catalysts have been somewhat neglected in recent years and little was published on the examination and activity of such catalysts until Sinfelt and co-workers (14–18) reported their work on the hydrogenolysis of ethane. Aben and others (19) found the activity of nickel per exposed metal atom, for the hydrogenation of benzene, to be independent of metal crystallite size or the support used. Van Hardeveld and Hartog (20) found that deuterium exchange in benzene, but not deuteration, was a function of crystallite size.

The present work was part of a general

program to study the relation between catalytic activity and the physical and chemical properties of catalysts containing Group VIII metals.

EXPERIMENTAL

Catalysts and their examination. All catalysts used in this work were modifications of an industrial nickel-alumina catalyst supplied as $\frac{1}{8}$-inch pellets. It was prepared by coprecipitation of the nitrates and the pellets were calcined at 450°C for 4 hr. The catalyst contained alkali metal and in the reduced state contained 75% by weight of nickel. The pellets were ground and sieved. The 40–50 mesh (ASTM) fraction will be subsequently referred to as Catalyst X.

Six samples of Catalyst X were pretreated in a flow of nitrogen (70 ml/min) for 16 hr at selected temperatures between 340° and 1160°C to give Catalysts A to F. The same mesh fraction of pellets which had been used in an industrial plant was pretreated in a flow of nitrogen for 16 hr at 500°C to give Catalyst G. The catalysts were stored in a dry inert atmosphere and removed in weighed quantities, as required.

The alkali metal could affect the form and activity of reduced Catalysts A to G. To test these possibilities samples of B and E were Soxhlet-extracted with distilled water to produce Catalysts B^1 and E^1 with much lower alkali contents. This treatment also removed some alumina which, when dried, was in the form of boehmite.

Metal surface areas were calculated from hydrogen chemisorption measurements on the assumption that each exposed nickel atom adsorbed one hydrogen atom. A surface area per nickel atom of 6.5 $Å^2$ was used (21). It was not possible to prepare alumina in exactly the same form as that in the catalyst so any small amount of chemisorption on the support or promoter was neglected.

The volumetric adsorption experiments were carried out in a conventional glass vacuum system in which an ultimate dynamic vacuum of at least 10^{-5} torr was obtainable. Gold foil protected the catalyst from mercury vapor. The catalyst, in the oxide form, was weighed in the adsorption vessel which was then glass-blown on to the

vacuum system. Hydrogen (70 ml/min) was passed through the catalyst as the temperature was raised at a reproducible rate from room temperature to 500°C over a period of 1 hr and that temperature was maintained for 16 hr. The adsorption vessel was sealed in the presence of hydrogen and evacuated at 400°C for 3 hr before it was cooled to room temperature. The amounts of hydrogen chemisorbed at room temperature were determined for a series of pressures up to 300 torr and the volume chemisorbed at 200 torr was taken as a measure of monolayer coverage. When the chemisorption was completed the catalyst was evacuated to 10^{-5} torr and cooled to -197°C for nitrogen adsorption experiments. Complete nitrogen isotherms were not plotted for all the catalysts but several points were taken in the p/p_0 range 0 to 0.3. Surface areas were calculated by use of the BET equation. On completion of adsorption experiments the adsorption vessel was weighed before and after removal of catalyst. This difference in weight gave the surface areas per gram final weight.

X-Ray line-broadening gave the average crystallite size of nickel or nickel oxide. Since the catalysts were pyrophoric in the reduced state, we prepared and examined the samples in dry inert atmosphere. The catalysts were ground to a fine powder and packed into Lindemann glass capillaries (wall, 0.01 mm; diameter, 0.5 mm) which were then sealed. The samples were examined in a 9-cm powder diffraction camera and the average crystallite size determined from the microdensitometer trace of Debye-Scherrer photographs. K_α splitting was negligible in the lines used. The half-height width was taken as the linewidth; it was corrected for experimental broadening with a specimen of "infinite" crystallite size, packed in a similar capillary. Warren's equation (22) gave the pure linewidth. The Scherrer constant was taken as unity. Examination of a larger number of catalysts of this type in our laboratories has shown that grinding had no effect on the determination of crystallite size (23).

Reduced catalysts for electron microscopic examination were embedded in methacrylate

without coming in contact with air. Aeon Laboratories, Egham, sectioned the embedded catalysts and examined them in the electron microscope.

Apparatus and procedure. The reaction studies were carried out in a flow system with a fixed-bed reactor at atmospheric pressure. The microreactor (A) was a stainless steel tube (length, 8 inch; bore, $\frac{5}{16}$ inch, and wall $\frac{1}{8}$ inch) wound with a mica-insulated heating coil which was adjusted to give isothermal heating. An injection port, brazed to the inlet of the reactor, allowed injection of liquids through a Suba Seal serum cap. The assembly was thermally insulated with asbestos lagging and a layer of high-temperature cement. A chromel-alumel thermocouple, held in a $\frac{1}{16}$-inch coaxial sheath, measured the temperature, which remained constant to $\pm 2°C$ at $500°C$ over a period of 16 hr. Each experiment used 0.3 g of catalyst held in place by fused quartz chips of 40–50 ASTM size.

The reaction mixture contained hydrogen, propane, and nitrogen as diluent. Gas flows were monitored by rotameters calibrated at a standard upstream pressure. Negretti and Zambra valves controlled the pressure and transducers measured it. Apart from experiments to determine the effect of reactant partial pressures, flow conditions were standardized as follows: partial pressures were nitrogen, 0.5; hydrogen, 0.4375; and propane, 0.0625 atms. The total flow at room temperature was 160 ml/min. The large excess of hydrogen was used to prevent complications due either to polymerization and dehydrocyclization or to carbide formation. The gas mixture was sampled before and after the reactor with Loenco sampling valves. A 12 ft $\times$ $\frac{1}{8}$-inch GLC column packed with 3% dihexylsebacate on silica gel separated the products at $53°C$. The carrier gas was helium and detection was by a flame-ionization detector.

In the flow experiments the catalysts, in the oxide form, were reduced *in situ*. They were heated in a stream of hydrogen (70 ml/min) under fixed conditions from room temperature to $500°C$ and held at that temperature for a further 16 hr. The temperature was then lowered to between $200°$

and $250°C$ and standard flow conditions were established. After 1 hr, the activity of the catalysts was determined at a series of temperatures; a period of 0.5 hr was allowed for the catalyst activity to come to equilibrium at each temperature. In experiments to find the effect of varying the partial pressure of the reactants each determination was bracketed by two under standard conditions; a period of 0.5 hr was allowed between each determination.

A larger reactor (B) was used to test the effect of reaction on the crystallite size of the nickel; it had seven sampling tubes welded at 2-inch intervals along the wall. The reactor (14 inches long, 1-inch bore, and $\frac{1}{8}$-inch wall) was heated by a furnace that was adjusted to give isothermal heating. Temperatures were measured by a chromel-alumel thermocouple held in a coaxial sheath of $\frac{1}{4}$-inch od. Six catalyst samples (0.5 g each) were packed between the sampling points. No diluent was added during these experiments. After reaction the reactor was discharged in an inert atmosphere and the first and last catalyst sections were retained for X-ray examination.

Materials. Research grade propane (Phillips) was used in most of this work. Chromatographic analysis showed no detectable impurities; these would have been detected if present at a concentration above 0.01%. In early experiments, where mentioned in the text, pure grade propane (Phillips) was used. It contained small amounts (up to 0.02%) of methane and ethane and a smaller amount of butane. The methane and ethane were allowed for in the calculation of conversion. Both grades contained less than 1 ppm of sulfur and a check on pure grade gave a maximum value of 0.6 ppm.

Hydrogen (Air Products) was purified by passage through a Deoxo unit, to convert traces of oxygen to water, and then through molecular sieves at $-132°C$; the nitrogen was passed over copper filings at $340°C$ to remove oxygen and then through molecular sieves at $-132°C$. The hydrogen and nitrogen used for the adsorption work were Pure Grade X as supplied by British Oxygen Ltd; they were used without further purifica-

tion. The hydrogen for reduction of samples before adsorption measurements was purified as above except that the molecular sieves were at room temperature.

Perylene (Aldrich Chemical Co. Inc.) and research grade benzene (Phillips) were used without further purification.

RESULTS

Characterization of Catalysts

The pretreatment of temperatures, total surface areas, and metal surface areas of Catalysts A to G are shown in Table 1. Total surface areas varied from 174 to 21 m²/g and metal surface areas from 56 to 2 m²/g.

