

## **Hydrogenolysis of N-heptane over Nickel Supported Catalysts: Influence of Experimental Conditions on Selectivity**

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**Abstract.** The hydrogenolysis of n-heptane over 2%, 4%, 6% and 8% Ni/Al<sub>2</sub>O<sub>3</sub> was studied in a flow reactor using a pulse technique. The rate of reaction in relation to the reactor temperature was observed and its dependency on the partial pressure of hydrogen and n-heptane was also determined.

Catalysts at 6% and 8% nickel loading show appreciable catalytic activity as compared to the other two catalysts. Similarly, the effect of temperature on the reaction rate is very prominent on the high nickel loading catalysts with greater rate increase at more elevated temperature. The rate was also found to be greatly influenced by an increase in n-heptane partial pressure while higher partial pressure of hydrogen appears to impede the ease by which the reaction proceeds. Hydrogenolysis with nickel catalysts is observed to produce methane preferentially with ethane, propane, butane, pentane and hexane as minor products. A plausible mechanism is presented supporting  $\alpha$ -scission cleavage of the n-heptane.

### **Introduction**

In the study of hydrogenolysis of paraffinic hydrocarbons over nickel catalysts, attention has mainly been given to the splitting of ethane or propane [1-6]. Cimino and Co-workers [7] reported that hydrogenolysis of ethane on nickel catalysts can be explained in terms of mechanism involving preliminary dehydrogenation of ethane to an unsaturated radical C<sub>2</sub>H<sub>2</sub> on the surface, followed by attack of the surface by hydrogen. It was observed by Kochloefl and Bazant [8] that the predominant reaction in hydrogenolysis of octane, decane and hexane involved successive degradation to methane and paraffins with one carbon atom less. Similar results have been

reported by Kikuchi *et al.* [9] and Matsumoto *et al.* [10] for the hydrogenolysis of n-pentane on nickel catalysts. On the other hand, a carbonium ion mechanism has been proposed for the hydrogenolysis of the n-pentane on Pt/SiO<sub>2</sub> catalyst to interpret both the characteristic distribution of the initial hydrogenolytic products and considerable skeletal isomerization during hydrogenolysis [10].

In the present work, the hydrogenolysis of n-heptane using catalysts with different concentration of nickel over alumina is studied. It is also aimed to establish the effect of reaction temperature, hydrogen pressure and hydrocarbon pressure on the reaction rate, product distribution and selectivity.

### Materials and Methods

The n-heptane was obtained from Koch Laboratories Ltd. Chromatographic analysis showed no detectable impurities. The hydrogen gas was further purified by passing it through silica gel and molecular sieves.

The supported metal catalysts investigated containing different percentages of nickel (2,4,6 and 8%) were prepared by impregnating  $\gamma$ -alumina (Merck) with solutions of Ni(NO<sub>3</sub>)<sub>2</sub> (BDH) in deionized water. After impregnation, the catalysts were calcined at 623 K for four hours and reduced in flowing hydrogen at 623 K for 36 hrs. The surface areas of the prepared catalysts were determined by hydrogen chemisorption.

In a typical run 0.1 gm catalyst was reduced under hydrogen flow (40 ml/min) at 623 K overnight. The reactor was allowed to cool down and, with hydrogen and n-heptane partial pressure set at 710 and 30 torr respectively, the reaction rate was determined at temperatures from 553-593 K. While maintaining the reactor temperature at 573 K, a series of measurements was made at varying partial pressures of both n-heptane (9.5-35 torr),  $P_{H_C}$ , and hydrogen (155-933 torr),  $P_{H_2}$ .

Reaction rate measurements on the hydrogenolysis of n-heptane were made at low conversion level (< 10%) to avoid diffusion. Hydrocarbon reactant and products were determined by a Varian gas liquid chromatograph with a flame ionization detector and 1/8" column packed with 30% DC-200 in Chromosorb W at 70°C.

The rate of reaction is calculated from the relation

$$r = (F/W) \times (X) \quad (1)$$

where  $F$  represents the feed rate of n-heptane to the reactor in cc per min.,  $W$  represents the weight in gms of the catalyst and  $X$  represents the fraction of n-heptane converted to products. The reaction rate ( $r$ ) is thus expressed as cc/min/gm of catalyst.

