Hydrogenolysis of n-Pentane on Nickel Catalyst

EIICHI KIKUCHI AND YOSHIRO MORITA

From the Department of Applied Chemistry, School of Science and Engineering, Waseda University, Tokyo, Japan

The reaction of normal pentane and hydrogen on a nickel–silica gel catalyst was studied in a flow system under a hydrogen pressure of less than 50 atm. Under the range of temperatures studied (300–400°C), the predominant reaction was the consecutive removal of terminal methyl groups as methane, and the formation of hydrocarbons containing one less carbon atom.

The product distributions varied widely with both variation of the partial pressure of hydrogen and with the reaction temperature. At high partial pressures of hydrogen or low temperatures mainly butane and corresponding amounts of methane were produced. At low partial pressures of hydrogen or high temperatures the pentane was more extensively degraded. Velocity of pentane hydrogenolysis increased with partial pressure of pentane and was inversely proportional to partial pressure of H_2. The results could be explained by the mechanism involving cracking of terminal carbon–carbon bonds of adsorbed hydrocarbon radicals.

INTRODUCTION

In the hydrogenolysis of paraffinic hydrocarbons over a nickel catalyst, attention has mainly been given to the splitting of ethane or propane (1–7). In the literature, the hydrogenolysis of these hydrocarbons was found to be strongly inhibited by hydrogen. Cimino et al. (8) showed that the kinetics could be explained satisfactorily in terms of a mechanism involving preliminary dehydrogenation of ethane to an unsaturated radical C_2H_x on the surface, followed by attack of the surface radical by hydrogen. Most of the work described in the literature, however, was carried out at low temperatures and pressures less than atmospheric.

Since catalytic hydrocracking has recently been emphasized in petroleum industry, investigations of hydrogenolysis of higher hydrocarbons (9–13) have also been initiated. In these investigations, it has been shown that, on nickel catalyst, the splitting of C–C bonds proceeds selectively, whereas on catalysts containing platinum, tungsten, and rhodium [for example (12,

14)] isomerization and other reactions are also accelerated. In the case of nickel catalysts, interest has mostly been shown in the selectivity in the splitting of C–C bonds. Haensel and Ipatieff (9, 10) investigated the selective demethylation of branched-chain paraffinic hydrocarbons by reaction with hydrogen, in which methyl groups not attached to a quaternary carbon were selectively removed to leave neopentane as a final product. In the hydrogenolysis of straight-chain paraffins, it was observed by Kochloefl and Bažant (13) that the predominant reaction involved successive degradation to methane and to paraffins containing one less carbon atom. The selectivity in the splitting of the terminal C–C bond, however, was somewhat lower in the straight chain than in the hydrogenolysis of branched-chain paraffins.

We have studied the hydrogenolysis of petroleum hydrocarbons on nickel catalysts with respect to the production of methane as one of the components of town gas (15, 16). In the present work, the hydrogenolysis of n-pentane was carried out in the tem-

perature range of 300–400°C, and under the pressure of less than 50 atm. It was the purpose of the present work to determine the effect of the hydrogen pressure and reaction temperature on the selectivity, and also to consider the mechanism of this reaction.

EXPERIMENTAL METHODS

Materials. Pentane used in the present work was a commercial reagent denominated as G.R. grade. Its purity, determined by gas chromatography, was nearly 100%. Cylinder hydrogen was used after purification by the Deoxo unit.

Catalyst. The nickel catalyst used in the present work contained 8.0 wt % nickel, and was prepared from nickel carbonate precipitated on silica gel. The silica gel used as the support was obtained by calcination (800°C, 3 hr) of the hydrogel precipitated from sodium silicate by addition of hydrochloric acid. The acidity of the support was determined by amine titration (*n*-butyl amine) with dimethyl yellow (pKa 3.3) as indicator. It was in the range 8.44×10^{-3} to 9.83×10^{-3} meq/g. These values probably indicate that the catalyst used is essentially neutral. The catalyst was calcined at 450°C for 2 hr in air.