TABLE 1

TEMPERATURE OF PRETREATMENT AND SURFACE AREAS OF CATALYSTS A TO G

Catalyst	Pretreatment temperature (°C)	Total surface area (m²/g)	Metal surface area (m²/g)
A	340°	174	56
B	500°	170	42
C	560°	137	37
D	670°	127	25
E	760°	116	14
F	1160°	47	5
G	500°	21	2

Catalysts A to F were examined both as the oxide and freshly reduced forms by X-ray methods. Figure 1 shows values of the average crystallite sizes for nickel oxide. We used reflections from the (111), (200), and (220) planes of nickel oxide and for the reduced catalysts the (111) and (200) reflections of nickel. The crystallite size of the metal paralleled that of the oxide except in Catalyst F, where some relative reduction in nickel crystallite size took place. There was also a small trace of poorly crystallized aluminate in this catalyst before but not after reduction.

Reactor B was used to study the effect of reaction on the average crystallite size of the metal in Catalysts A to F since the heat evolved in the reaction might cause greater crystallite growth at the inlet. (The maximum heat of reaction was about 36 kcal/mole in the temperature range studied.) The
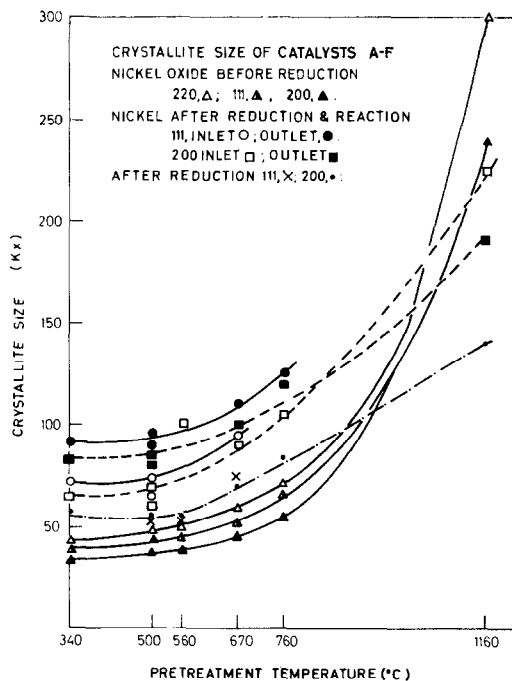

FIG. 1. Graph showing the relationship between crystallite size and temperature of pretreatment.

reaction temperature was controlled at 250° and 290°C on alternate days for a total of 10 days. Analysis of the product gases showed that most of the reaction occurred over the first catalyst section, and at very high conversions (>75%), a temperature rise of a few degrees was found in the inlet section.

The average crystallite sizes of the inlet and outlet sections are shown in Fig. 1. Traces of oxide were found in some samples as a result of the difficulties in preparing and examining samples; no nickel crystallite size is given where overlap of lines occurred. All catalysts showed crystallite growth during reaction, but contrary to expectation, the outlet sample had usually a significantly larger crystallite size. Separate experiments at 300°C with gas mixtures of the composition present at the inlet and outlet showed that changes in gas composition did not affect the crystallite growth over a period of 50 hr. But when both inlet and outlet samples were compared directly after reduction the average crystallite sizes of the outlet samples were about 10% to 20%

larger than those of the inlet samples already shown in Fig. 1.

Since the removal of alkali and alumina from Catalysts B[1] and E[1] could have had a marked effect on their physical and chemical properties, further experiments were necessary to study the changes in metal area, microporosity, acidity, and the form of metal crystallites.

The pore-size distribution of the reduced catalysts, calculated from nitrogen adsorption, showed only a maximum at a diameter of approximately 20 Å or less and thus were not of much use for interpreting changes in the pore structure.

It seemed more valuable to obtain t plots for the catalysts, although the interpretation of these plots is the subject of much discussion. Lippens and de Boer (24) believed that the difference in surface areas ($S_t - S_w$),

calculated from the slopes in a t plot, was a measure of the surface area in micropores, but Sing (25) has recently suggested that micropore volume (M_v), as determined by backward extrapolation to the vertical axis, is a more meaningful value.

Figure 2 shows the result of plotting the nitrogen adsorbed, X_m, against the thickness of the adsorbed layer t. The relationship between p/p_0 values and t was that reported by Lippens and others (26). In Table 2 values of S_t, S_w, and M_v, obtained from these plots by methods described in the literature (24, 25) are given together with S_{BET} and metal surface area. In general the micropore volume, M_v, or surface area in micropores, $S_t - S_w$, decreased with increasing temperature of pretreatment, i.e., from A to F, but increased when the catalyst was Soxhlet-extracted. The increase was
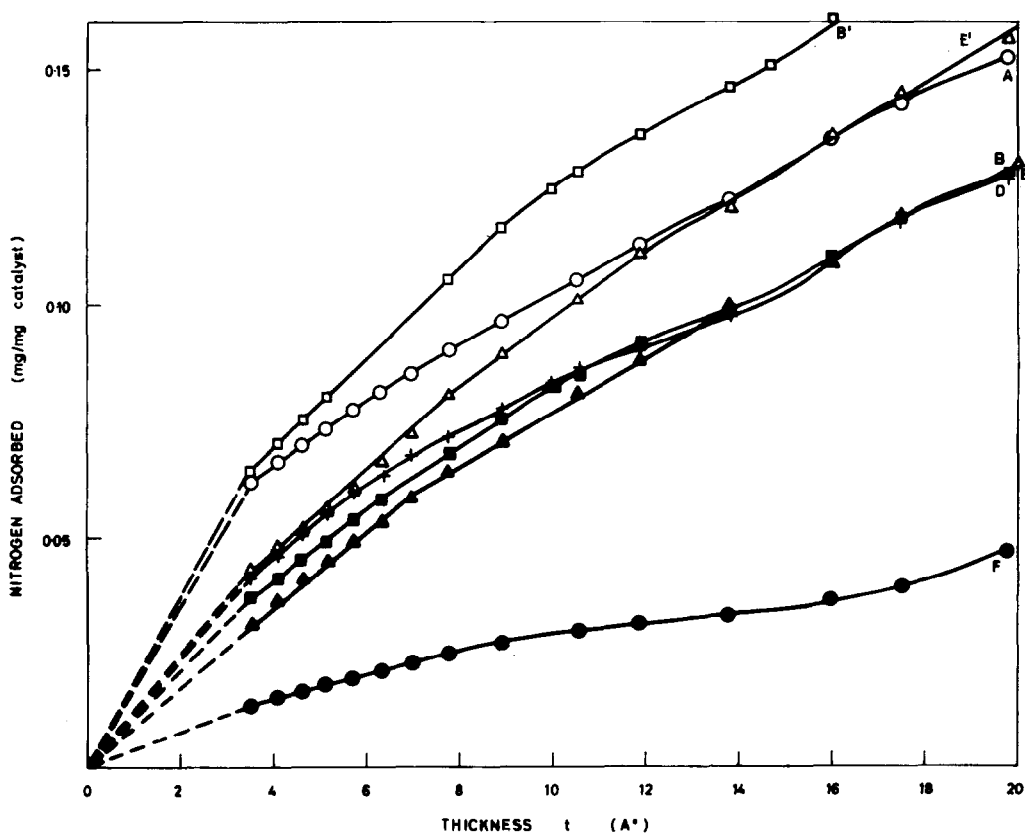

FIG. 2. The t plots obtained from selected catalyst samples.

TABLE 2

SURFACE AREAS AND MICROPORE VOLUMES
DERIVED FROM t PLOTS OBTAINED ON
SELECTED CATALYSTS OF KNOWN
METAL SURFACE AREA

Catalyst	MSA[a] (m²/g)	S_{BET} (m²/g)	S_t (m²/g)	S_w (m²/g)	M_v (cc/g)
A	56	171	217	105	4.60×10^{-2}
B	42	133	145	87	1.20×10^{-2}
B¹	50	197	226	119	3.77×10^{-2}
D	25	120	129	96	1.48×10^{-2}
E	14	106	105	73	0.62×10^{-2}
E¹	37	138	151	108	1.42×10^{-2}
F	5	43	47	33	0.50×10^{-2}

[a] Metal surface area.

more marked in Catalyst B¹ than in E¹. With the exception of Catalyst B, the BET surface areas were in good agreement with those determined in the volumetric apparatus but the six samples give the results $S_w < S_{BET} < S_t$, although the values of C in the BET equation were between 200 and 300 and so were not excessively large. Where com-

parison was possible, the adsorption isotherms determined volumetrically were in good agreement with those determined gravimetrically.