The dependence of the rate on partial pressure of hydrocarbon and hydrogen can be deduced from the following equation:

$$r = kP_{H_C}^n P_{H_2}^m \quad (2)$$

where  $n$  and  $m$  are the calculated orders of reaction with respect to hydrocarbon and hydrogen respectively.

The selectivity ( $S$ ) of each product was calculated from the following equation [8]:

$$S = 7C_n / \sum_{i=1}^6 iC_i \quad (3)$$

where  $C_i$  is the mole percent of each product.

The percentage product distribution ( $P$ ) given by the ratio between the mole percent of each product and the total n-heptane conversion was obtained using the following equation [7]:

$$P = \%C_i = (C_i / \sum_{i=1}^6 C_i) \times 100 \quad (4)$$

The theoretical amount of methane was calculated from the following mass balance equation [10]:

$$C_i^0 = C_6 + 2C_5 + 3C_4 + 4C_3 + 5C_2 \quad (5)$$

The above equation assumes that ethane is stable and further breakdown to methane does not occur.

**Table 1. Catalyst surface area as determined by H<sub>2</sub> chemisorption**

Catalyst	Area (m <sup>2</sup> /gm catalyst)
2% Ni/Al <sub>2</sub> O <sub>3</sub>	0.285
4% Ni/Al <sub>2</sub> O <sub>3</sub>	0.597
6% Ni/Al <sub>2</sub> O <sub>3</sub>	1.088
8% Ni/Al <sub>2</sub> O <sub>3</sub>	2.539

### Results and Discussion

The specific metal surface areas of the various catalysts as determined from the hydrogen chemisorption measurements are listed in Table 1. It can be noted that since the higher the nickel content the greater is the surface area of the catalyst, it seems that decreasing the nickel concentration does not lower the average crystallite size as would have been expected if the nickel aggregates were smaller.

The results of the present work agree very well with Taylor and Co-workers [11] for the reaction of ethane and hydrogen over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. They explained the large difference in the catalytic properties of dilute nickel catalysts from those containing higher nickel by suggesting that this observation can well be explained by the interaction of the metal with the support, and such interaction can be most pronounced at low nickel concentrations. The first increment of nickel impregnated on the surface of the support could selectively interact with the most energetic sites on the surface leading to heterogeneity of the nickel sites. The detailed mechanism of this interaction is not known explicitly. However, it seems reasonable to expect that the metal interacts electronically with the support since electron transfer in general, occurs at the junction between a metal and semiconductors.

The variation in catalytic activity in relation to nickel concentration is illustrated in Fig. 1. It is apparent that catalysts with low nickel content exhibit relatively low catalytic activity which is approximately tenfold less active when compared with the high nickel bearing catalysts at 573 K. This observation demonstrates a significant diversity with regard to the mechanism of their catalytic action. The data show an interesting parallel with earlier results of Hill and Selwood [12] on benzene hydrogenation over nickel on alumina catalysts. These investigators reported a critical nickel concentration, about 5% below which the catalysts were inactive. They also found that the magnetic properties of nickel in these catalysts varied markedly. The specific ferromagnetism increases substantially with nickel concentration. They suggested

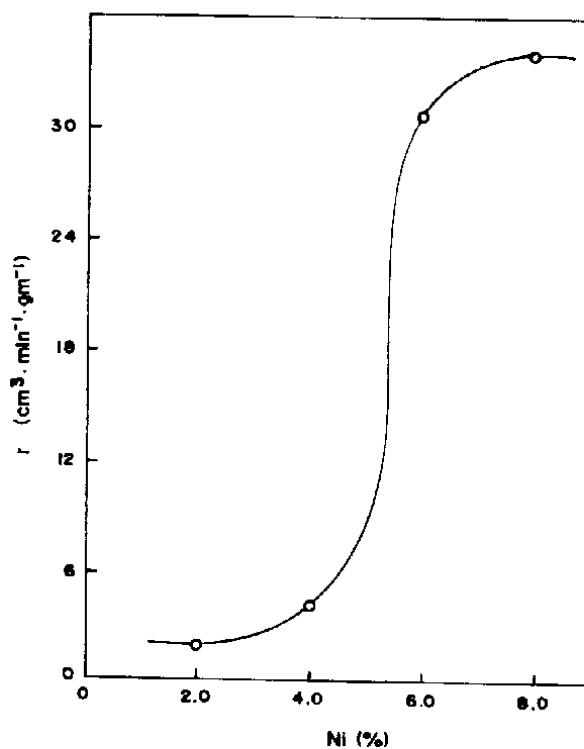


Fig. 1. Reaction rate as a function of nickel content at 573 K

that at low nickel concentration few nickel particles are large enough to produce ferromagnetism and that the low catalytic activity results because the aggregates of nickel atoms are too small. In other words, they proposed that a geometric factor is involved such that a minimum size aggregate of nickel atoms is required to effectively catalyze the hydrogenation of benzene.

