JOURNAL OF CATALYSIS 24, 153–160 (1972)

The Kinetics and Mechanism of the Catalytic Hydrogenation of Cyclopropane

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Received April 13, 1971

Kinetic data are presented for the reaction of cyclopropane with hydrogen over four supported nickel catalysts. Both hydrogenation and hydrocracking reactions occur to yield propane, ethane, and methane; but, on the basis of the kinetic evidence, it is suggested that the reactions proceed through a series mechanism involving a common rate controlling step. Analysis of the kinetic data by the method of Hougen and Watson gave, as the best fit rate equation for all four catalysts, $r = kK_cp_c(1 + K_cp_c)^{-1}$. The values of the cyclopropane adsorption equilibrium constant K_c obtained from the kinetic data by regression analysis are quite similar for all four catalysts and agree well with independently measured values derived from experimental equilibrium isotherms for cyclopropane adsorption. It is suggested that the rate determining step is the cleavage of the cyclopropane ring to form the 1–3 diadsorbed species from a physically adsorbed or weakly chemisorbed precursor. This mechanism appears to be consistent with evidence from deuterium exchange studies. Results of catalyst pretreatment studies are briefly summarized.

INTRODUCTION

The kinetics of the catalytic hydrogenation of cyclopropane and the corresponding deuterium exchange reaction have been extensively studied; but, although much valuable information has been accumulated, there is still considerable uncertainly concerning the reaction mechanism. The reaction was reported by Willstatter and Bruce (*1*) in 1907 but the first kinetic studies were carried out half a century later by Bond and co-workers (*2–9*), who studied the reaction over pumice supported Group VIII metals (Pt, Pd, Rh, Ir) and metal films (Ni, Pd, Pt) and by Benson and Kwan (*10*) who used a commercial $Ni/SiO_2 — Al_2O_3$ catalyst. During the past decade the reaction has been extensively studied by several independent research groups. Boudart *et al.* (*11*) and McKee (*12*) have reported kinetic data for supported and unsupported platinum catalysts while a comparative study of a series of silica and silica-alumina supported catalysts (Ni, Pt, Ir, Os, Pd, Rh, Ru) has been carried out by Sinfelt *et al.* (*13*), Taylor *et al.* (*14*) and Dalla Betta *et al.* (*15*). Studies of chemisorption and deuterium exchange on evaporated metal films have been reported by Anderson and Avery (*16*), Knor *et al.* (*17*), and Merta and Ponec (*18, 19*). The early kinetic studies of Bond served to delineate the main features of the reaction kinetics but some of the conclusions concerning the reaction mechanism would appear to require modification in the light of the more recent data. A useful general review of the literature through 1968 is given by Wallace (*20*).

In a previous publication (*21*), the present authors reported preliminary kinetic data for a series of differently supported nickel catalysts and the observed differences in the specific activity and selectivity of the catalysts were discussed in relation to metal–support interaction and crystallite size effects. In the present paper, more extensive kinetic data for the same catalysts are presented and interpreted in terms of a simple reaction mechanism, which appear to be consistent with the evidence from published chemisorption and deuterium exchange studies.

APPARATUS AND EXPERIMENTAL METHODS

The kinetic data were obtained using a standard differential flow reactor coupled to a Perkin-Elmer model 880 gas chromatograph. Details are given elsewhere (*21*, *22*). Specific metal areas of the catalysts used were measured by hydrogen chemisorption using a Cahn electrobalance and the BET areas were measured with a Perkin-Elmer Sorptometer. Details of the catalysts employed are summarized in Table 1.