Because the X-ray method gives only an average value and neglects small crystallites, most catalysts were examined in the electron microscope. X-Ray measurements emphasized the need for this information because examination of these catalysts, and others of the same type (*23*), often showed that the relative intensities of lines were not those expected for regular cubic crystals. However, it was impossible to estimate crystallite-size distribution in electron micrographs because of the nature of the catalyst. These difficulties were due to low contrast between the metal and the base material and to overlapping of crystallites. Although in several catalysts it was difficult even to determine the lower limit, the approximate limits of metal crystallite size in the catalysts examined are shown in Table 3. The maximum size of crystallites did not increase
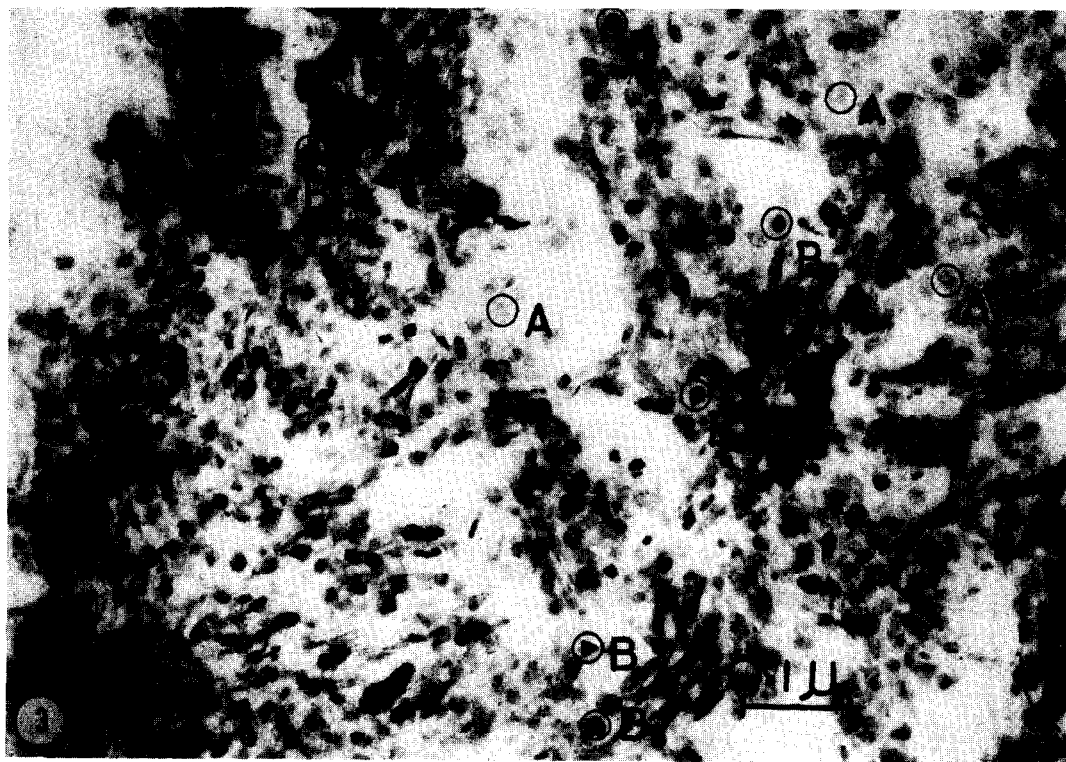

FIG. 3. Electron micrograph of Catalyst C.

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TABLE 3

RANGE OF CRYSTALLITE SIZES FOUND
IN CATALYSTS EXAMINED IN THE
ELECTRON MICROSCOPE

Catalyst	Approx. crystallite size range (Å)	Catalyst	Approx. crystallite size range (Å)
B	<100 to 500	E	50 to 450
B¹	<100 to 850	E¹	100 to 350
C	<100 to 250	F	50 to >1000
D	<100 to 300	G	200 to >2000

regularly with increasing temperature and some samples, e.g., B¹, contained anomalously large nickel particles. Small crystallites were associated with continuous areas of porous base material whereas larger ones were often free of base.

The general appearance of the metal crystallites can be seen in Figs. 3, 4, and 5. There appear to be three types of crystallites: A, thin platelets with a high degree of symmetry, some of which were even found in Catalyst F; B, crystallites which appeared as three, four, five, and six-sided shapes and often showed internal contrast patterns; and C, irregular crystallites. Lateral sections of platelets were also found and can be seen in Figs. 4 and 5. In B¹ and E¹ there was a large preponderance of crystallites of type A but the support appeared to be the same as that observed in unextracted samples, i.e., η- or γ-alumina.

Although increased acidity is unlikely to cause cleavage of a C_3 species, it could perhaps provide an alternative adsorption route for a species that could migrate to the metal. But adsorption of ammonia at room temperature on extracted and unextracted catalyst yielded Langmuir plots that showed only about 4% increase in ammonia adsorption.

Reaction Studies

The activities of Catalysts A to F for hydrogenolysis of pure grade propane were studied, under standard conditions in reactor A, over the temperature range 200° to 255°C.
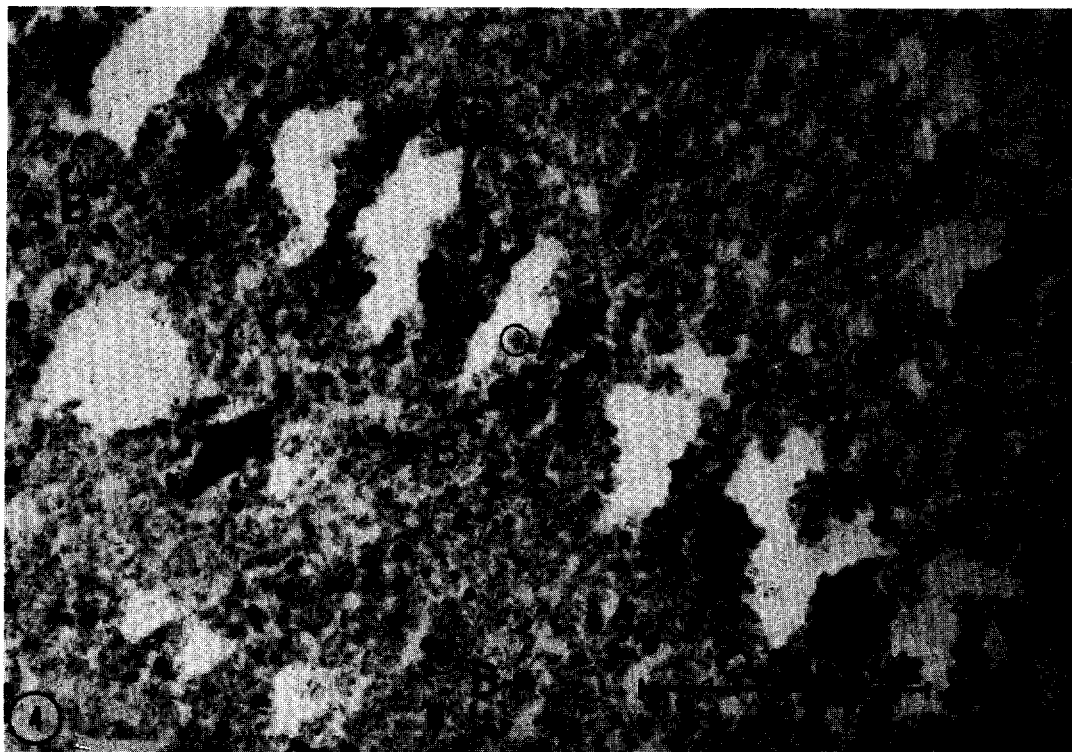