Apparatus and procedures. The hydrogenolysis was carried out in a flow system schematically illustrated in Fig. 1. Hydrogen was admitted from a high pressure cylinder into the apparatus after a purification (Deoxo unit) to remove oxygen impurity. The gas flow rate was measured by an orifice-type flow meter. The pentane was added quantitatively to the hydrogen flow from cylindrical pump. The gases were premixed and preheated prior to the reaction.

The reactor was constructed from a 10 mm inside diameter stainless steel (SUS 27) tube of 270 mm length with a constriction near the middle to hold the catalyst basket. About 30–100 mg of the catalyst (crushed to particles of a size from 30 to 60 mesh) was packed, diluted with 10- to 30-fold inactive carborundum to remove the heat evolved by the reaction. The total volume of the catalyst bed was 3.0 ml. A magnesia coated chromel-alumel thermo-

couple was placed at the center of the catalyst bed.

Prior to reaction, the catalyst was reduced to 550°C for 7 hr by hydrogen. By such treatment, catalytic activity and selectivity did not change appreciably for about 5 hr in our reaction conditions. And then the catalyst was reactivated in hydrogen stream for 1 hr prior to another reaction period. As methane was not observed in the effluent gas during the reactivation, deposition of carbonaceous material on the catalyst was considered to be negligible.
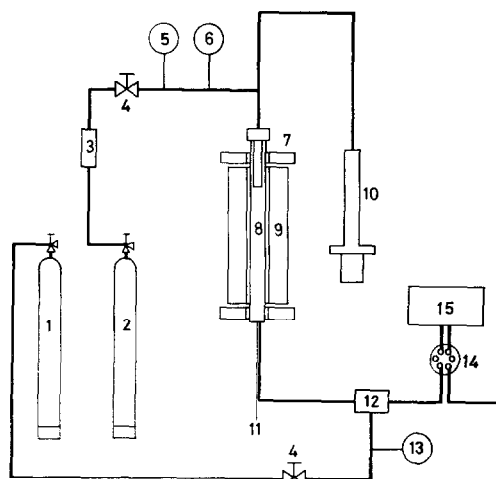

FIG. 1. Flow sheet of the reactor assembly: 1, nitrogen cylinder; 2, hydrogen cylinder; 3, Deoxo unit; 4, flow control valve; 5, pressure gauge; 6, flow meter; 7, preheating block heater; 8, reactor; 9, reactor heater; 10, liquid hydrocarbon feed pump; 11, thermocouple; 12, pressure control valve; 13, pressure gauge; 14, gas sampling cock (6 ways); 15, gas chromatographic unit.

After the reduction of the catalyst, the catalyst was cooled to the reaction temperature in a stream of hydrogen. The pressure and flow rate of hydrogen were adjusted by a pressure control valve and a needle valve, respectively, and then the pentane was admitted to the hydrogen stream. Feed rate of pentane was in the range of $1.74 \times 10^{-4} \sim 6.96 \times 10^{-3}$ moles/min, and ratio of flows of hydrogen to pentane was changed in the range of 5 ~ 100. Feed ratio of hydrogen/pentane and also total pressure were changed to examine
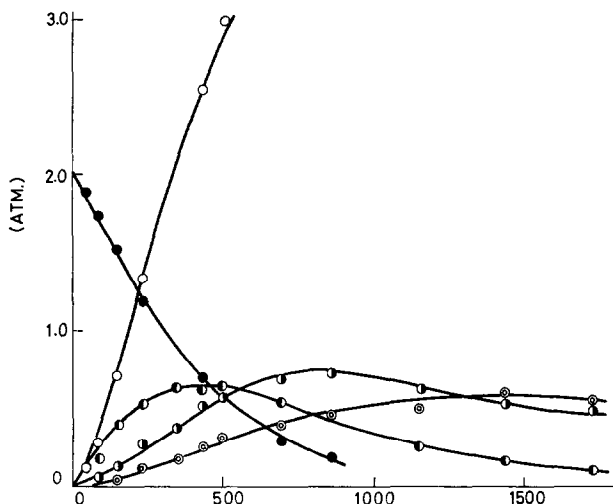
Fig. 2. The partial pressure of various hydrocarbons observed during the decomposition of pentane (2.0 atm) with hydrogen (30 atm) at 350°C: ●, pentane; ◐, butane; ◑, propane; ◎, ethane; ○, methane.

