JOURNAL OF CATALYSIS 16, 363-369 (1970)

The Hydrogenation of Cyclopropane over Supported Nickel Catalysts

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Received July 15, 1969

Kinetic data are reported for the reaction of cyclopropane with hydrogen over a series of nickel catalysts supported on alumina and silica–alumina. Metal areas of the catalysts were measured by hydrogen chemisorption. Both hydrogenation to propane and hydrocracking to equimolar amounts of ethane + methane occur. Over all the catalysts, both reactions are zero order in hydrogen and approximately 0.6 order in cyclopropane. Activation energies are given and it appears the activation energy for the hydrocracking reaction is approximately 2–4 kcal greater than that for the hydrogenation reaction. The selectivity of the catalyst (rate of hydrogenation/rate of hydrocracking) appears to be quite sensitive to the nature of the support and the metal dispersion. The total specific activity based on nickel area is however approximately the same for all the catalysts studied. It is tentatively suggested that both reactions proceed through a series path involving a common overall rate-determining step.

INTRODUCTION

The study of supported metal catalysts has attracted much attention in recent years owing to the industrial importance of this type of catalyst. Although observations suggesting complex interaction between metal and support were reported 20 years ago (*1*), real progress in this field has become possible only recently with the development of techniques for measuring metal surface areas and crystallite sizes. Since the fraction of "edge" and "corner" atoms increases as the metal crystallite size is decreased it is possible, *a priori*, that the metal crystallite size may have an effect on the catalytic properties quite apart from any specific metal–support interaction effects. The problem of metal–support interaction may, therefore, be conveniently considered in two parts: (i) To what extent does the chemical nature of the support affect the catalytic properties of the metal? (ii) For a given metal and support, how are the catalytic properties affected by the degree of dispersion of the metal (the crystallite size)?

Although the existence of both these effects has been demonstrated, the extent to which they are significant is still debatable. For a number of hydrogenation reactions, extensive studies have shown that the magnitude of these effects is small. The support appears to act only as an inert carrier of the metal so that the specific activity (based on metal surface area) is approximately constant and independent of either the nature of the support or the crystallite size. Such behavior was observed for the hydrogenation of benzene over platinum, palladium and nickel supported on silica, alumina, silica–alumina and magnesia (*2*, *3*) and for the hydrogenation of cyclopropane over various supported platinum catalysts (*4*).

Very different behavior was found, however, by Sinfelt and co-workers in their study of ethane hydrogenolysis (*5–10*). A series of catalysts containing 10% nickel on silica showed approximately constant specific activity (*5*). By contrast the specific activity of nickel supported on silica–alumina was much lower and was strongly dependent on crystallite size (*6*, *8*, *9*). Shephard, in his recent study of propane hydrogenolysis over catalysts containing 75% nickel on alumina (*11*), found the specific activity approximately independent of crystallite size but very sensitive to small changes in the support composition (e.g., removal of traces of alkali).

A somewhat similar conclusion was reached by Dorling and co-workers (*12*) as a result of their extensive study of the hydrogenation of ethylene over platinum–silica catalysts. No significant variation in activity with crystallite size was observed although it was shown that the methods used to effect changes in crystallite size (e.g., sintering at elevated temperatures) may produce small changes in the composition of the support which profoundly affect the specific activity, leading to an apparent crystallite size effect.

Previous studies of metal–support interaction effects have been concerned mainly with variations in the specific activity rather than in the selectivity of the catalyst. In the present paper, kinetic data are presented for the reaction of cyclopropane with hydrogen over a series of supported nickel catalysts. Both hydrogenation to propane and hydrocracking to methane and ethane occur making this a convenient system for studying the effect of the support on catalyst selectivity.

EXPERIMENTAL METHODS

Kinetic Studies

The kinetic data were obtained using a differential flow reactor operating at approximately atmospheric pressure. Reaction rates and reactant partial pressures were calculated from measurements of the gas flow rate and composition.