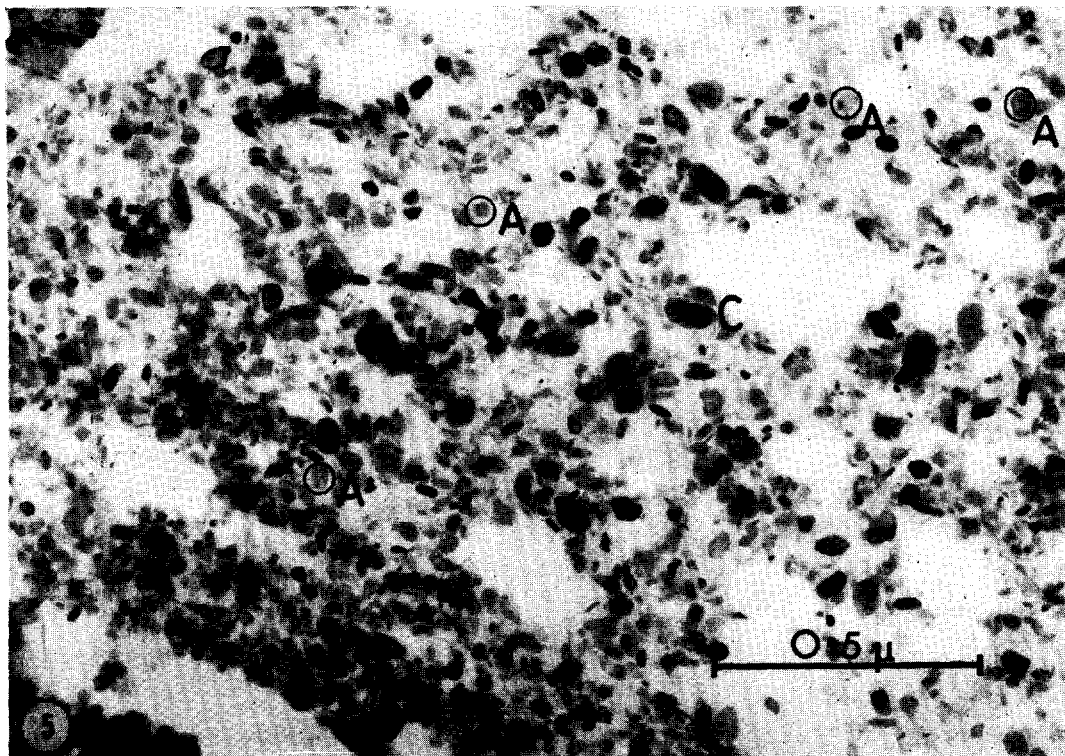FIG. 4. Electron micrograph of Catalyst E.

FIG. 5. Electron micrograph of Catalyst F.

The results are shown as Arrhenius plots in Fig. 6; values for the apparent activation energies shown in Table 4 are very similar.

Because damage to the reactor necessitated the construction of a new one which had a slightly different cross section, the measurements of the activities of Catalysts B to F were repeated for comparison purposes using research grade propane. Figure 7 compares the results with those given by the

TABLE 4
VALUES OF APPARENT ACTIVATION ENERGY
(KCAL/MOLE) ON ALL CATALYSTS

Catalyst	Figure 6		Figure 7	
A	51			
B	48		49	
C	47	48	50	
D	50		52	50
E	48		50	
F	44		49	
G			34	
F″			54	
B¹, E′			54	

Catalyst G and Table 4 shows derived values for apparent activation energies. The value obtained from G was always 35 ± 1 kcal/mole; the apparent activation energies on the other catalysts were about 50 kcal/mole, i.e., essentially the same as before.

The apparent activation energy seemed unusually high for this type of reaction. Some tests were therefore made to check for the presence of diffusion effects, which usually appear as a decrease in apparent activation energy but can sometimes increase the apparent activation energy (27). A standard weight of catalyst was taken, rather than a standard volume, because of the difficulties in packing exactly the same volume. Samples of catalysts, ground to a fine powder of less than 200 mesh ASTM, gave apparent activation energies similar to those obtained on the 40–50 mesh size. The largest variation was found in the Arrhenius plot from ground sample F shown in Fig. 7 as F″. The apparent activation energy was 54 kcal/mole.
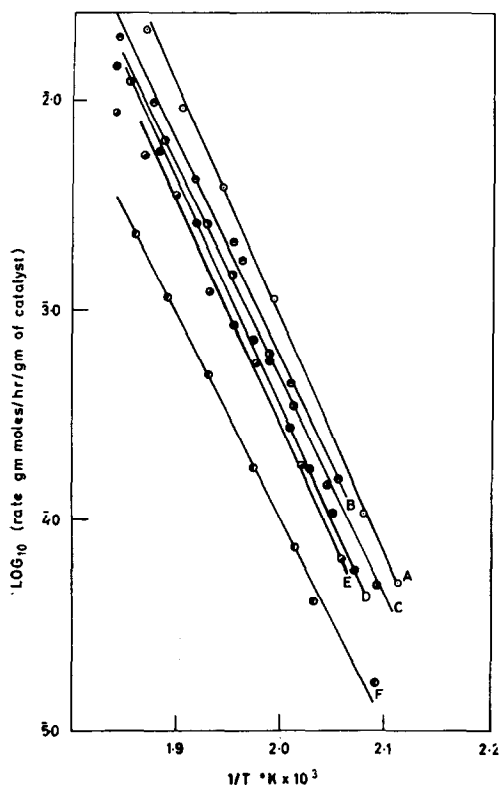
FIG. 6. Arrhenius plots obtained from Catalysts A to F.

Reduction of the hydrogen-to-propane ratio by alteration of the partial pressure of hydrogen resulted in a decrease in the apparent activation energy. Variation of the hydrogen partial pressure from 0.4375 to 0.1875 atm lowered the apparent activation energies on B from 50 to 41, on E from 50 to 42, and on G from 36 to 30 kcal/mole. These reductions were not due to any permanent poisoning effects, as resumption of standard conditions restored the original activity.

As a test of the possible effects of carbonaceous deposits on activity some catalysts were treated by injecting 4 ml of perylene solution (2 × 10⁻⁴ g in 4 ml C₆H₆). This treatment resulted in significant decrease in activity to less than 3% of the original value on catalyst B¹ at 222°C and to less than 1% on D at 244°C. The reaction mixture gradually restored the activity, and treatment with hydrogen at 360°C overnight brought it back almost to its original value. The

apparent activation energy did not fall below that for the standard reaction—in fact it increased—but gradual removal of the residue made it difficult to obtain accurate measurements of activity at a series of temperatures on poisoned catalysts.

Of experiments carried out on each catalyst to determine the effect of varying either the partial pressure of propane or that of hydrogen, each was bracketed by two others under standard conditions. This procedure avoided errors due to possible changes in activity. Most of the experiments were made at temperature that gave conversion, under standard conditions, of about 1% or less; the results obtained from reaction on catalysts A to G are shown in Table 5. The pressure dependencies were calculated from changes in the relative activities. For the purposes of presentation, the data are described by the familiar empirical rate equation

$$\text{Rate} = k[\text{C}_3\text{H}_8]^n[\text{H}_2]^{-m}$$

This type of equation is often written with the tacit assumption that k does not vary at a fixed temperature. The use of the equation often implies also that n and m do not vary with temperatures. Therefore, additional experiments were carried out on Catalyst B to investigate the effect of temperature on the pressure dependencies; the results are shown in Table 6.

Table 7 shows the values of n and m calculated from experiments on several catalysts at different temperatures, together with the percentage conversion under standard conditions. With conversions of 1% or less, under standard conditions, Catalysts A to F gave values of approximately 1 and 2 for n and m, respectively. Catalyst G gave much lower values for both n and m. As the reaction temperature on B was raised the value of m decreased.

To study the effect of alkali in these catalysts activities were measured in Catalysts B¹ and E¹ in which the alkali content had been markedly reduced.

Their activity under standard reaction conditions increased by a factor of at least 10, as shown in Fig. 7. However, chemisorption of hydrogen on B¹ and E¹ showed that
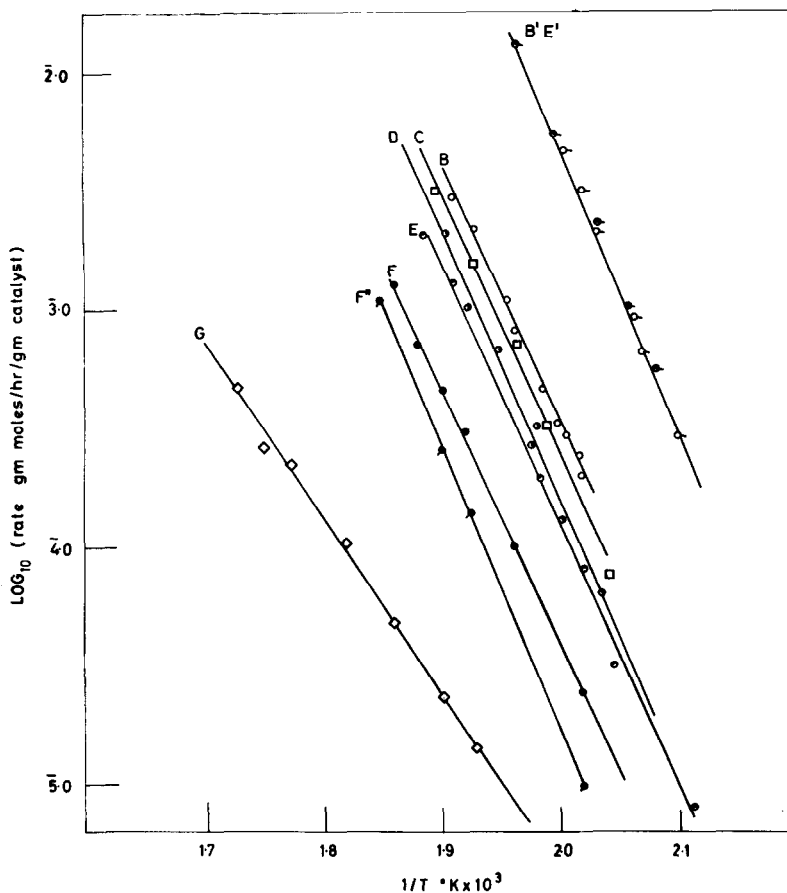
FIG. 7. Arrhenius plots obtained from Catalysts B to G, finely divided F (F″), and Soxhlet-extracted samples B¹ and E¹.