effect of partial pressure of components. About 5 min were required to reach steady state of the reaction system. The effluent gas in the following 10 min was analyzed.

The products were analyzed by a gas chromatographic unit connected to the reactor, by using a thermal conductivity detector. The chromatographic column was packed with DOP/Celite (3 m) + DMF/ activated alumina (1 m), and the carrier gas was hydrogen.

RESULTS

The products of n-pentane hydrogenolysis included all the normal paraffins containing one to four carbon atoms. Isomerization was not observed in the course of the hydrogenolysis under our conditions. The reaction products are shown in Fig. 2, with variation of the reciprocal space velocity (W/F), where W is weight of catalyst (g), and F is molar feed of pentane (moles/min), respectively.

The main product was methane throughout the period of contact. The amount of each product except for methane showed a maximum. Shorter period of contact produced hydrocarbons with larger number of carbon atoms. It is, therefore, reasonable that the hydrogenolysis of pentane proceeds in consecutive steps. An analogous course of hydrogenolysis has already been

observed by some authors [for example (9, 13)].

The pentane disappearance $(-\Delta p_{C_5})$ and methane formation (Δp_{C_1}) were examined by changing the partial pressure of hydrogen, without changing the partial pressure of pentane. Conversion of pentane (X) can be calculated by Eq. (1) and it is equal to the decrease of pentane partial pressure $(-\Delta p_{C_5})$ divided by initial partial pressure of pentane $(p_{C_5}{}^0)$, namely $(-\Delta p_{C_5}/p_{C_5}{}^0)$.

$$X = \frac{C_1 + 2C_2 + 3C_3 + 4C_4}{C_1 + 2C_2 + 3C_3 + 4C_4 + 5C_5}$$

$$= \frac{\sum_{i=1}^{4} iC_i}{\sum_{i=1}^{5} iC_i}, \quad (1)$$

where C_n is molar fraction of the hydrocarbon containing n carbon atoms in product. The initial velocity of pentane disappearance (V) and that of methane formation (V_{C_1}) defined as Eqs. (2) and (3) were obtained from the initial gradients of the curves shown in Figs. 3 and 4, respectively.

$$V = dX/d(W/F)$$
$$= -d(\Delta p_{C_5}/p_{C_5}{}^0)/d(W/F), \quad (2)$$

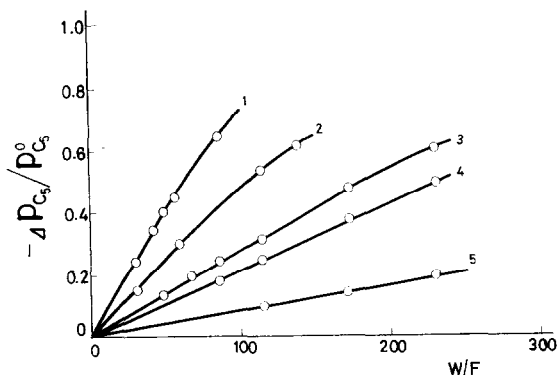$$V_{C_1} = d(\Delta p_{C_1}/p_{C_5}{}^0)/d(W/F). \quad (3)$$

FIG. 3. Dependence of pentane disappearance at 350°C ($p_{C_5}^0 = 0.5$ atm) on the partial pressure of hydrogen: 1, 2.5 atm; 2, 5 atm; 3, 12 atm; 4, 20 atm; 5, 30 atm.