### Effect of temperature

It was found in this investigation that the reaction rate of n-heptane hydrogenolysis over a series of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts increases with increasing reaction temperature and nickel concentration. The catalysts with low nickel content have very low activity at temperatures below 553 K and start to increase slightly above this temperature. However, a direct correlation between the activity of high nickel concentration catalysts and temperature exist prominently with a sharp increase in activity at elevated temperature as illustrated by the Arrhenius plots in Fig. 2.

The apparent activation energy values over the various Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for n-heptane hydrogenolysis at a temperature range of 543-583 K as listed in Table 2 are approximately constant. This does not agree with the findings of Taylor *et al.* [11],

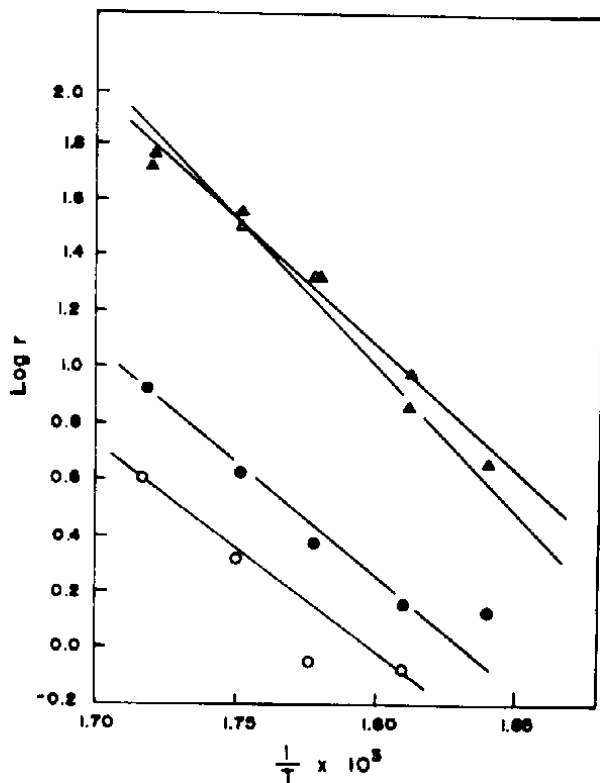


Fig. 2. Arrhenius plot of the different nickel catalysts, o: 2% Ni/Al<sub>2</sub>O<sub>3</sub>, ●: 4% Ni/Al<sub>2</sub>O<sub>3</sub>, △: 6% Ni/Al<sub>2</sub>O<sub>3</sub> and ▲: 8% Ni/Al<sub>2</sub>O<sub>3</sub>

Table 2. Kinetic parameters for n-heptane hydrogenolysis over nickel catalyst

Catalyst	$n^a$	$m^b$	$E_a^c$	$r^d$
2% Ni/Al <sub>2</sub> O <sub>3</sub>	0.30 + 0.11	-1.0 + 0.03	152.0 + 1.4	1.51 × 10 <sup>13</sup>
4% Ni/Al <sub>2</sub> O <sub>3</sub>	0.57 + 0.15	-1.5 + 0.02	153.2 + 0.5	4.47 × 10 <sup>13</sup>
6% Ni/Al <sub>2</sub> O <sub>3</sub>	0.43 + 0.13	-1.3 + 0.03	153.2 + 0.7	2.80 × 10 <sup>14</sup>
8% Ni/Al <sub>2</sub> O <sub>3</sub>	0.60 + 0.13	-0.8 + 0.05	158.5 + 1.3	1.20 × 10 <sup>15</sup>

<sup>a</sup> Reaction order with respect to n-heptane pressure

<sup>b</sup> Reaction order with respect to hydrogen pressure

<sup>c</sup> Apparent activation energy, kJ/mole

<sup>d</sup> Pre-exponential factor in units of rate

who reported that the activation energy and the catalytic activity observed with dilute nickel catalysts are significantly lower than the high concentration nickel catalysts. Taking the apparent activation energy to be the same over all the catalysts, the difference in catalytic activity will then have to be attributed to a variation in the pre-exponential factor ( $r'$ ) from the relationship

$$r = r' \exp(-E_a/RT) \quad (6)$$

It is clear from this investigation as indicated in Table 2 that the lower activities are accompanied with low values of  $r'$  ( $1.5 \times 10^{13} - 4.47 \times 10^{13}$ ) while the high activities are accompanied with greater values of  $r'$  ( $2.8 \times 10^{14} - 1.2 \times 10^{15}$ ). This may be attributed to the more abundant number of active centers as the metal surface area increases and consequently gives higher values for the pre-exponential factor.