TABLE 5
RELATIVE RATES MEASURED ON CATALYSTS A TO G TOGETHER
WITH THE EXPERIMENTAL CONDITIONS USED

$P_{C_3H_8} \times 10^2$ (atm)	$P_{H_2} \times 10^2$ (atm)	Rate relative to that obtained under standard conditions (r_x/r_{av})						
		Catalyst A 231°C	Catalyst B 213°C	Catalyst C 240°C	Catalyst D 223°C	Catalyst E 238°C	Catalyst F 247°C	Catalyst G 312°C
6.25	50.0	—	0.69	0.70	—	0.74	0.75	0.88
6.25	37.50	1.40	1.47	1.33	1.40	1.44	1.36	—
6.25	31.25	2.04	2.13	1.98	2.05	2.10	1.85	1.38
6.25	25.00	3.34	3.94	3.07	3.70	3.19	2.75	1.65
6.25	18.75	5.05	7.31	5.11	6.70	—	4.04	1.84
3.13	43.75	0.50	0.47	0.52	0.62	0.51	0.49	—
4.69	43.75	0.76	—	—	—	0.79	—	—
5.00	43.75	—	—	—	0.74	—	—	0.97
6.25	43.75	1.00	1.00	1.00	1.00	1.00	1.00	1.00
7.50	43.75	—	—	—	1.11	—	—	1.13
9.38	43.75	1.45	1.32	1.44	1.39	1.47	1.42	1.34
11.25	43.75	—	—	—	1.58	—	—	—
12.50	43.75	2.00	2.00	1.96	—	1.83	2.00	1.50

TABLE 6
RELATIVE RATES MEASURED ON B, B¹ AND E¹ TOGETHER
WITH THE EXPERIMENTAL CONDITIONS USED

$P_{C_3H_8} \times 10^2$ (atm)	$P_{H_2} \times 10^2$ (atm)	Rate relative to that under standard conditions (r_x/r_{av})					
		Catalyst B 225°C	Catalyst B 236°C	Catalyst B 250°C	Catalyst B 260°C	Catalyst B¹ 213°C	Catalyst E¹ 206°C
6.25	50.00	0.87	0.71	0.77	0.67	0.76	—
6.25	37.50	1.52	1.28	—	1.21	1.64	1.36
6.25	31.25	—	2.02	1.55	1.61	2.38	1.83
6.25	25.00	3.43	3.02	2.25	2.13	4.13	4.14
6.25	18.75	6.29	4.78	3.16	2.78	7.87	—
3.13	43.75	0.50	0.45	0.53	0.55	—	—
5.00	43.75	—	—	—	—	0.80	0.86
6.25	43.75	1.00	1.00	1.00	1.00	1.00	1.00
7.50	43.75	—	—	—	—	—	1.20
9.38	43.75	1.58	1.98	1.12	1.57	1.30	1.42
12.50	43.75	1.95	2.51	1.79	2.02	1.82	—

the metal surface areas had only increased by maximum factors of 1.2 and 3.6, respectively. Thus there was a considerable increase in the specific activity of these catalysts.

Variation of the reactant partial pressures on these catalysts resulted in the relative rates shown in the last two columns of Table 6. The calculated values of n and m arc shown in Table 7. On average, n decreased slightly and m increased after Soxhlet extraction.

Attempts to study the reaction on finely

TABLE 7
THE PRESSURE DEPENDENCIES OF PROPANE (n)
AND HYDROGEN (m) OBTAINED FROM CHANGES
IN RELATIVE ACTIVITY TOGETHER
WITH REACTION CONDITIONS
AND DERIVED VALUES OF f

Catalyst	Reaction temperature (°C)	n	m	Standard conversion (%)	f
A	231	0.96	2.04	1.02	1.7
B	214	0.95	2.30	0.16	1.1
	225	1.02	2.00	0.42	2.1
	236	1.09	2.05	1.33	2.4
	250	0.96	1.47	4.6	2.9
	260	0.99	1.34	11.6	3.3
C	240	0.94	2.08	1.24	1.5
D	223	0.87	2.24	0.15	0.55
E	238	0.94	2.15	1.1	1.3
F	247	0.97	1.88	0.53	2.1
G	312	0.59	0.99	0.91	1.3
B¹	213	0.91	2.40	1.00	0.53
E¹	206	0.82	2.20	0.67	0.16

divided nickel powders were unsuccessful because these sintered into discs very easily and no measurement of activity was possible.

Selectivity

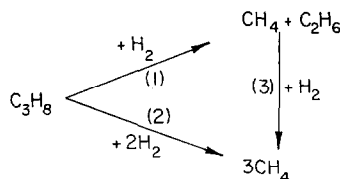The formation of products can be represented diagrammatically as follows:

Thus complete hydrogenolysis of propane to methane can occur by two consecutive reactions or by reaction (2) which is in competition with reaction (1). As it is known that ethane is much less reactive than propane (28, 29) we assumed that reaction (3) was negligible under our conditions and treated the system as two simultaneous reactions. We defined selectivity as the fraction of propane in which only one carbon–carbon bond is broken, i.e., reaction (1).

Figure 8 shows a plot of selectivity of reaction on various catalysts against reaction temperature; the points from experiments, under standard conditions, on Catalysts A to G fall within a broad band. The Soxhlet-extracted catalysts give higher selectivities than the normal catalysts: but finely divided catalyst showed no significant change
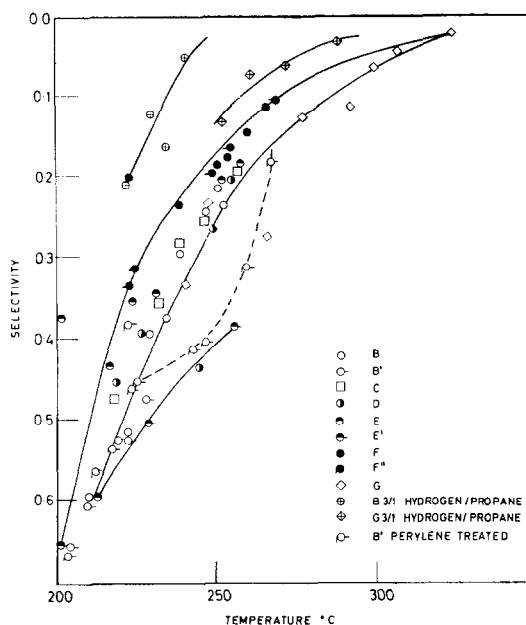
FIG. 8. Variation of selectivity to ethane formation with reaction temperature on several catalysts under standard and varied conditions.

in selectivity. A sample of B¹ poisoned with perylene gave higher selectivities than B¹, but reaction after hydrogen treatment at 360°C gave selectivities similar to those obtained from B¹ over a range of temperatures. Reaction with lower hydrogen-to-propane ratio showed decreased selectivity over temperature range studied and the data in Table 8 show that selectivity also decreased at a constant reaction temperature as the ratio of hydrogen to propane was decreased. These decreases were real and were not merely due to increased reaction.

TABLE 8

VARIATION OF SELECTIVITY WITH HYDROGEN PARTIAL PRESSURE AT A CONSTANT TEMPERATURE ON CATALYSTS B, B¹, AND D

$P_{H_2}/P_{C_3H_8}$:	8	7	6	5	4	3
Catalyst B, 228°C	—	0.43	0.4	0.29	0.24	0.20
Catalyst B¹, 213°C	0.5	0.48	—	0.39	—	0.23
Catalyst D, 227°C	—	0.37	0.32	0.21	0.24	0.20

DISCUSSION

Catalysts

As expected, in Catalysts A to F, decrease of the metal surface area with the temperature of pretreatment (Table 1) was not due to the decrease in total area. This is shown in Fig. 9, where the metal surface area and total surface area were plotted against pretreatment temperature. When the total surface area had been decreased to 120 m²/g—a decrease of 30%—the metal surface area had been reduced by 63%. Thus the nickel oxide/nickel system was much less stable to sintering than the alumina.