Satisfactory linear relationships can be obtained between the initial velocities of pentane disappearance and the reciprocal hydrogen partial pressure, as shown in Fig. 5. Velocity of pentane hydrogenolysis was expressed in equation of type $V = k \, p_{C_5}^{0.7-0.8} \, p_{H_2}^{-1}$. The reaction is strongly suppressed by hydrogen, and it seems likely that hydrogen competes with the hydrocarbon for adsorption sites on the metal surface.

In Fig. 6, the ratios of the initial velocity of methane formation to that of pentane disappearance are plotted versus partial pressure of hydrogen. The ratio is reduced to unity by increasing the partial pressure

of hydrogen or decreasing the reaction temperature, but it does not become less than unity.

Typical distribution and selectivity of reaction products for a number of operating conditions are summarized in Table 1. Selectivity of each product was calculated by Eq. (4).

$$\text{Selectivity of } C_nH_{2n+2} = 5C_n / \sum_{i=1}^{4} iC_i. \quad (4)$$

The relations of the selectivities of products and conversion (X) are illustrated in Figs. 7 and 8 for $V_{C_1}/V = 1.00$ and 1.43, respectively. As shown in Fig. 7, only methane and butane are initially formed, and the remaining hydrocarbons are formed successively in the case of $V_{C_1}/V = 1.00$. On the other hand when the partial pressure of hydrogen decreases, V_{C_1}/V becomes greater than unity, where ethane and propane are also formed as primary product as well as methane and butane. In both cases, the following relation is obtained for the amount of the hydrocarbons formed, as shown in Table 1:

$$C_1 = C_4 + 2C_3 + 3C_2. \quad (5)$$

This relation proves that the reaction proceeds by way of successive demethylations and no cracking of C_2. Values less than 1.0 could arise from splitting of other carbon–carbon bonds than terminal, but the present
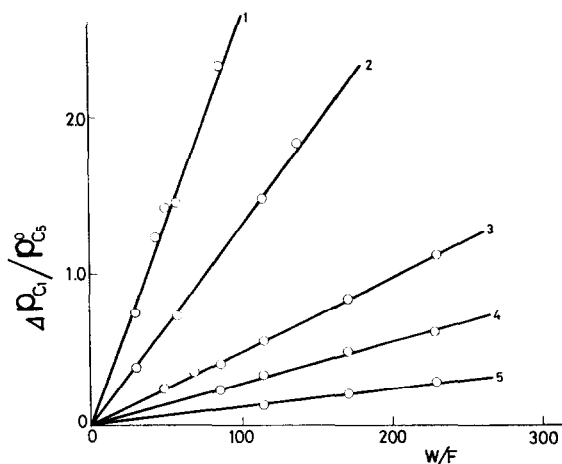

FIG. 4. Dependence of methane formation on the partial pressure of hydrogen, for runs shown in Fig. 3.

<div align="center">TABLE 1</div>
<div align="center">DISTRIBUTION AND SELECTIVITY OF PENTANE HYDROGENOLYSIS PRODUCT</div>