This is similar to the situation in ethylene hydrogenation over metal films, where the apparent activation energy is reported to be constant over a series of metals despite large variations in catalyst activity [13]. The fact that the apparent activation energy for n-heptane hydrogenolysis is comparable over the various supported nickel catalysts in the present work, however, does not necessarily mean that the true activation energy is constant. For instance, if the surface is only sparingly covered by the reactive intermediates that are suggested for the reaction mechanism, the apparent activation energy  $E_a$  is related to the true activation energy  $E_t$  by the expression

$$E_a = E_t - q \quad (7)$$

where  $q$  is the heat of adsorption. It is possible that  $q$  and  $E_t$  both vary by the same amount, thus causing  $E_a$  to be essentially independent of the variation of the nickel concentration in Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

### Effect of pressure

The effect of the partial pressure of n-heptane and hydrogen on the rate of reaction can be expressed in the form of a simple power law (eq.2), with  $n$  and  $m$  representing the calculated order of reaction for both n-heptane and hydrogen, respectively.

The effect of hydrogen partial pressure which was varied from 155-933 torr on the rate of n-heptane hydrogenolysis was studied at 573 K and 30 torr n-heptane partial pressure. Results are given in Fig. 3. The rate of n-heptane hydrogenolysis decreases with increasing hydrogen partial pressure for the series of catalysts. The

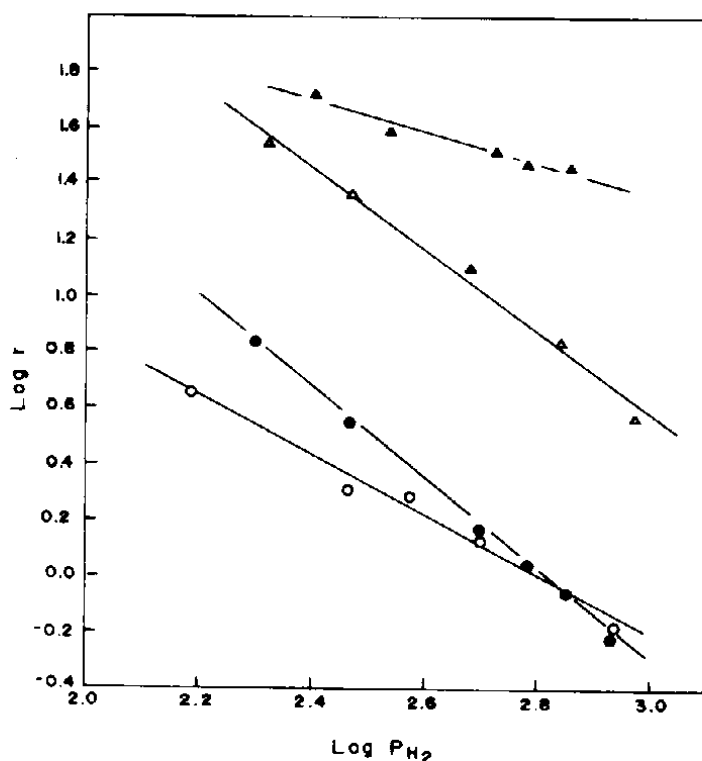


Fig. 3. Effect of the partial pressure of hydrogen (torr) on the rate of hydrogenolysis ( $\text{gm-mol.gm-cat}^{-1}.\text{min}^{-1}$ ) at  $P_{H_2} = 30$  torr. O: 2% Ni/Al<sub>2</sub>O<sub>3</sub>, ●: 4% Ni/Al<sub>2</sub>O<sub>3</sub>, △: 6% Ni/Al<sub>2</sub>O<sub>3</sub> and ▲: 8% Ni/Al<sub>2</sub>O<sub>3</sub>

mechanism of Langmuir - Hinshelwood of competitive adsorption on the surface of catalyst can well explain this behaviour, where the hydrogen atoms occupy the most available sites on the surface at higher pressures [14]. This behaviour was also noticed by Zahraa and Al-Khowaiter [15] for the hydrogenation of cyclohexene on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Grain and Gault [16] reported the same phenomenon for the hydrogenolysis of pentanes on a 10% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