TABLE 1
DETAILS OF CATALYSTS

Harshaw catalyst	(wt %) Nickel	Support material	Metal area from hydrogen chemisorption experiments (m^2/g)	BET area (m^2/g)
Ni-0104	58	Kieselguhr	63.0	82
Ni-0707	14	Alumina	2.8	172
Ni-1430	40	Alumina	5.7	225
Ni-0901	5	Alumina-silica	~0.2	<1

Catalyst Pretreatment

It has been recognized that the preparation and subsequent pretreatment of metal catalysts may have a substantial effect on the catalytic properties but, for the hydrogenation of cyclopropane, reported data are somewhat inconsistent. Thus for nickel films, Knor *et al.* (*17*) state that the preadsorption of either hydrogen or cyclopropane has no effect on the subsequent reaction; whereas for supported nickel catalysts, preadsorption of hydrogen has been shown by Taylor *et al.* (*14*) to lead to preferential hydrocracking. To determine the effect of pretreatment on the present catalysts, several different pretreatment procedures were employed.

Hydrogen pretreatment. The catalysts was reduced in a stream of hydrogen at 360°C for 12 hr (standard reduction procedure). Prior to the kinetic run the catalyst was cooled to reaction temperature with the hydrogen flow maintained. This was the procedure used in the majority of runs and is referred to as the "standard pretreatment."

Helium pretreatment. After standard reduction the catalyst was cooled to reaction temperature in a helium stream.

Hydrocarbon pretreatment. After standard reduction the catalyst was cooled to 200°C in hydrogen. It was then purged with a stream of the appropriate hydrocarbon for a period of 1 hr at 200°C and finally cooled to reaction temperature with the hydrocarbon stream maintained.

Sintering procedure. In place of the standard reduction process the catalyst was reduced in hydrogen at 450°C for 18 hr.

The initial behavior of each catalyst was investigated prior to the kinetic runs. For all four catalysts it was observed that the activity dropped rapidly during the first 10–20 min on stream and then leveled off at a much lower level, which remained essentially constant for a period of several hours. The kinetic data were obtained during this period of approximately constant activity and showed satisfactory reproducibility. The initial behavior of the catalyst Ni-0707, which is shown in Fig. 1, is typical. Curve A was obtained by passing the reactants over the catalyst continuously while curve B was obtained by alternating 15 min periods of reaction, during which both cyclopropane and hydrogen were

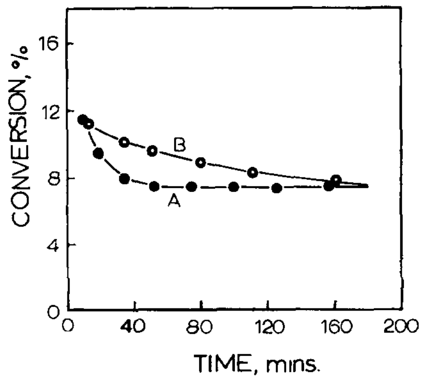
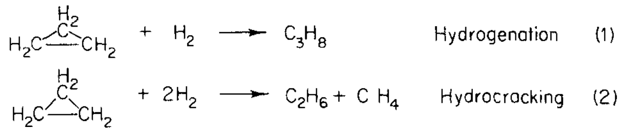


FIG. 1. Initial behavior of catalyst Ni-0707.

passed, with similar periods during which hydrogen alone was passed over the catalyst.

It seems likely that the decline in the activity of a fresh catalyst results from the poisoning of the surface by carbonaceous residues formed from the reactants. Thus, in the constant activity region, the reaction probably takes place on only a small fraction of the original metal surface. Independent evidence in favor of this hypothesis was obtained by Knor *et al.* (*17*) who showed that the quantity of oxygen required to inhibit the catalytic activity of a nickel film was much greater for a fresh film than for a film on which the reaction had been previously carried out.

All catalysts subjected to the standard pretreatment catalyzed both hydrogenation and hydrocracking reactions:



Sintering the catalyst (Ni-0104) at 450°C caused a substantial decrease in activity to about 20% of the activity obtained with the standard reduction procedure at 350°C. However, the selectivity, defined as the ratio of hydrogenation to hydrocracking, was substantially greater for the sintered catalyst (~7.0 compared with ~4.0). Pretreatment with either He, CH_4, C_2H_6, or C_3H_8 caused no significant change in either activity or selectivity compared with the standard hydrogen pretreatment suggesting that these gases are not adsorbed to any appreciable extent under reaction conditions and that they do not displace adsorbed hydrogen from the catalyst surface. On this basis, any inhibiting effect of the products of reaction may be expected to be small. By contrast, pretreatment with cyclopropane had a drastic effect on both the activity and selectivity. The activity was greatly decreased and no hydrocracking was observed. It seems likely that, under the conditions employed in the cyclopropane pretreatment, cyclopropane reacts with and displaces hydrogen to leave the catalyst surface covered with strongly chemisorbed fragments or polymeric residues formed by interaction between the chemisorbed species. The formation of such polymeric residues, was observed by Merta and Ponec (*18*) and if it is assumed that the hydrocracking reaction requires a larger number of adjacent surface sites than the hydrogenation reaction, such an effect would explain both the reduction in activity and the corresponding increase in selectivity. This poisoning effect was shown to be reversible and prolonged treatment with hydrogen at 360°C restored the activity and selectivity to approximately the same levels as were obtained under standard pretreatment conditions.

KINETICS AND MECHANISM

The general features of the reaction kinetics have already been described in our earlier paper (*21*) in which we discussed the specific activity and selectivity of the different supported catalysts. It was shown that, over the four catalysts studied the rates of both hydrogenation and hydrocracking reactions could be correlated approximately according to a simple power law rate equation:

$$r = k' p_H{}^m p_c{}^n, \qquad (3)$$

where

r = reaction rate (g moles/hr m^2 nickel area);
p_H = hydrogen partial pressure (atm);
p_c = cyclopropane partial pressure (atm);
k' = reaction rate constant (per m^2 nickel area).

For all four catalysts and for both the hydrogenation and hydrocracking it was found that the exponents had essentially the same values : $m \simeq 0$, $n \simeq 0.6$. Furthermore, although the catalysts showed considerable differences in the relative rates of hydrogenation and hydrocracking, the total specific reaction rate per unit nickel area was quite similar for all four catalysts. These observations suggest that the rates of both hydrogenation and hydrocracking reactions are governed by a common rate limiting step.

In an attempt to obtain further insight into the reaction mechanism, the kinetic data were analyzed according to the method of Hougen and Watson. The fit of the kinetic data to 65 different Langmuir-Hinshelwood rate expressions, corresponding to what were considered the most physically reasonable assumptions concerning the reaction mechanism, was tested by linearized multiple regression analysis. Details both of the models tested and the statistical analysis of the results are given elsewhere (*22*). It was found that for all four catalysts and for the hydrogenation and hydrocracking reactions considered separately, as well as for the overall reaction, the kinetic data could be best fitted by one of the simplest rate equations:

$$r = \frac{kK_cp_c}{(1 + K_cp_c)}. \tag{4}$$

The majority of the kinetic data were obtained at 60°C and the values of the constants K_c and k calculated from the kinetic data for the overall reaction are listed in Table 2. In Fig. 2, total reaction rate is plotted against cyclopropane partial pressure for two of the catalysts studied. The corresponding plots for the other two catalysts are similar.

TABLE 2

k AND K_c VALUES FOR THE SERIES OF NICKEL CATALYSTS AT 60°C

Catalyst	k (per m² Ni)	K_c (atm^{-1})
Ni-0707	0.0061	2.12
Ni-1430	0.0063	2.80
Ni-0104	0.0079	3.39
Ni-0901	0.0050	3.71
SA-5N-VII D[a]	—	2.50[b] [Ref. (*10*)]

[a] Ni-silica-alumina catalyst.

[b] Extrapolated value.

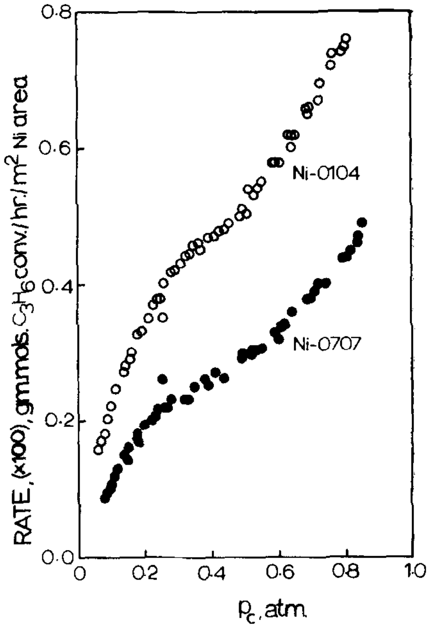


FIG. 2. Plot of reaction rate vs cyclopropane partial pressure for Ni-0707 and Ni-0104 catalysts at 60°C.