| Temp. (°C)	$p_{C_5}^{\circ}$ (atm)	$p_{H_2}^{\circ}$ (atm)	V_{C_1}/V	$X(\%)$	Distribution (mole %) Selectivity				$C/\sum_{i=2}^{4}(5-i)C_i$
					C_1	C_2	C_3	C_4	
350	2.0	50	1.00	5.0	52.0	0.5	3.0	44.0	1.01
					1.09	0.01	0.06	0.92	
				11.1	53.3	2.2	7.4	34.3	0.957
					1.23	0.05	0.17	0.79	
				20.4	57.2	3.3	11.8	27.7	0.935
					1.36	0.08	0.28	0.66	
				24.1	59.2	3.4	12.3	25.2	0.987
					1.45	0.08	0.30	0.62	
				27.0	59.4	3.7	12.5	24.4	0.980
					1.47	0.09	0.31	0.60	
				42.5	61.0	4.6	13.5	20.9	0.990
					1.57	0.12	0.35	0.54	
350	2.0	20	1.43	10.0	60.8	5.8	11.5	23.5	0.951
					1.51	0.14	0.29	0.59	
				20.0	61.8	5.9	11.5	21.9	0.987
					1.58	0.15	0.29	0.56	
				29.5	62.5	6.5	11.6	20.0	0.997
					1.64	0.17	0.31	0.53	
				33.5	62.9	7.0	11.6	19.5	0.987
					1.66	0.18	0.31	0.51	
				55.0	63.0	6.5	11.6	18.0	1.04
					1.72	0.18	0.32	0.49	
350	0.5	5.0	2.42	15.0	77.0	8.5	8.3	5.6	1.61
					2.72	0.30	0.29	0.20	
				29.4	79.1	8.6	7.5	4.7	1.74
					2.87	0.31	0.27	0.17	
				53.0	80.5	8.7	6.8	3.9	1.85
					3.01	0.32	0.25	0.15	
				61.2	81.3	8.5	6.6	3.7	1.92
					3.06	0.32	0.25	0.14	
350	0.5	2.5	3.81	34.8	85.9	6.6	4.7	3.1	2.66
					3.42	0.26	0.19	0.12	
				42.3	87.1	6.1	4.1	2.6	2.99
					3.57	0.25	0.17	0.11	
				64.7	88.7	5.7	3.6	2.1	3.66
					3.72	0.24	0.15	0.09	
				85.5	93.8	3.5	1.8	0.9	6.25
					4.27	0.16	0.08	0.04	
400	0.5	5.0	4.45	23.5	73.6	3.4	1.4	0.7	6.83
					4.38	0.16	0.07	0.03	
				44.0	96.3	2.4	1.0	0.3	10.1
					4.57	0.11	0.05	0.01	
				55.6	97.5	2.0	0.7	0.0	12.6
					4.67	0.10	0.03	0.01	
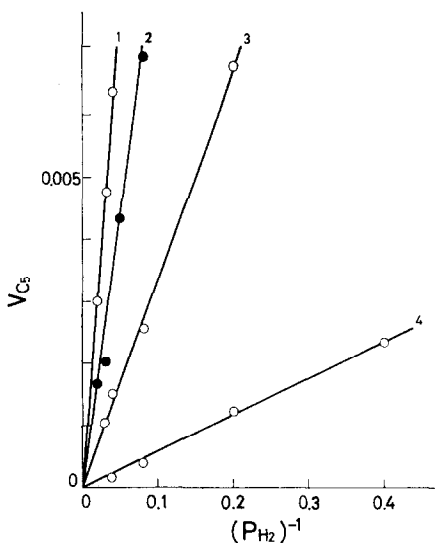
FIG. 5. Initial velocity of pentane disappearance (V) vs. reciprocal partial pressure of hydrogen: 1, $p_{C_5}{}^0 = 0.5$ atm, 400°C; 2, $p_{C_5}{}^0 = 2.0$ atm; 350°C; 3, $p_{C_5}{}^0 = 0.5$ atm, 350°C; 4, $p_{C_5}{}^0 = 0.5$ atm, 300°C.

values only slightly less than 1.0 are probably the result of analytical uncertainties.