Metered streams of hydrogen and cylopropane were passed through the reactor which contained about 0.5 g of catalyst mixed with Pyrex glass beads and was maintained at a constant temperature in an ultrathermostat (±0.1°C). The gas composition at reactor inlet and outlet was determined chromatographically using a Perkin-Elmer model 880 gas chromatograph fitted with a silica gel column and thermal conductivity detector. Hydrogen was used as a carrier gas so that the hydrogen in the reaction mixture was not detected. Methane, ethane, propane, and cyclopropane were determined and the hydrogen concentration was obtained by difference. Precise control of the flow rate was achieved by using a "Cartesian Manostat" and the total flow rate was measured at the reactor outlet by a soap bubble meter. Pretreatment and regeneration of the catalyst were carried out *in situ* with the thermostat replaced by an electric furnace. Temperatures inside the reactor were measured by two chromel–alumel thermocouples.

Reduction of catalysts with hydrogen prior to the kinetic studies was carried out at 360°C for a period of 12 hr. Slow deactivation of the catalyst was observed during the course of the kinetic runs. After an initial period (2–3 hr) of fairly rapid deactivation the activity remained approximately constant for at least 10 hr, during which period the kinetic data were obtained. This period of constant activity could be extended by purging the catalyst intermittently with hydrogen during the course of the run. Even after deactivation the catalyst could be regenerated to approximately the same steady-state activity by repetition of the hydrogen pretreatment at 360°C.

Materials

Hydrogen. Matheson prepurified hydrogen (99.95% min) was passed through a Deoxo unit to remove any traces of oxygen and through a tube packed with 5A molecular sieve to remove traces of moisture formed in the Deoxo unit.

Cyclopropane. Matheson cyclopropane was used without further purification. No impurities were detected chromatographically.

Catalysts. The catalysts used were supplied by the Harshaw Company and were crushed to 100–140 mesh before use to eliminate pore diffusional resistance. Experiments carried out with larger particles showed that at temperatures below 100°C pore diffusional resistance is negligible for catalyst particles smaller than 40 mesh. Details of the catalysts studied are summarized in Table 1.

Surface Area Measurements

Total areas were determined by measuring the adsorption of nitrogen at liquid nitrogen temperatures using a Perkin-Elmer model 212D Sorptometer. Nickel surface areas were determined from hydrogen chemisorption isotherms measured at 250°C in order to minimize physical adsorption on the support. The procedure was essentially similar to that used by Yates *et al.* (*5*) and by Brooks and Christopher (*13*). The samples of catalyst used for the hydrogen adsorption measurements were subjected to the same pretreatment as was employed for the kinetic studies. The isotherms, which were determined gravimetrically using a Cahn R. G. recording electrobalance, showed little further uptake of hydrogen at pressures between 100 and 300 mm Hg: monolayer coverage was therefore assumed. Surface areas were calculated by assuming that each exposed nickel atom adsorbs one hydrogen atom so that the effective area covered is approximately 12 Å^2/hydrogen molecule (*13*). For the catalyst of smallest area, the quantity of hydrogen adsorbed was too small to measure accurately and the value obtained for the nickel area is, therefore, very approximate.

No direct measurements of metal crystallite size were carried out. However, an approximate measure of the degree of dispersion may be obtained from the catalyst composition and nickel area by calculating the fraction R of the total nickel atoms which are accessible to hydrogen. If it is assumed that the metal is present as approximately spherical crystallites of uniform size, the mean crystallite diameter may be calculated but for most purposes the parameter R is probably a more useful measure of the extent of dispersion.

RESULTS AND DISCUSSION

The pretreatment procedure adopted in the kinetic studies is outlined above. Preliminary experiments showed that the behavior of the catalyst is profoundly influenced by the pretreatment and an approximately steady-state activity is reached only after 2 or 3 hr under operating conditions. The necessity for conducting a sufficient series of preliminary experiments before meaningful kinetic data can be obtained cannot therefore be overemphasized.