It is possible that because of migration of the alkali metal during pretreatment, some of the metal surface was covered and this also contributed to the loss of metal area. However, it is unlikely that such migration was significant since the fractional loss was greatest at the lower temperatures.

The crystallite size of the nickel in reduced catalysts closely followed that of the corresponding oxide but there seemed to be a significant decrease in the nickel crystallite size of Catalyst F. The decrease in crystallite size was similar to that reported by Adler and Keavney (3) and Gruber (7) in the breakup of platinum oxide during reduction. The other catalysts did not show this effect, but sintering during reduction could have masked it. Because various crystallite shapes were seen in the catalyst a good agreement was not expected between metal surface areas obtained by chemisorption and those calculated from average crystallite size. But Fig. 10 shows that a good empirical relationship was obtained between the metal surface area and crystallite size. Thus X-ray methods gave a good indication of the available metal surface area in this batch of catalysts.

After the reduction process itself the average crystallite size of nickel was greater at the outlet of reactor B than at the inlet; this indicated that the water formed during reduction accelerated sintering of the nickel oxide/nickel catalyst.

The results in Fig. 1 showed that the average crystallite size of nickel increased during reaction itself. Despite the slightly
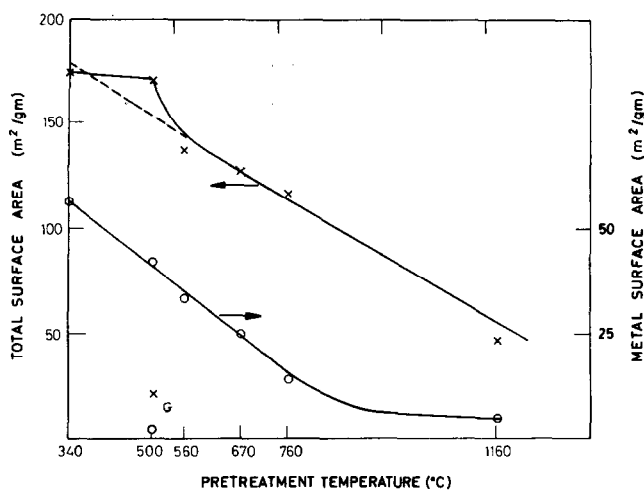
FIG. 9. Graph showing the variation of surface areas with the pretreatment of Catalysts A to F (on curves) and G (off curve).

higher temperature at the inlet, the larger crystallite size at the outlet was maintained while the samples sintered further during reaction. This sintering was not a function of the gas composition itself because the experiments with simulated gas compositions did not show any differences. Therefore, the rates of sintering during reaction at the inlet and outlet must have been about the same. Independent work on catalysts of the same type gave a similar result (*30*); the rate of long-term crystallite growth under a standard atmosphere was largely independent of initial crystallite size after reduction.

When the catalysts were examined in the electron microscope three types of crystallite were found. The hexagonal platelets (A) were present in all catalysts with a similar ratio of length to thickness, suggesting that growth in any direction was related to the crystallite length in that direction. The various shapes with well-defined diffraction contrast (B) were very like crystallites in nickel films described by Allpress and Sanders (*31*), who explained the various shapes seen in terms of multiple twinning on the (111) faces. We have not yet been able to study electron diffraction from crystallites in our catalysts or use dark-field techniques to identify the growth planes. But the contrast patterns indicate the presence of stacking faults of some type in these crystallites. Van Hardeveld and Hartog recently reported similar effects in supported nickel catalysts (*20*). The third type of crystallite (C) resulted from extensive sintering and its properties probably approach those of bulk metal.
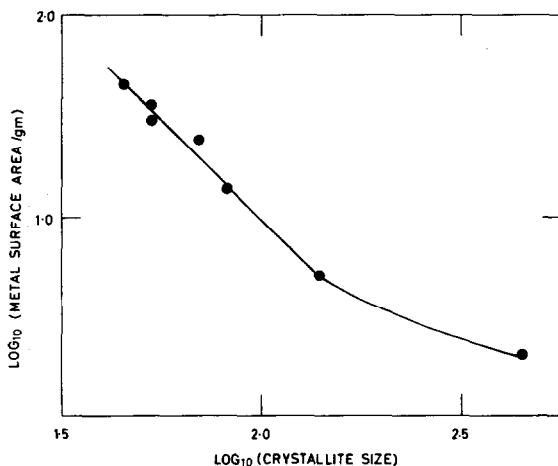
The presence of three types of crystallites may indicate modification of the sintering by changes in the support or in the support–metal bonding. Thus reduction in the alkali metal content could affect the bonding to make two-dimensional growth more favor-

FIG. 10. Graph showing the relationship between the metal surface area and crystallite size.

able than three-dimensional. A preponderance of platelets would result. Type C probably resulted from massive sintering when crystallites touched each other. The attempts to use nickel powder showed how easy it was to sinter nickel particles under these experimental conditions.

Adsorption studies in the microbalance showed $S_{BET} < S_t$. De Boer and others (32) reported the same effect for microporous material and attributed it to the large values of C in the BET equation. However, the values of C quoted were substantially larger than values of 200 to 300 found in this work and other effects can give the same result. De Boer and others (33) found $S_{BET} < S_t$ in work on graphitized carbons and attributed (34) this effect to stepwise adsorption on a homogeneous surface. This type of adsorption did not take place on our catalysts but further work is required before the effect can be attributed solely to microporosity.

The t plots in Fig. 2 and the results in Table 2 show that the microporosity in reduced catalysts, expressed as either $S_t - S_w$ or M_v, decreased with increased temperature of pretreatment. The data in Table 2 showed that $S_t - S_w$ had increased in the extracted catalysts. B^1 gave a value of 107 m²/g compared to 58 m²/g for B and E^1 gave a value of 43 m²/g compared to 32 m²/g for E. The calculated volumes in micropores, M_v, also showed increases; M_v of B^1 was three times that of B and that of E^1 was more than twice the value of E. Thus, irrespective of the method of calculation from the t plot, the Soxhlet extraction increased the microporosity.

This treatment also resulted in increased metal surface areas from 42 m²/g in B to 50 m²/g in B^1 and from 14 to 37 m²/g in E^1. It was not known how much of these increases was due to straightforward removal of alkali metal (or alumina) from the surface and how much was due to other processes such as widening of pore mouths to increase the total surface area available.

Reaction studies

The Arrhenius plots in Fig. 6 gave the catalytic activities of catalysts A to F at

203° and 253°C. These are plotted against metal surface area in Fig. 11. Because the catalyst samples for the reactor were weighed in the oxide form, the metal surface areas are now those calculated on the same basis. Figure 7 gave values for the activities of Catalysts B to G at 203°, 227°, and 253°C and these are plotted against metal surface area in Fig. 12.

With the exception of sample A the activity of these catalysts was proportional to metal surface area. This agrees with the results of other workers. Yates and others reported (15) a constant specific activity for the hydrogenolysis of ethane on several impregnated nickel on silica catalysts. Nickel on various supports also showed constant specific activity for other reactions such as hydrogen–deuterium exchange or phenol hydrogenation (35) and benzene hydrogenation (19, 20).

The higher specific activity of A is discussed later together with those of Catalysts B^1 and E^1.

The apparent activation energy found on these catalysts was much larger than the values of 34 and 35 ± 5 kcal/mole reported for reaction on nickel on kieselguhr (28) and nickel films (29). Only when the metal surface area was very low, in Catalyst G, or when the ratio of hydrogen to hydrocarbon in the reaction mixture was low, did the values we found approach those found by other workers.