Equation (4) may be written in linearized form as:

$$\frac{1}{r} = \frac{1}{kK_cp_c} + \frac{1}{k}, \tag{5}$$

from which it is apparent that a plot of $1/r$ vs $1/p_c$ should give a straight line. The data for the two catalysts shown in Fig. 2 are plotted in this way in Fig. 3 and it is evident that the model does indeed provide

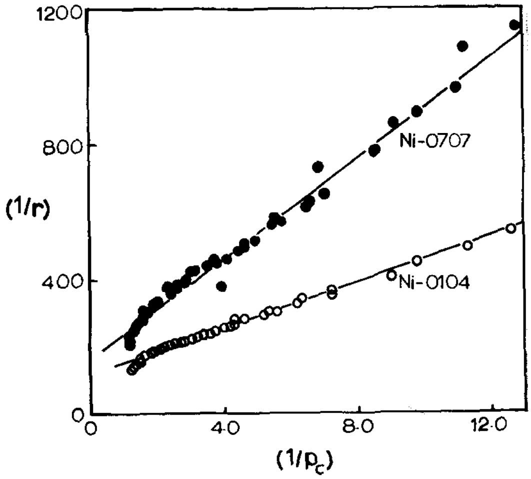


FIG. 3. Linearized plot of kinetic data according to eq. (5); test of model [$r = kK_cp_c(1 + K_cp_c)^{-1}$].

a satisfactory correlation of the experimental data, although, in the region of high pressures, a small, but significant, deviation is evident.

This type of Langmuir-Hinshelwood rate equation corresponds to a simple system involving only a single reactant which is nondissociatively adsorbed according to a Langmuir isotherm and which decomposes at a rate, which is directly proportional to surface concentration. For the present system this suggests:

1. Over the entire range of partial pressures covered by this study ($70 < p_H < 700$ Torr) the surface concentration of hydrogen remains essentially constant.
2. The adsorption of cyclopropane and hydrogen is noncompetitive.
3. The surface concentration of adsorbed cyclopropane is governed by a simple Langmuir type of isotherm.
4. The rate of the overall reaction is determined by the rate of reaction of the adsorbed cyclopropane and is therefore proportional to the surface concentration of this species.

According to this interpretation the constant K_c is the surface equilibrium constant for the adsorption of cyclopropane and k is the rate constant for the surface decomposition of this species. Although, on a weight basis, the catalysts exhibit considerable differences in activity, the difference in the specific activity based on unit nickel area is quite small as shown by the rate constants given in Table 2. Furthermore, the values of K_c show only a relatively minor variation between the different catalysts; and the average value of K_c (~3.0) is in satisfactory agreement with the value of 2.5 calculated from the experimental isotherm data of Benson and Kwan (*10*). For the Ni-0707 catalyst, extensive kinetic data were obtained over a range of different temperatures so that the temperature dependence of both k and K_c could be established. The Arrhenius plot for the rate constant k is given in Fig. 4 and the activation energy calculated from the slope of this plot is 13.15 kcal. The corresponding plot for the cyclopropane adsorption equilibrium constant K_c is shown in Fig. 5; and the heat of adsorption, calculated from this plot is 6.3 kcal in reasonable agreement with the value of 7–8.8 kcal determined by Benson and Kwan from their adsorption isotherms. These values are only slightly greater than the latent heat of evaporation of cyclopropane (~4.8 kcal) (*25*) suggesting that either physical adsorption or a very weak type of chemisorption is involved.