Kinetic data were obtained for each catalyst over a range of hydrogen and cyclopropane partial pressures from 0.1 to 0.9 atm at temperatures within the range 30 to 90°C. Both hydrogenation and hydrocracking reactions were observed over all catalysts but methane and ethane were always present in the products in equimolar amounts showing that secondary hydrocracking of ethane did not occur. An extensive series of experiments (approx 60 runs for each catalyst) was carried out at 60°C to determine the form of the kinetic rate equation. The kinetic data for both hydrogenation and hydrocracking reactions were fitted by regression analysis to power law expressions of the form:

$$r = k\, p_{\mathrm{H}}{}^{m} \cdot p_{C}{}^{n},$$

TABLE 1
DETAILS OF CATALYSTS

Catalyst	Ni(%)	Support	BET area (m^2/g)	Ni area (m^2/g)	R
Ni-0104	58	Kieselguhr (SiO_2–Al_2O_3)	82	63	0.163
Ni-0901	5	SiO_2-Al_2O_3	<1.0	~0.2	0.006
Ni-1430	40	Al_2O_3	225	5.7	0.022
Ni-0707	14	Al_2O_3	172	2.8	0.03
Sinfelt (14)	10	SiO_2-Al_2O_3	—	6.8	0.1
	10	SiO_2	—	13.3	0.2

where r = reaction rate (g moles of cyclopropane converted per hr per g of catalyst); k = rate constant per g of catalyst; p_H = hydrogen partial pressure (atm); p_c = cyclopropane partial pressure (atm). The resulting exponents and rate constants are summarized in Table 2. The less extensive series of runs which were carried out at other temperatures, within the range 30–90°C, showed no significant changes in the exponents. Activation energies for both reactions calculated from the slopes of the Arrhenius plots, are included in Table 2, together with estimated limits of error.

TABLE 2
SUMMARY OF KINETIC DATA

	Hydrogenation				Hydrocracking				
Catalyst	k_1 (per g at 60°C)	m_1	n_1	E_1 (kcal)	k_2 (per g at 60°C)	m_2	n_2	E_2 (kcal)	Selectivity at 60°C $= k_1/k_2$
Ni-0901 Ni/SiO_2–Al_2O_3	7.95 $\times 10^{-4}$	−0.01	+0.47	10.6 ± 0.2	9.33 $\times 10^{-5}$	−0.03	+0.35	15.5 ± 1.7	8.5
Ni-0104 Ni/SiO_2–Al_2O_3	0.367	−0.02	+0.54	15.1 ± 0.6	8.2 $\times 10^{-2}$	−0.06	+0.57	16.0 ± 1.8	4.5
Sinfelt (14) Ni/SiO_2–Al_2O_3		−0.2	+0.6	13.8		−0.5	+0.6	13.2	3.5
Ni-0707 Ni/Al_2O_3	7.24 $\times 10^{-3}$	−0.03	+0.67	10.8 ± 0.6	5.58 $\times 10^{-3}$	−0.06	+0.52	13.8 ± 1.5	1.3
Ni-1430 Ni/Al_2O_3	1.9 $\times 10^{-2}$	−0.09	+0.51	12.0 ± 0.5	8.89 $\times 10^{-3}$	+0.04	+0.51	16.0 ± 1.2	2.1
Sinfelt (14) Ni/SiO_2		−0.1	+0.8	13.0		−0.3	+0.4	16.0	0.96

The hydrogen order is almost exactly zero for both reactions over all the catalysts studied. Furthermore, for each catalyst the cyclopropane order is approximately the same for both hydrogenation and hydrocracking. (Differences in the exponents of less than 0.15 are probably not significant.) The selectivity, defined as the ratio of the rate of hydrogenation to hydrocracking, is therefore approximately independent of both hydrogen and cyclopropane pressures and is given by k_1/k_2. Some idea of the consistency of the kinetic data may be obtained from Fig. 1 which shows the rates of hydrogenation and hydrocracking plotted against cyclopropane pressure and from Fig. 2 in which the selectivity is plotted against the mole ratio of cyclopropane to hydrogen in the feed.

The kinetic rate equations obtained by Sinfelt *et al.* working at cyclopropane pressures very much lower than those used in the present study ($p_c \simeq 0.03$ atm) (*14*, *15*) are included in Table 2 for comparison. In spite of the difference in the partial pressure range, the rate equations are quite similar to those obtained in the present study. Since the number of experimental runs is not quoted it is difficult to estimate whether the small negative hydrogen order observed is significant.

The rate constants in Table 2 show pronounced differences in the activity of the different catalysts but these rate constants, based on unit catalyst weight, do not take into account the large differences in active area. Rate constants based on unit nickel surface area are given in Table 3. In spite of the relatively large differences in the rates of the individual reactions (hydrogenation and hydrocracking) which reflect the variation in selectivity among the catalysts, it is apparent that the total reaction rate per unit nickel area is approximately the same for all catalysts varying only over the range 0.0044 to 0.007.

