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Hydrogenolysis of Isopentane on Nickel

Products from the hydrogenolysis of hydrocarbons often yield valuable information on the mechanism of the splitting process; bonds at different locations in the molecule may split at different rates. Subsequent reactions must be considered if the conversion of feed is substantial, or if the products are more reactive than the feed hydrocarbon. Characteristic splitting patterns of metals have been described (*1–7*). On supported ruthenium the data for butanes and pentanes could be explained by a 1,2-type chemisorbed species (*1*, *2*). The bonds of *n*-butane had an equal probability of splitting, but isopentane cracked preferentially at the long end of the chain, the bonds to the tertiary carbon being relatively stable. Isobutane was the principal primary product. On ruthenium branched isomers were less reactive than normal paraffins of the same carbon number, and in the normal paraffins the different bonds are broken at about the same rate (*1*, *2*, *8*).

Nickel catalysts preferentially attack terminal carbon–carbon bonds; successive demethylations have been found for *n*-pentane (*5*, *6*), *n*-hexane (*4*, *7*), octanes, and decanes (*3*). Branched paraffins were more reactive than the corresponding normal isomer on nickel (*3*). Skeletal rearrangements have not been reported on either nickel or ruthenium.

We are reporting here data on the hydrogenolysis of isopentane in a differential reactor on a nickel catalyst supported on a low area, porous silicon carbide and containing magnesia as a structural promoter (*8*). The experiments were made at 1.2 atm with an excess of hydrogen and at 233 to 282°C. Selectivity plots at 248°C are shown in Fig. 1; the solid curves are calculated values. The selectivities defined as moles of product per mole of isopentane reacted are plotted as a function of the conversion of isopentane. The ratio of the selectivities of *n*- to iso-butane on nickel is about 2, which is very different from ratios of about 0.05 found on ruthenium (*1*, *2*).

These data were fitted to equations for the reaction network of Kempling (*1*, *2*) by nonlinear least squares. These equations represent the data satisfactorily, but it was possible to evaluate only groups of rate constants and splitting factors. Table 1 compares the rate constants for isopentane on nickel of Fig. 1 with similar data of Kempling (*2*) on ruthenium. Significant results are the ratios f'/f and k''_{i4}/k''_{4n}, both indicating that on nickel methyl groups on the tertiary carbon are removed faster than a methyl attached to a secondary carbon. On ruthenium the methyls of tertiary carbons are removed very slowly. In Table 1, f' and f denote the fraction of isopentane losing a methyl at the ethyl end and at the tertiary carbon, respectively; k''_x denotes the overall first-order rate constant for hydrogenolysis of hydrocarbon x; k'_x and k^*_x are the rate constants for desorption and splitting of hydrocarbon x, respectively; and i4, n4, and i5 refer to isobutane, *n*-butane, and isopentane.

Parameters for the power rate law, $r = Ap_{H_2}{}^{m}p_{iC5}{}^{n}\exp(-E/RT)$ for the hydrogenolysis of isopentane on the present nickel catalyst and on supported ruthe-

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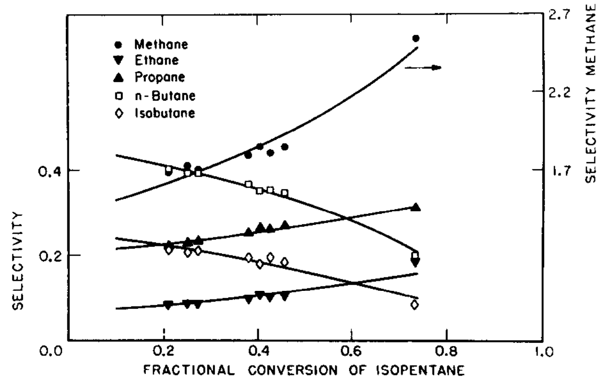

FIG. 1. Selectivities in the hydrogenolysis of isopentane on supported nickel at 248°C. Curves are calculated and points experimental.

nium were:

	m	n	E (kcal/mol)
Present nickel catalyst	−1.6	0.8	43.3
Ruthenium on alumina (*2*)	−1.1	.7	43.2

In the rate equation p_{H_2} and p_{iC_5} are the partial pressures of H_2 and isopentane; A, m, and n are constants, and E the activation energy. The Sinfelt (*9*) interpretation of the power rate law suggests that four and three hydrogen atoms are removed in the dissociative chemisorption of isopentane by Ni and Ru, respectively.

Thus, carbon–carbon bonds involving the tertiary carbon of isopentane react slowly on ruthenium and rapidly on nickel. A 1,2-chemisorbed species involving the tertiary carbon seems to be an important intermediate in the reaction on nickel.

TABLE 1

Parameters of the Reaction Network for the Hydrogenolysis of Isopentane (*2*)

Parameter	Nickel 248°C	Ruthenium (*2*) 110°C
$k'_{i4}f/(k'_{i4} + k^*_{i4})$	0.25	0.82
k''_{i4}/k''_{i5}	0.55	0.03
$k'_{n4}f'/(k'_{n4} + k^*_{n4})$	0.46	0.07
k''_{n4}/k''_{i5}	0.42	0.64
f'/f	1.84[a]	0.095
k''_{i4}/k''_{n4}	1.31	0.05

[a] Calculated assuming that $k'_{i4}/(k'_{i4} + k^*_{i4}) = k'_{n4}/(k'_{n4} + k^*_{n4})$.

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REFERENCES

1. Kempling, J. C., Ph.D. thesis, McMaster University, 1971.
2. Kempling, J. C., and Anderson, R. B., "Catalysis" (J. W. Hightower, Ed.), Vol. 2, p. 1099. Elsevier, Amsterdam, 1973.
3. Kochloefl, K., and Bazant, B., *J. Catal.* **10**, 140 (1968).
4. Matsumoto, H., Saito, Y., and Yorieda, Y., *J. Catal.* **19**, 101 (1970).
5. Kikuchi, E., and Morita, Y., *J. Catal.* **15**, 217 (1969).
6. Kikuchi, E., Isumuri, M., and Morita, Y., *J. Catal.* **22**, 226 (1971).
7. Matsumoto, H., Saito, Y., and Yorieda, Y., *J. Catal.* **22**, 182 (1971).
8. Machiels, C. J., and Anderson, R, B., *J. Catal.*, **58**, 253, 260, 268 (1979).
9. Sinfelt, J. H., *J. Catal.* **27**, 468 (1972).

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