The literature values of activation energies for the hydrogenolysis of ethane on nickel show great variation. Balandin (36) found values of 20 kcal/mole with a slight excess of ethane: 45–50 with a slight excess of hydrogen and 19 kcal/mole when the metal surface had been swept with nitrogen. Morikawa and others (37) found a value of 43 kcal/mole. All these workers were using 15% nickel on kieselguhr. Anderson and Baker (29, 39) reported values of 69 and 58 kcal for nickel films while Taylor (16) and others found values of 20 to 40 kcal/mole depending on the support and metal content. A reduction of apparent activation energy in the hydrogenolysis of butane on palladium has also been reported by Anderson and Avery (40); they found a decrease from 38
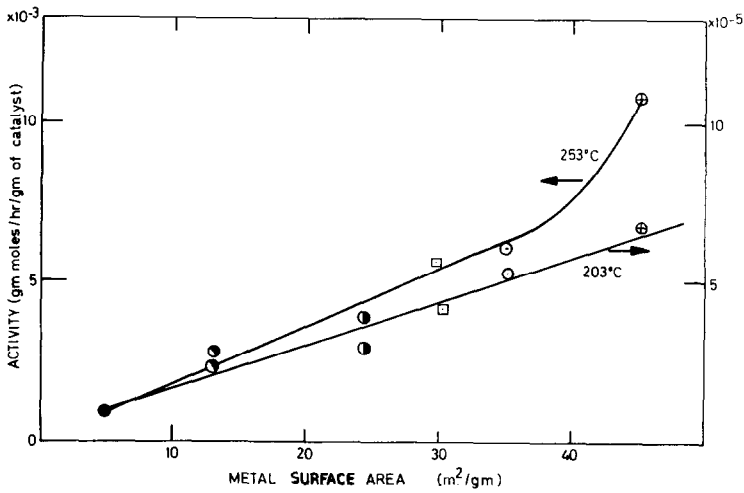
F. E. SHEPHARD

FIG. 11. Plots of the relationship between metal surface area and activity of catalysts at 203° and 253°C: A, ⊕; B, ⊙; C, ⊡; D, ◐; E, ◖; F, ●.
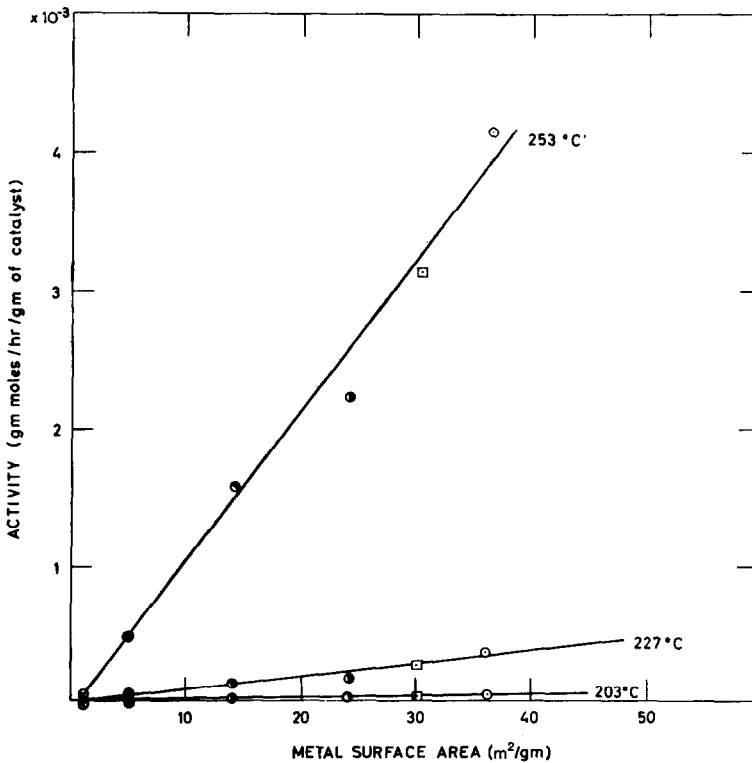

FIG. 12. Plots of the relationship between metal surface area and activity of catalysts at selected temperatures: G, ⊗; other symbols as in Fig. 11.

to 13 kcal/mole when the hydrogen partial pressure was reduced by about 50%.

The values of apparent activation energy from Catalysts B^1, E^1 and A to F were all close to 50 kcal/mole although B^1 and E^1 gave slightly higher values. If the true activation energy was varying from catalyst to catalyst there would need to be remarkable compensation by the heat of adsorption terms to give this constant value. Thus, although metal content or crystallite form may affect the true activation energy of a reaction, the high value of apparent activation energy in this work was due mainly to heat of adsorption terms. The low value found on Catalyst G may reflect changes in the adsorption characteristics of nickel when crystallites are very large. There was no evidence of diffusion effects. The lower activity of F'' was probably due to a slight change in contact time.

The reaction on these catalysts was strongly inhibited by hydrogen. A rate equation with a high negative power of hydrogen has been reported before for the hydrogenolysis of propane (28) on nickel, and it has been interpreted in the following manner (41).

The propane lost hydrogen on the surface to give the following equilibrium:

$$C_3H_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_3H_f)_{ads} + (8 - f)/2\ H_2 \qquad (1)$$
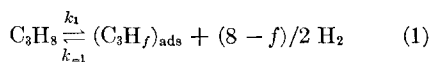
The authors assumed that the slow step was the cleavage of the adsorbed species into fragments and that it involved a molecule of hydrogen.

$$(C_3H_f)_{ads} + H_2 \rightarrow (CH_x)_{ads} + (C_2H_y)_{ads} \qquad (2)$$

They also assumed that the fragments formed were rapidly removed to the gas phase as methane and ethane. The fraction of the surface, θ, covered with $(C_3H_f)_{ads}$ species was then derived from Eq. (1) as follows:

$$k_1 P_{C_3H_8}(1 - \theta) = k_{-1}P_{H_2}^{(8-f)/2}(\theta)$$

whence

$$\theta = \frac{K_1 P_{C_3H_8}/P_{H_2}^{(8-f)/2}}{1 + K_1 P_{C_3H_8}/P_{H_2}^{(8-f)/2}} \qquad (3)$$

with $K_1 = k_1/k_{-1}$. It is well known that an

expression such as (3) can be replaced in a restricted pressure range by

$$\theta = K_1^n[P_{C_3H_8}/P_{H_2}^{(8-f)/2}]^n$$

where $\theta < n < 1$. The rate of the overall reaction, with Eq. (2) as the slow step, became

$$\begin{aligned} \text{rate} &= k\theta P_{H_2} \\ &= kP_{C_3H_8}P_{H_2}^{[1-n(8-f)/2]} \\ &= kP_{C_3H_8}P_{H_2}^{-m} \end{aligned} \qquad (4)$$

By substituting the experimental value of n and a suitable value of f in Eq. (4) they found good agreement between experimental and theoretical values of m.

On Catalysts A to G the necessary values of f in this work fell between 0.55 and 3.3 under all conditions. These are significantly higher than the zero values found by previous workers (15, 41). Reaction on Soxhlet-extracted catalysts gave lower values of f at the same temperature, e.g., 0.53 on B^1 compared to 1.1 on B. If comparison was made at similar standard conversions the Soxhlet-extracted catalyst still gave lower values of f. E^1 gave a value of 0.16 at 0.67% conversion and that of E was 1.3 at 1.1% conversion. If the theoretical treatment is approximately valid our results can be interpreted as showing that alkali metal in these nickel-alumina catalysts resulted in adsorbed hydrocarbon species which were less dissociated than those on undoped catalysts. The effect of the alkali metal was similar to that reported by Cimino and others (41) in a study of ethane hydrogenolysis on promoted iron catalysts. They found that the addition of 0.05% K_2O to the supported iron catalysts had little effect on the rate equation but a value of 0.6% K_2O increased the derived f value from 2 to 4. These workers also found a decreased activity on the addition of alkali but no measurements of metal surface area were made.

Inhibition by hydrogen decreased as the reaction temperature was increased although there was no simple relationship between the value of m and the temperature. So the empirical rate equation at one temperature was not sufficient to describe the reaction over a wide temperature range.

This empirical interpretation of the kinetics can rationalize some of the results but is not really satisfactory; for example, the derived value of f (Table 3) increases with reaction temperature on Catalyst B from 1.1 to 3.3. The conversions at the two highest temperatures were rather high but the trend was established at lower conversions and on other catalysts. These values would lead to the conclusion that propane was less dehydrogenated at higher temperatures but this conclusion seems unlikely to be correct and is contrary to the work of Galwey and Kemball (42). Another weakness of this treatment, already mentioned in the literature (43), is that no adsorbed species except C_3H_f was considered to affect the surface coverage. The rate equation itself is derived on the assumption that k is constant at a fixed reaction temperature. The present work showed that the apparent activation energy varied when hydrogen pressure was varied at a fixed reaction temperature. Unless the pre-exponential term within k also varied by an appropriate amount the derived rate equation itself is incorrect.

Galwey (44, 45) and Anderson and Baker (39) have found desorption of products to be the rate-controlling step in reactions of adsorbed alkanes with hydrogen on nickel. Anderson and Baker based their conclusions on the fact that they obtained reasonable agreement between experimental and theoretical product composition in the temperature range studied.