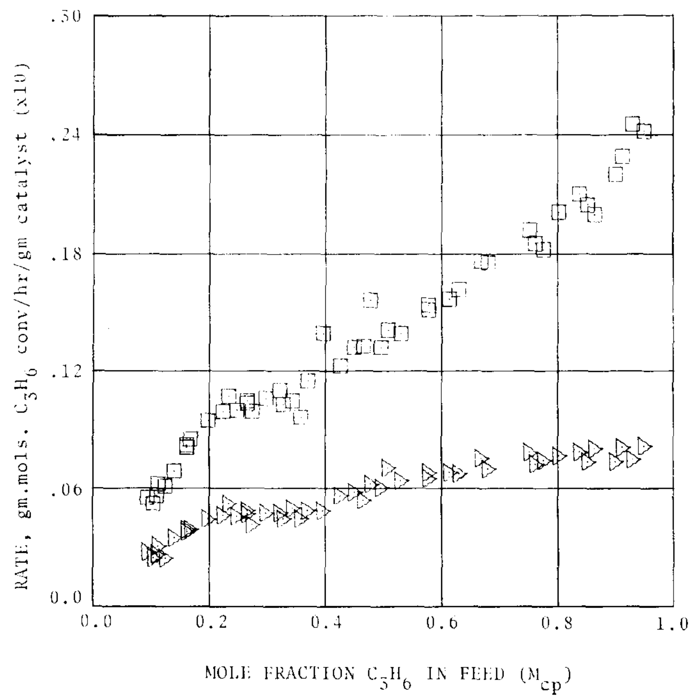


Fig. 1. Rate vs. mole fraction C_3H_6 in feed for catalyst Ni-1430; reaction temperature, 59.6°C; ⊡, hydrogenation; △, hydrocracking.

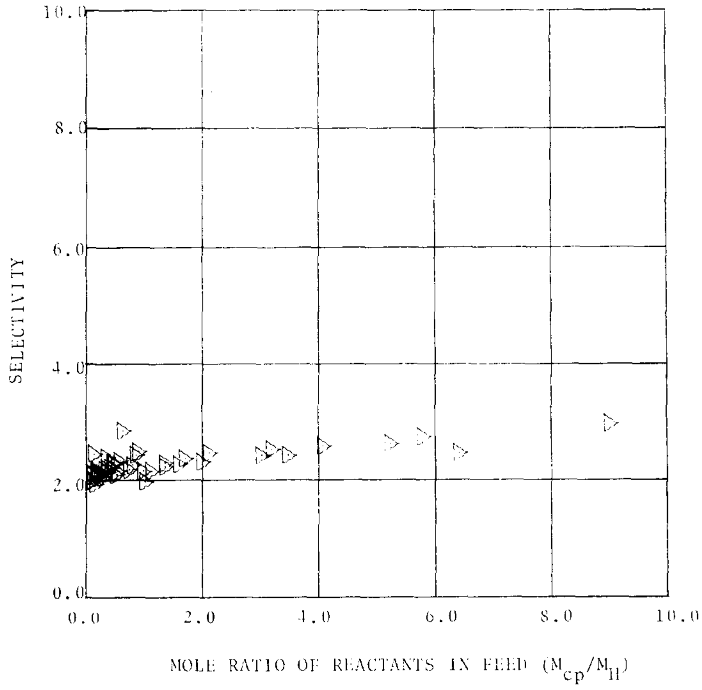


Fig. 2. Selectivity vs. mole ratio of reactants in feed for catalyst Ni-1430.

TABLE 3
SPECIFIC RATE CONSTANTS AT 60°C

Catalyst	Support	R	k'_1	k'_2	Total specific activity = $k'_1 + k'_2$	Selectivity = k_1/k_2
Ni-0104	SiO_2–Al_2O_3	0.163	0.0057	0.00128	0.007	4.5
Ni-0901		0.006	0.0039	0.00045	0.0044	8.5
Ni-0707	Al_2O_3	0.03	0.0026	0.002	0.0046	1.3
Ni-1430		0.022	0.0033	0.0016	0.0049	2.1

[a] k' is calculated by dividing the specific rate constant k in Table 2 by the nickel area (m^2/g).