Table 2 also indicates that the values of reaction order with respect to hydrogen is negative for all catalysts. These negative values can be regarded as an indication of hydrogen preferential adsorption which can lead to a speculation that at elevated hydrogen pressure the active surface of the catalyst is predominantly occupied by strongly adsorbed hydrogen atoms consequently preventing contact with the n-heptane molecules. The negative values of the order of reaction has also been reported by Taylor for ethane hydrogenolysis over nickel [5] and other supported metals [12].

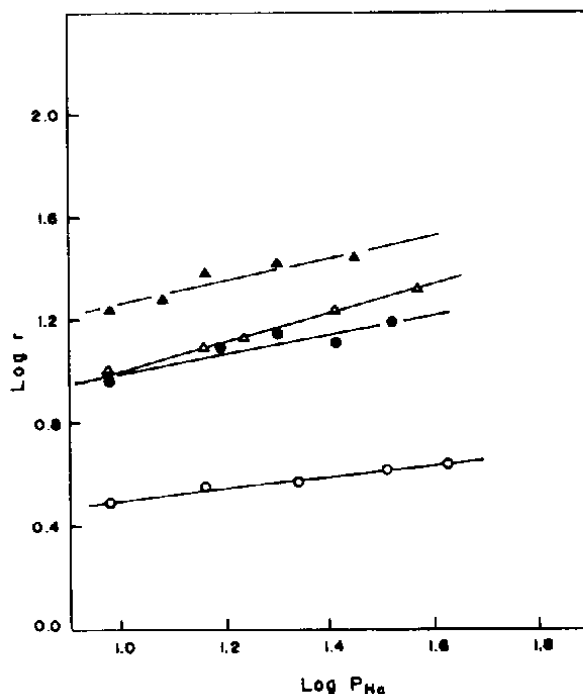


Fig. 4. Effect of the partial pressure of n-heptane (torr) on the rate of hydrogenolysis ( $\text{gm}\cdot\text{mol}\cdot\text{gm}\cdot\text{cat}^{-1}\cdot\text{min}^{-1}$ ) at  $P_{\text{H}_2} = 710$  torr, O: 2% Ni/Al<sub>2</sub>O<sub>3</sub>, ●: 4% Ni/Al<sub>2</sub>O<sub>3</sub>, △: 6% Ni/Al<sub>2</sub>O<sub>3</sub> and ▲: 8% Ni/Al<sub>2</sub>O<sub>3</sub>

The effect of n-heptane partial pressure on the rate of n-heptane hydrogenolysis was studied at 573 K and 710 torr hydrogen partial pressure. The results are illustrated graphically in Fig. 4. It is clear that n-heptane hydrogenolysis is directly dependent on the n-heptane partial pressure with faster reaction rate at greater hydrocarbon partial pressure for all the observed catalysts.

It is important to note that the values for the reaction order with respect to the hydrocarbon for all the catalysts are positive and comparable with other reported studies on propane [4; 17], on pentane [16] and on hexane, octane and decane [8]. The positive order suggests that the hydrocarbon is weakly adsorbed on the active surface of the catalyst resulting in a greater number of more reactive reaction cycles.

### Selectivity and mechanism

In the hydrogenolysis of n-heptane using the different nickel catalysts, no isomerization and aromatization have been observed under the given conditions. The main product obtained is predominantly methane, and the selectivity of the

minor products composed of ethane, propane, butane, pentane and hexane is very low. The selectivity and percentage product distribution are shown in Tables 3,4 and 5 at different temperatures and at various n-heptane and hydrogen partial pressure.