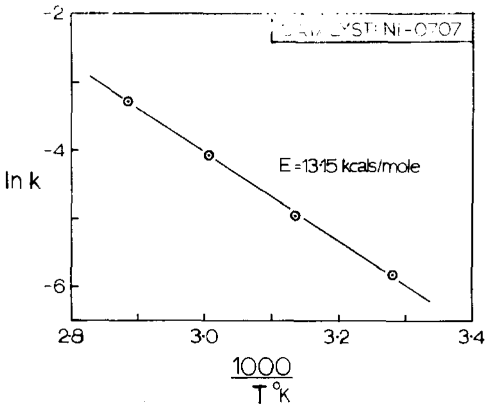


FIG. 4. Arrhenius plot for rate constant k.

The sigmoid shape of the rate curves shown in Fig. 2 is reminiscent of the Type II isotherms which are commonly observed for physical adsorption and it is clear that the representation of such curves by a simple Langmuir equation is an oversimplification. A rather better fit of the data could be obtained by the use of one

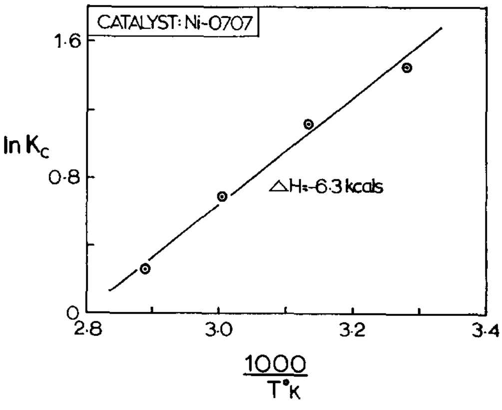


FIG. 5. Temperature dependence of adsorption equilibrium constant K_c.

of the isotherm equations commonly used to describe physisorption isotherms. In general, however, such equations contain more than one adsorption constant and, for the interpretation of the kinetic data, the increased complexity is not justified.

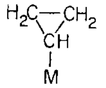
In attempting to interpret these observations from the kinetic studies in terms of a reaction mechanism, the following additional evidence, derived from studies of chemisorption and deuterium exchange, must be considered.

5. It has been shown that, on a nickel catalyst, hydrogen is adsorbed more strongly than cyclopropane (*9, 10*). In the light of this observation, the assumption that, under reaction conditions, the surface is essentially saturated with hydrogen is clearly reasonable.

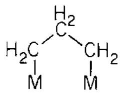
6. In the adsorption of cyclopropane on clean metal surfaces it is observed that the initial rapid adsorption is followed by a slower process during which more cyclopropane is adsorbed and the electrical resistence of the metal increases (*10, 17*). This suggests that two different types of adsorbed species are involved: a weakly adsorbed species which is formed rapidly and a more strongly adsorbed species which is formed by a relatively slow subsequent reaction.

7. The overall rates of the hydrogenation and deuterium exchange reactions are quite similar suggesting that both processes may proceed through a common rate limiting step.

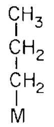
8. In deuterium exchange studies, it is found that no significant quantity of deuterocyclopropanes is formed and the quantity of monodeuterated propane in the products is also quite small (*26, 27*). These observations provide strong evidence that cleavage of the cyclopropane ring is necessary before significant exchange can occur. On this basis, the existence of dissociatively adsorbed species such as


(A)

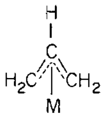
which have been suggested as possible reaction intermediates, seems improbable. Furthermore, the formation of a relatively small amount of monodeuterated propane suggests that cleavage of the cyclopropane ring leads initially to the 1–3 diadsorbed species


(B)

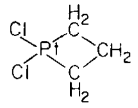
rather than to mono-adsorbed species such as


(D)

or π-allyl species



as suggested by Merta and Ponec (*18*). Further it has been reported (*23*) that cyclopropane reacts with Pt(IV) halides in aqueous solution to form species such as



which is analogous in structure to species (B).