DISCUSSION

As a result of kinetics on the hydrogenolysis of ethane and propane on nickel and iron catalysts, Cimino et al. (8) postulated that dissociation of the hydrocarbon into adsorbed radicals and hydrogen takes place on the metal surface.
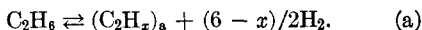
$$C_2H_6 \rightleftarrows (C_2H_x)_a + (6 - x)/2H_2. \qquad (a)$$
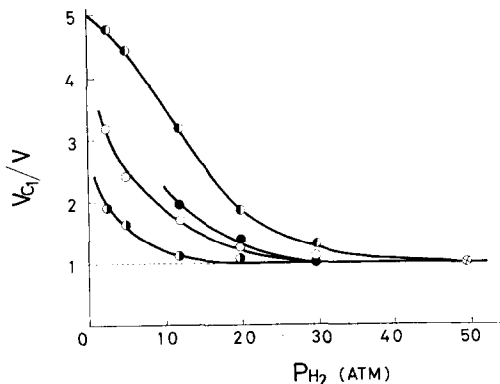
FIG. 6. Variation of V_{C_1}/V ratio with partial pressure of hydrogen and reaction temperature: 300°C (◑), 350°C (○), 400°C (◐) for $p_{C_5}{}^0 = 0.5$ atm; 350°C (●) for $p_{C_5}{}^0 = 2.0$ atm. ⊗; ◑ and ●.
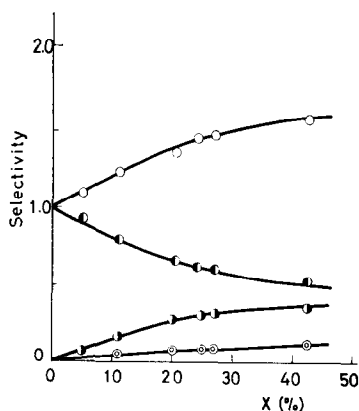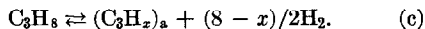

FIG. 7. Selectivities of products at $V_{C_1}/V = 1.00$ (350°C): ○, methane; ◑, butane; ◑, propane; ◎, ethane.

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

$$(C_2H_x)_a + H_2 \rightarrow CH_y + CH_z. \qquad (b)$$

This was believed to be the slow step in the reaction, the removal of the monocarbon fragments as CH_4 being rapid. A similar mechanism was proposed for the hydrogenolysis of propane, the initial step being the dissociation;

$$C_3H_8 \rightleftarrows (C_3H_x)_a + (8 - x)/2H_2. \qquad (c)$$

As an alternative mechanism, is was proposed by Anderson and Baker (12) that the overall reaction velocity is controlled by the velocity of product desorption, and that
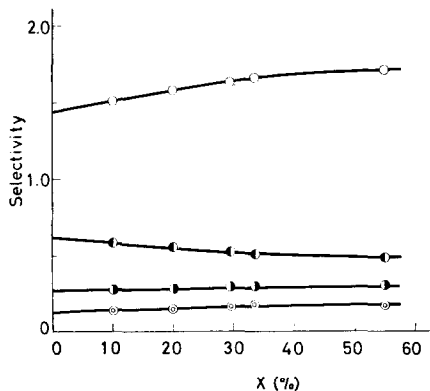

FIG. 8. Selectivities of products at $V_{C_1}/V = 1.43$ (350°C): ○, methane; ◑, butane; ◑, propane; ◎, ethane.

product distributions can be determined only by the velocity of adsorption/desorption. According to their proposition, mono-carbon surface residues must be far more numerous than any other since the ease of adsorption/desorption increases markedly in the sequence methane, ethane, propane.

It was observed in the present work that product distribution changed widely with variation of the partial pressure of hydrogen and with the reaction temperature. With low partial pressure of hydrogen and/or at high temperature, methane was formed as the predominant product, with relatively small amounts of higher hydrocarbons as shown in Table 1. These product distributions are similar to those observed by Anderson and Baker.

On the other hand, with high partial pressure of hydrogen and/or at low temperature, the reaction of pentane yielded corresponding amounts of methane and butane as primary product as shown in Fig. 7. In this case, product distributions can hardly be explained by supposition that reaction velocity is controlled by product desorption.