**Table 3. Effect of temperature on product distribution and selectivity at  $P_{H_C} = 30$  torr and  $P_{H_2} = 710$  torr over different Ni/Al<sub>2</sub>O<sub>3</sub> catalysts**

Ni/Al <sub>2</sub> O <sub>3</sub> %	K	P/S	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>1</sub> <sup>o</sup> cal	C <sub>1</sub> /C <sub>1</sub> <sup>o</sup> cal
2	553	P	45.10	9.50	10.70	10.90	11.30	12.50	—	—
		S	1.16	0.25	0.28	0.28	0.29	0.32	4.10	0.30
	573	P	61.70	5.30	8.70	7.70	7.70	8.90	—	—
		S	1.95	0.17	0.28	0.24	0.24	0.28	3.44	0.57
	593	P	83.20	1.40	7.40	3.20	2.50	2.50	—	—
		S	3.94	0.06	0.35	0.15	0.12	0.12	2.52	1.56
4	553	P	47.50	10.90	9.90	10.20	10.60	10.90	—	—
		S	1.30	0.30	0.27	0.28	0.29	0.30	4.30	0.32
	573	P	56.10	11.40	8.10	7.50	7.80	9.20	—	—
		S	1.73	0.35	0.25	0.23	0.24	0.28	4.20	0.41
	593	P	76.20	7.00	5.20	4.00	3.61	3.93	—	—
		S	3.25	0.30	0.22	0.17	0.15	0.17	3.39	0.96
6	553	P	50.60	8.40	9.10	8.81	9.61	13.40	—	—
		S	1.37	0.23	0.25	0.24	0.26	0.36	3.70	0.40
	573	P	65.70	7.10	6.90	5.90	6.30	8.10	—	—
		S	2.25	0.24	0.24	0.20	0.21	0.28	3.40	0.70
	593	P	80.90	5.30	5.70	3.20	2.40	2.50	—	—
		S	3.80	0.25	0.27	0.20	0.14	0.11	3.10	1.20
8	553	P	50.00	9.50	9.50	9.10	10.20	11.7	—	—
		S	1.37	0.26	0.26	0.25	0.28	0.32	4.00	0.34
	573	P	67.20	7.30	7.13	5.80	5.90	6.70	—	—
		S	2.40	0.26	0.25	0.21	0.21	0.24	3.60	0.70
	593	P	78.80	7.20	5.00	3.20	2.90	2.90	—	—
		S	3.60	0.32	0.23	0.15	0.13	0.13	3.40	1.05

P = percent product distribution

S = selectivity

**Table 4. Effect of n-heptane partial pressure on product distribution and selectivity over different Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at 573 K and P<sub>H<sub>2</sub></sub> = 710 torr**

Ni/Al <sub>2</sub> O <sub>3</sub> %	P <sub>HC</sub>	P/S	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>1</sub> <sup>o</sup> cal	C <sub>1</sub> /C <sub>1</sub> <sup>o</sup> cal
2	9.5	P	80.00	4.70	4.70	3.30	3.20	4.00	–	–
		S	3.51	0.21	0.21	0.15	0.14	0.18	2.80	1.20
	32.0	P	78.96	4.20	4.40	3.30	3.80	5.30	–	–
		S	3.36	0.18	0.19	0.14	0.16	0.22	2.61	1.28
	67.0	P	72.60	5.10	5.50	4.30	5.10	7.50	–	–
		S	2.72	0.19	0.20	0.16	0.19	0.28	2.92	0.93
4	12.0	P	81.60	7.50	4.10	2.40	2.20	2.30	–	–
		S	3.99	0.36	0.20	0.12	0.11	0.12	3.30	1.20
	43.0	P	77.80	7.70	5.10	2.90	2.90	3.50	–	–
		S	3.45	0.35	0.23	0.13	0.13	0.16	3.50	0.99
	74.0	P	78.00	8.60	5.30	3.10	2.80	2.00	–	–
		S	3.51	0.39	0.24	0.14	0.13	0.09	3.66	0.96
6	9.5	P	79.40	6.30	4.90	3.00	3.00	3.00	–	–
		S	3.61	0.29	0.22	0.14	0.13	0.15	3.20	1.10
	36.0	P	77.40	6.20	4.90	3.30	3.60	4.60	–	–
		S	3.32	0.26	0.21	0.14	0.16	0.20	3.10	1.10
	67.0	P	77.90	6.10	4.80	3.20	3.60	4.40	–	–
		S	3.36	0.26	0.21	0.14	0.16	0.19	3.10	1.10
8	12.0	P	82.60	4.20	4.70	2.70	2.60	3.20	–	–
		S	3.90	0.20	0.22	0.13	0.12	0.15	2.70	1.40
	43.0	P	80.00	5.90	4.20	2.80	2.90	4.10	–	–
		S	3.62	0.27	0.19	0.13	0.13	0.18	2.93	1.20
	71.9	P	81.10	4.90	4.30	2.70	2.90	4.00	–	–
		S	3.61	0.22	0.19	0.12	0.13	0.18	2.64	1.36