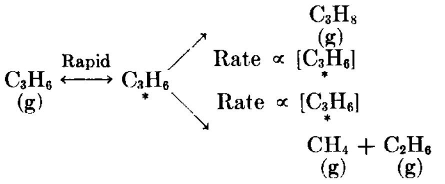
The results of this study thus suggest that, for the reaction of cyclopropane with hydrogen over supported nickel catalysts, changes in the nature of the support and the metal dispersion have very little effect on the total specific activity but a significant effect on the selectivity. The selectivities of the silica–alumina supported catalysts are higher than those of the catalysts supported on alumina alone. In the case of each type of catalyst the higher metal dispersion (larger value of R) is associated with lower selectivity but a more extensive series of experiments over a series of catalysts having the same support but different metal dispersions is required before the relative importance of crystallite size and specific metal–support interaction can be assessed.

The selectivities reported by Sinfelt are generally similar to the values obtained in the present study and may be compared with a value of approximately 6.0 observed by Knor *et al.* (*16*) for evaporated nickel films at 0°C. A direct comparison of total specific activity with the present data is difficult since the order of magnitude difference in cyclopropane pressure and the difference in the temperature range renders such a comparison very sensitive to the precise values of reaction orders and activation energy. It appears, however, that the differences in the total specific activities of Sinfelt's catalysts was much greater than the differences observed in the present study.

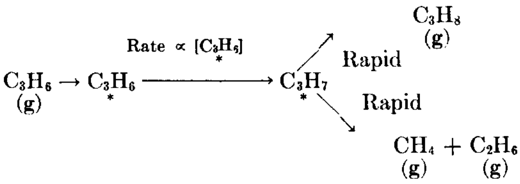
The activation energies show some variation among the catalysts but the activation energy for hydrocracking is consistently higher than that for hydrogenation. This leads to the not unexpected conclusion, that the selectivity of the catalyst decreases, although quite slowly, with temperature.

Although this study is not primarily concerned with the reaction mechanism, some qualitative conclusions may be drawn from the kinetic data. The zero-order dependence on hydrogen implies that there is always an excess of hydrogen on the surface but that the adsorption of cyclopropane is not significantly impeded by the presence of hydrogen. This can be explained if it is assumed that cyclopropane is strongly adsorbed and can therefore displace hydrogen from the surface but that, even when the surface is saturated with cyclopropane, there are still sites available for hydrogen adsorption. Under these conditions the surface concentration of adsorbed cyclopropane would depend only on the cyclopropane pressure. Some evidence in favor of this idea comes from the work of Merta and Ponec (*17*) who showed that a nickel film saturated with cyclopropane could still adsorb further carbon monoxide without displacing the hydrocarbon from the surface.

The question of whether the hydrocracking reaction proceeds through a series or a parallel reaction path has not been unambiguously resolved. Under the conditions of the present study, the rate at which gaseous propane reacts is negligible. This was established experimentally using a propane/hydrogen inlet gas and confirms the observations of Taylor *et al.* (*14*) and Anderson and Avery (*18*). It is, however, still possible that both reactions proceed through the same adsorbed intermediate. If this is so, and if the rate of each reaction is proportional to the surface concentration of this intermediate, the observed similarity in the orders of the hydrogenation and hydrocracking reactions would be explained. These conditions could be fulfilled by either a "parallel" reaction path:



or by a "series" reaction sequence:



The negligible reaction rate with gaseous propane could be due to a slow adsorption step. The latter sequence, which postulates a single rate-controlling step for the overall reaction, can explain the approximately constant overall specific activity coupled with the variable selectivity of the differently supported catalysts if it is assumed that subtle changes in the nature of the catalyst have little effect on the initial overall rate-controlling hydrogenation step but a significant effect on the relative rates of the (rapid) secondary steps. On the basis of the parallel reaction scheme, the constant total specific activity would appear to be entirely fortuitous. More extensive studies are required, however, before any definite conclusions about the reaction mechanism can be drawn.

ACKNOWLEDGMENTS

The hydrogen chemisorption measurements were carried out at New York University by kind permission of Dr. John Happel. Financial support by the National Research Council of Canada is gratefully acknowledged.

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