From the results obtained in the present work, amounts of methane were observed as shown in Table 1 to be equal to $C_4 + 2C_3 + 3C_2$ in many cases except for the lowest partial pressure of hydrogen (2.5 atm, 350°C) and a high temperature (400°C). From these observations it can be deduced that the splitting of C–C bonds takes place at the terminal position of the carbon chain, and not at the inner position. And it was also found that in some cases (at high partial pressure of hydrogen) the formation of methane at zero conversion was equal to the pentane disappearing and for other conditions $\Delta C_1 > -\Delta C_5$ as shown in Fig. 6. Thus we may represent the situation as follows (the hydrogen atoms formed by dissociation being omitted for simplicity).
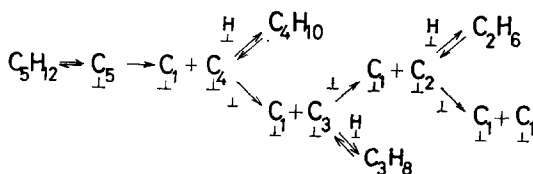
The adsorbed hydrocarbon radical will be hydrogenated and desorbed if hydrogen present is sufficient. However, when this radical is exposed to a bare metal site, this radical will be decomposed to a mono-carbon radical and a radical having one less carbon atom.

This situation can be considered to be essentially identical to the mechanism proposed by Taylor et al. (8). 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.

REFERENCES

1. MORIKAWA, K., BENEDICT, W. G., AND TAYLOR, H. S., J. Am. Chem. Soc. 58, 1795 (1936).
2. MORIKAWA, K., TRENNER, N., AND TAYLOR, H. S., J. Am. Chem. Soc. 59, 1103 (1937).
3. KEMBALL, C., AND TAYLOR, H. S., J. Am. Chem. Soc. 70, 345 (1948).
4. YATES, D. J. C., TAYLOR, W. F., AND SINFELT, J. H., J. Am. Chem. Soc. 86, 2996 (1964).
5. TAYLOR, W. F., YATES, D. J. C., AND SINFELT, J. H., J. Phys. Chem. 68, 2962 (1964).
6. TAYLOR, W. F., SINFELT, J. H., AND YATES, D. J. C., J. Phys. Chem. 69, 3857 (1965).
7. BALANDIN, A. A., SLOVOKHOTOVA, T. A., SHOLIN, A. F., AND UGOLTSEVA, L. A., Kinetika i Kataliz 6, 115 (1965).
8. CIMINO, A., BOUDART, M., AND TAYLOR, H. S., J. Phys. Chem. 58, 796 (1954).
9. HAENSEL, V., AND IPATIEFF, V. N., J. Am. Chem. Soc. 68, 345 (1946).
10. HAENSEL, V., AND IPATIEFF, V. N., Ind. Eng. Chem. 39, 853 (1947).
11. CIAPETTA, F. G., AND HUNTER, J. G., Ind. Eng. Chem. 45, 147 (1953).
12. ANDERSON, J. R., AND BAKER, B. G., Proc. Roy. Soc. (London), Ser. A 271, 402 (1963).
13. KOCHLOEFL, K., AND BAZANT, V., J. Catalysis 10, 140 (1968).
14. HAENSEL, V., AND DONALDSON, G. R., Ind. Eng. Chem. 43, 2102 (1951).
15. MORITA, Y., KIKUCHI, E., AND YAMAMOTO, K., J. Chem. Soc. Japan, Ind. Chem. Sect. 70, 670 (1967).
16. KIKUCHI, E., MORITA, Y., AND YAMAMOTO, K., J. Chem. Soc. Japan, Ind. Chem. Sect. 70, 1662 (1967).

$$C_5H_{12} \rightleftharpoons \underset{\perp}{C_5} \rightarrow \underset{\perp}{C_1} + \underset{\perp}{C_4}$$