It was suggested by Addy and Bond (*6, 7*) and later by Anderson and Avery (*16*) that the deuterium exchange reaction proceeds via the initial formation of a weakly adsorbed species and that the rate limiting step involving rupture of the cyclopropane ring is the subsequent formation of the 1–3 diadsorbed species. If it is assumed that such a process can occur, not only on a clean metal surface but also on a surface which is largely covered with hydrogen, this type of mechanism can provide a satisfactory explanation of the principal features of the kinetics of hydrogenation and chemisorption as outlined above. Such a reaction mechanism is shown diagrammatically in Fig. 6. It is assumed that species (C), which is either physically adsorbed or weakly chemisorbed by π-bonding cannot undergo deuterium exchange. The rate of formation of this species from the gas phase is supposed to be sufficiently rapid to ensure that equilibrium is maintained and the surface concentration is assumed to be given by a Langmuir type of expression. The transition from species (C) to species (B), the more strongly diadsorbed species, is assumed to be the rate controlling step for hydrogenation, hydrocracking, and exchange reactions. These subsequent steps are assumed to take place rapidly and no detailed evidence concerning the reaction path is available although the sequences suggested seem reasonable. According to this mechanism, the relative rates of hydrogenation and hydrocracking may be sensitive to quite small differences in the nature of the catalyst surface; but both reactions, being controlled by a common rate determining step, would be expected to show similar kinetic orders and differences in the total specific activity of the different supported nickel catalysts may perhaps be expected to be relatively minor. The principal objection to the proposed mechanism is the difficulty of visualizing the formation of the adsorbed species (C) and (B) on a surface which is essentially saturated with hydrogen. This conceptual difficulty may, however, be more apparent than real, since, for example, the adsorption of nitrogen on a hydrogen-covered surface is an established step in the ammonia synthesis reaction, and Tamaru (*24*) has shown that hydrogen does not inhibit further nitrogen chemisorption. The hydrogen layer would be expected to be highly mobile so that the rate of formation of species (B) would be dependent on both the surface concentration of species (C) and the probabiliy of two adjacent sites becoming vacant at the same time. For a saturated surface, this probability would remain essentially constant and independent of hydrogen pressure.

The evidence on which the proposed reaction mechanism is based is largely indirect and the mechanism must therefore be regarded as somewhat tentative. To obtain direct experimental evidence concerning a reaction mechanism is always difficult, but the hypothesis that the reaction rate is directly proportional to the

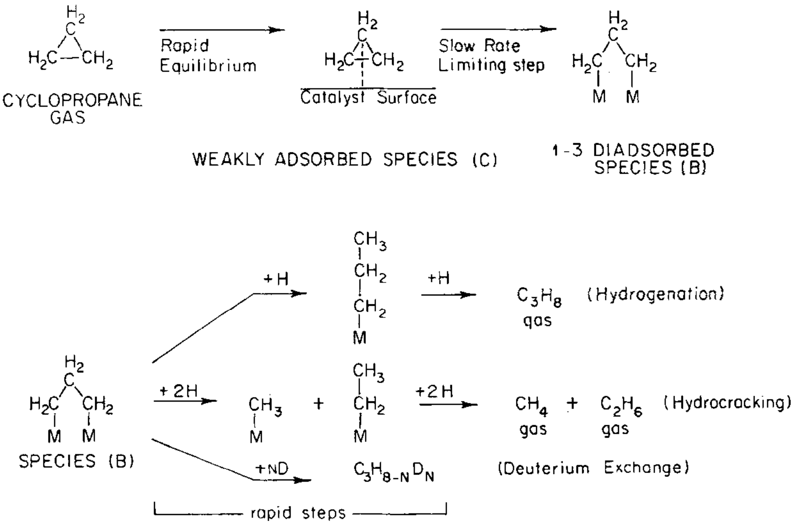


FIG. 6. Reaction scheme.

surface concentration of weakly adsorbed cyclopropane could, perhaps, be tested by gravimetric measurement of the adsorption of cyclopropane on a hydrogen-covered catalyst, under conditions such that the reaction rate is sufficiently slow to allow the surface concentration of cyclopropane to be estimated.

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