P = percent product distribution

S = selectivity

**Table 5. Effect of hydrogen partial pressure on product distribution and selectivity over different Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at 573 K and P<sub>H<sub>2</sub></sub> = 30 torr.**

Ni/Al <sub>2</sub> O <sub>3</sub> %	P <sub>H<sub>2</sub></sub>	P/S	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>1</sub> <sup>o</sup> cal	C <sub>1</sub> /C <sub>1</sub> <sup>o</sup> cal
2	295	P	86.50	4.50	3.50	1.50	1.30	2.70	—	—
		S	4.50	0.24	0.18	0.08	0.07	0.14	2.41	1.86
	590	P	81.40	4.10	3.50	2.20	2.90	5.90	—	—
		S	3.60	0.18	0.15	0.10	0.13	0.26	2.30	1.56
	870	P	82.4	1.70	2.90	2.90	3.20	7.00	—	—
		S	3.50	0.08	0.12	0.12	0.14	0.31	1.80	1.90
4	210	P	85.00	3.40	2.10	1.60	1.80	6.50	—	—
		S	4.80	0.19	0.12	0.09	0.10	0.37	2.27	2.10
	610	P	81.60	4.00	4.42	2.70	2.50	4.90	—	—
		S	3.70	0.18	0.20	0.12	0.11	0.22	2.50	1.48
	855	P	77.50	3.80	4.10	2.60	3.80	8.20	—	—
		S	3.10	0.15	0.16	0.11	0.15	0.33	2.40	1.30
6	210	P	95.40	3.20	1.40	0.00	0.00	0.00	—	—
		S	6.30	0.20	0.09	0.00	0.00	0.00	1.40	4.50
	480	P	89.40	4.37	2.53	1.30	1.16	1.50	—	—
		S	5.00	0.24	0.40	0.07	0.06	0.08	2.20	2.27
	933	P	77.10	4.80	4.20	3.40	4.20	6.40	—	—
		S	3.10	0.20	0.20	0.14	0.17	0.26	2.70	1.15
8	200	P	84.80	6.80	3.90	2.10	1.16	1.20	—	—
		S	4.51	0.36	0.21	0.11	0.06	0.06	3.20	1.40
	340	P	78.50	6.50	5.60	3.40	2.90	3.10	—	—
		S	3.54	0.29	0.25	0.15	0.13	0.14	3.30	1.07
	710	P	73.50	6.20	5.30	4.10	4.60	6.40	—	—
		S	2.87	0.24	0.21	0.16	0.18	0.25	3.10	0.95

P = percent product distribution

S = selectivity

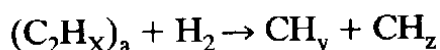
Higher selectivity for methane is enhanced by an increase in temperatures but is slightly diminished by greater hydrogen and n-heptane partial pressure.

In the present work, the ratios between the observed amount of methane and the calculated amount of methane from the mass balance equation (5) are less than unity (0.3-0.7) at low temperature, and approaches unity at higher temperatures. Moreover, the ratio is almost unity at hydrocarbon pressures between 9.5-74 torr with constant hydrogen pressure and temperature (710 torr and 573 K respectively).

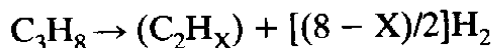
With the hydrocarbon partial pressure and the temperature kept constant at 30 torr and 573 K, respectively, the ratio is observed to be greater than unity (1.5-3.0) at minimal hydrogen pressure (200-500 torr), but shifts to lower ratios as the hydrogen pressure is increased from 590-940 torr.

As a result of kinetic study of the hydrogenolysis of ethane and propane on nickel and iron catalysts, Cimino *et al.* [7] postulated that association of hydrocarbon into adsorbed radicals and hydrogen takes place on the metal surface.

This reversible dissociation was assumed to be followed by the breaking of C-C bonds on the surface by interaction with hydrogen.



A similar mechanism was proposed by Anderson and Barker [18] for the hydrogenolysis of propane, the initial step being the dissociation



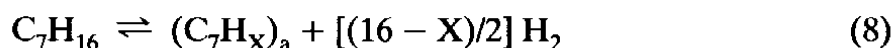
Kikuchi and Morita [9] proposed the  $\alpha$ -scission mechanism for the hydrogenolysis of pentane over nickel catalysts.