Because the surface concentration of the desorbing species was not known, their calculated product compositions were fitted to the observed compositions at one temperature T_0. Activation energies from the literature for desorption of products were used to calculate the percentage composition of products over a range of temperature. We treated the results in this work in a similar manner, and selected theoretical and experimental curves are shown in Fig. 13, together with curves reported by Anderson and Baker for the same reaction. The theoretical curves were all calculated from the experimental product compositions at 257°C. The agreement between the theoretical and experimental curves is good and could be improved

by taking a median value of T_0 for each catalyst sample.

Neither of the kinetic approaches was very rigorous and both had some points in their favor. However, the argument for desorption as the rate-controlling step is marginally stronger. It required no assumptions that were obviously incorrect and did not lead to any results which seem to be invalid.

Increased Specific Activity

Catalysts A, B^1, and E^1 showed increased specific activity which was not a function of any one property. The presence of very small crystallites could affect activity but neither X-ray nor electron microscopic examination gave information about such crystallites. The increase in specific activity was most marked in Catalysts B^1 and E^1. The nickel crystallites in these were predominantly of the platelet type which may be more favorable for hydrogenolysis.

There is some evidence in the literature that crystallite size can affect the properties of metals in chemisorption and catalysis. In a study of ethane hydrogenolysis on nickel-alumina catalysts, Carter and others (17) found that catalytic activity decreased at a greater rate than metal surface area. They attributed this effect to a higher specific activity of small crystallites. Other workers (46) reported that the crystallite size of supported nickel even affected the type of bonding with nitrogen.

The increased microporosity in these catalysts may indicate a structure which permitted the development of more active crystallites: it could also have affected the measurement of activity itself.

Unless there was a remarkable compensation between heats of adsorption and the true activation energy, the derived rate equations and the constant apparent activation energy suggest that the active sites on all catalysts, except perhaps G, were of the same type. If this was so, the higher specific activity of the Soxhlet-extracted catalysts and Catalyst A was due to an increase in the number, or availability, of active sites. Previous workers who found a constant apparent activation energy for hydrogenolysis of ethane on impregnated nickel
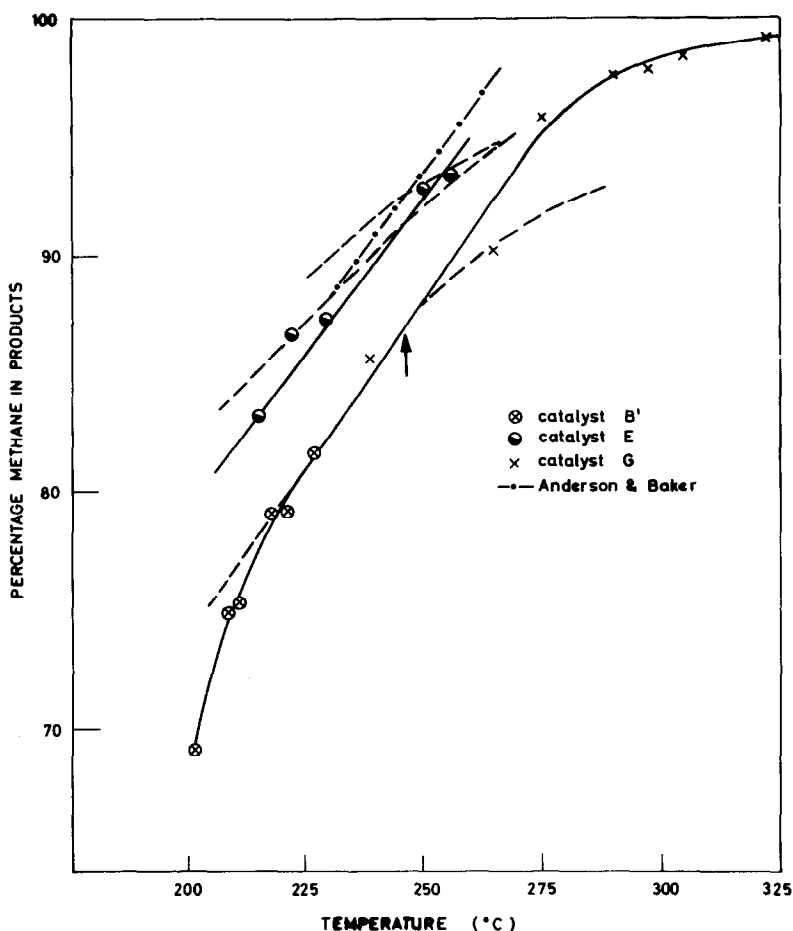
Fɪɢ. 13. Comparison of the theoretical and experimental percentage of methane in the products within the range of temperatures used for reaction.

catalysts were of the opinion that compensation between the true activation energy and heats of adsorption occurred (14) and that the pore structure had no effect. The situation in these coprecipitated catalysts may be different.

Schuit and van Reijen (1) found that some nickel in coprecipitated nickel-silica catalysts was accessible to hydrogen but not to other gases and postulated the presence of a silica skin on these areas. Work in these laboratories has shown (47) that molecules such as carbon dioxide can be trapped within the micropores of alumina during preparation; it seems equally possible for nickel surface to be present within pores which have ends wide enough to permit hydrogen, but not larger molecules, to enter. Then the removal

of alkali metal and alumina could increase the surface available to propane by a larger amount than the surface available to hydrogen.

Hydrogen chemisorption is widely used to calculate specific activity but the results often appear to be contradictory. For example, Sinfelt and co-workers have studied the hydrogenolysis of ethane on supported nickel catalysts. In one report (17) a series of catalysts (a) was prepared by heating samples of a nickel on silica-alumina catalyst at various temperatures. The catalysts heated at the lowest temperature had the highest specific activity and this was related to the small crystallite size of nickel. Another series of nickel on silica catalysts (b) contained different percentages of metal but

all received the same heat treatment in preparation. On these catalysts, the specific activity, and the apparent activation energy, increased with increased metal content. Thus the catalyst with probably the smallest crystallite size had the lowest specific activity. Although it is possible that the different supports may have affected the activity, both catalysts might have had "blocked pores" which admitted hydrogen but not ethane. The number of these pores and therefore the available metal within them could have decreased during high-temperature treatment of series (a) catalysts. The percentage of metal within "blocked pores" might have decreased as the total metal content was increased in series (b) catalysts. If specific activity was calculated on the hydrogen chemisorbed then apparent changes in activity would result even if the true specific activity was constant.

Thus while hydrogen chemisorption is useful for comparing the activity of closely related catalysts it is difficult to be sure that calculated changes in specific activity are real ones. So although observed specific activities were higher on A, B^1, and E^1 further work is necessary before the effect of the increases can be linked to particular catalyst properties.

Catalyst G was anomalous in that it yielded a rate equation and apparent activation energy which differed significantly from the others. However, the reaction temperature range required for this catalyst was much higher than that for the other samples and the differences mentioned are probably due only to the effect of higher temperature on the heats of adsorption.

Selectivity

The selectivity of reaction varied with reaction conditions and amount of alkali metal in the catalysts. It is known that the state of a metal surface can affect selectivity. In the deuterium exchange of p-xylene on nickel films the relative exchange rates of ring hydrogen and methyl hydrogen changed by a large factor when the films were sintered (48). Other workers have reported that the relative rates of exchange and deuteration of benzene depended on nickel crystallite size (20).

Any steric or electronic effects which reduced the chance of complete interaction of propane with the surface could lead to increased selectivity. If we assume that the large values of m in the empirical rate equations indicated strong chemisorption then selectivity should have decreased as the hydrogen partial pressure was reduced or the reaction temperature increased. Conversely, when m had larger values than normal, i.e., on catalysts B^1 and E^1, selectivity should have been higher. These were the effects found. The increased selectivity on the perylene-poisoned surface can also be explained by a steric effect which reduced the number of sites capable of interacting with the three carbon atoms of propane. This type of effect has been reported before; Bourne and others (49) found that partially sulfided nickel surfaces hydrogenated diolefins to monoolefins because the adsorbed sulfur prevented complete association with the surface.

Selectivity can be a function of porosity under certain conditions (50). If propane reacted in two consecutive first-order reactions the higher selectivity of catalysts B^1 and E^1 could be attributed to opening of pore mouths. But while Soxhlet extraction probably opened some "blocked pores," it obviously led to increased microporosity and therefore it is more likely that selectivity would have decreased. To explain selectivity changes on the perylene-poisoned catalyst would require blockage of small pores by perylene products and those at reduced hydrogen partial pressures would require partial blockage of wide pores by polymerization products. But we know that polymerization reactions were not important as the activity under standard conditions had the same value before and after experiments with decreased hydrogen partial pressure. It is more likely therefore that selectivity was not due to secondary effects but was a function of the various adsorbed species.

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