It is interesting to note that the higher selectivity for methane formation was observed to be in most cases within experimental error to its theoretical value as calculated from equation (3).

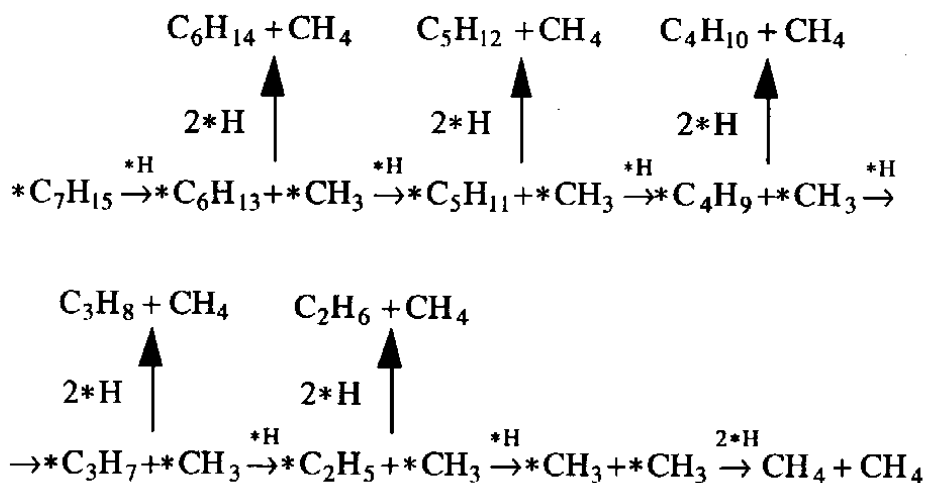
From these observations it can be deduced that the predominant reaction proceeds by carbon-carbon bond cleavage at the terminal position of the n-heptane carbon chain.

A ratio more than one may arise from the splitting of ethane which is not included in the mass balance equation (5), while the ratio less than unity may be due to the inner splitting of C-C bonds. However, the latter case would be considered as a side reaction, notably because the amount of other reaction products are small when compared with methane.

Thus, based on our results, we may safely suggest the predominant  $\alpha$ -scission mechanism for n-heptane hydrogenolysis which is initiated by the formation of the adsorbed species according to the following equation:



and which is clearly illustrated by the step wise scheme below,



The adsorbed intermediate radicals will be hydrogenated and desorbed from the active metal surface if hydrogen is present in excessive quantity. However, the presence of just a reasonable amount of hydrogen will permit longer exposure of the intermediate radicals to the bare metal site, resulting in the continuous decomposition to other radicals one carbon atom shorter and a molecule of methane for each reacted radical.

This situation can be considered to be essentially identical to the mechanism proposed by Cimino *et al.* [7] for the hydrogenolysis of ethane.

The above scheme leads to the expectation that product distributions will be influenced by hydrogen pressure which affects the amount of hydrogen adsorbed on nickel.

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## تفكيك الهبتان النظامي بوجود الهيدروجين على حفاز النيكل المدعوم أثر الظروف التجريبية على الانتقائية

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(سُلِّمَ في ١١/٥/١٤١٤ هـ؛ وقَبِلَ للنشر في ٤/٥/١٤١٥ هـ).

ملخص البحث. دُرِسَ تفكيك الهبتان النظامي في وجود الهيدروجين على حفاز ٢٪، ٤٪، ٦٪ و ٨٪ نيكل / الومينا في تفاعل تدفقي باستعمال تقنية النبضة. وقد سجلت سرعة التفاعل بالنسبة لدرجة الحرارة وضغوط المواد المتفاعلة.

أظهر الحفازان ٦٪ و ٨٪ نشاطاً كبيراً مقارنة بالبقية. كما كان أثر درجة الحرارة على السرعة أكبر في هاتين الحالتين، حيث كانت الزيادة في السرعة عالية عند درجات الحرارة المرتفعة، كما تأثرت السرعة كثيراً بضغط الهبتان، في حين أن زيادة ضغط الهيدروجين كانت معيقة لاستمرارية التفاعل. وقد وجد أن عملية التفكيك تؤدي إلى إنتاج الميثان بشكل مفضل مقارنةً بكل من الإيثان والبروبان والبيوتان والبتان والهكسان. وقد اقترحت ميكانيكية مشجعة تدعم حدوث انقسامات متتالية للهبتان.