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Hydrogenolysis of 2,3-Dimethylbutane on Supported Ruthenium, Nickel, Cobalt, and Iron

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The hydrogenolysis of 2,3-dimethylbutane was studied over supported catalysts of ruthenium, nickel, cobalt, and iron, some containing magnesia as a structural promoter, in a differential reactor system. The selectivity data were fitted to equations derived from reaction networks involving reversible dissociative chemisorption of the hydrocarbons and irreversible rupture of the carbon–carbon bonds of the adsorbed species. In the sequence—ruthenium, nickel, cobalt, iron—the product distribution shifts toward smaller hydrocarbons, CH_4 being the principal product on iron. On ruthenium tertiary carbon atoms are relatively stable, but on nickel and cobalt they are no more stable than secondary carbon atoms. At the temperatures used in these experiments, splitting of the adsorbed species was usually not slow compared to desorption.

INTRODUCTION

Studies of the hydrogenolysis of paraffins larger than ethane have often been concerned primarily with the distribution of products. For *n*- and isobutane and neo- and isopentane on ruthenium, the orders with respect to hydrogen were large and negative and those for the hydrocarbons were near unity (*1*, *2*). These results were similar to those from ethane hydrogenolysis over most transition metals (*3*, *4*, *7*), and a similar reaction scheme was proposed. The activation energies for the hydrogenolysis of higher hydrocarbons were lower than for ethane. The rate of hydrogenolysis increased with the number of carbon atoms in normal hydrocarbons, but on ruthenium branching decreased the rate. For *n*-heptane on unsupported Pt, Pd, Ru, Rh, and Ir, the range of activities was as large as with ethane (*9*).

Interesting results were obtained from reactions of large hydrocarbons with several nonidentical carbon–carbon bonds (*2*, *5*, *6*, *10*), but the experiments were generally limited to low conversions of feed hydrocarbon, so that only initial product distributions were obtained. The product distributions are very much dependent on the catalyst and on the temperature. For nickel, successive demethylation occurred at the terminal carbon(s) of the longest chain of the hydrocarbon molecule. At high temperatures and low pressures, more extensive cracking was observed at the same conversion. Selective splitting of terminal carbon–carbon bonds also occurred on palladium and rhodium. On platinum the splitting occurred with about equal probability for each carbon–carbon bond, and isomerization and dehydrocyclization

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took place in addition to hydrogenolysis. On ruthenium, random splitting was observed for normal alkanes, but for branched molecules bonds in the straight part of the chain were split preferentially. On cobalt and iron desorption has been postulated to be a rate limiting step (*6–8*), which may explain the relatively large amount of small products from these catalysts.

EXPERIMENTAL

The following catalysts were used in this study: ruthenium on alumina, nickel on silicon carbide, nickel–magnesia on silicon carbide, cobalt–magnesia on silicon carbide, and iron–magnesia on silica. The preparation and properties of these catalysts were described in a previous paper (*11*), as well as the reactor system. The hexane was introduced into the system as liquid using a multispeed pump (Harvard Apparatus Co.) with two 50-ml gastight syringes (Hamilton 1050). The hexane entered into the recycle loop through a hypodermic needle. The tubing and valves connecting the reactor, recycle pump, and in the effluent system were heated with heating tape to prevent condensation. The analytical system described in the previous paper (*11*) was able to separate in about 25 min all the products with the gas chromatographic columns operating isothermally. 2,3-Dimethylbutane from Aldrich was described as 97+%, but gas chromatography showed only traces of impurities.

A large excess of hydrogen was always used, the hexane to hydrogen ratio in the feed never exceeding 1:10, and all experiments were performed at a total pressure of 1.20 atm. For each catalyst, studies were made at a single temperature that was chosen to permit tests over a wide range of conversion of the hexane, usually from less than 5% to greater than 80%. The deactivation of the catalysts was very much more rapid than in the propane experiments, and the ruthenium catalyst lost activity particularly rapidly. The deactivated catalyst could be regenerated by treatment with hydrogen at temperatures 10 to 20°C higher than that of the previous operation. The 2,3-dimethylbutane was stored over Raney nickel, silica gel, and activated alumina in an attempt to remove impurities, but the catalysts still deactivated rapidly.

Because of the rapid deactivation, kinetic experiments were not made; however, the product distributions were not affected by the decreasing activity, and the selectivities were studied. The fractional conversion, X_6, of 2,3-dimethylbutane was determined from the composition of the effluent gas according to

$$X_6 = \left(\sum_{j=1}^{N} n_j Y_j\right) \Big/ \sum_{j=1}^{M} n_j Y_j, \qquad (1)$$

where j = a series of integers representing the different products in the effluent, n_j = carbon number of hydrocarbon j, N = total number of hydrocarbon products, $M = (N + 1)$, includes the feed hydrocarbon, and Y_j = mole fraction of hydrocarbon j in effluent. The selectivity, S_i, for a reaction product, i, is defined as the moles of that product formed per mole of 2,3-dimethylbutane reacted.

$$S_i = 6Y_i \Big/ \sum_{j=1}^{N} n_j Y_j. \qquad (2)$$

The maximum values of the selectivities for isopentane, isobutane, and *n*-butane are 1.0, for propane and ethane 2.0, and for methane 6.0. Isomerization and chain growth reactions were not observed. Blank experiments on the porous low-area silicon carbide, used as a support in some of the catalysts, showed no reaction of 2,3-dimethylbutane and H_2 at temperatures up to 400°C. Experimental errors in the selectivity data are estimated to be 6%.

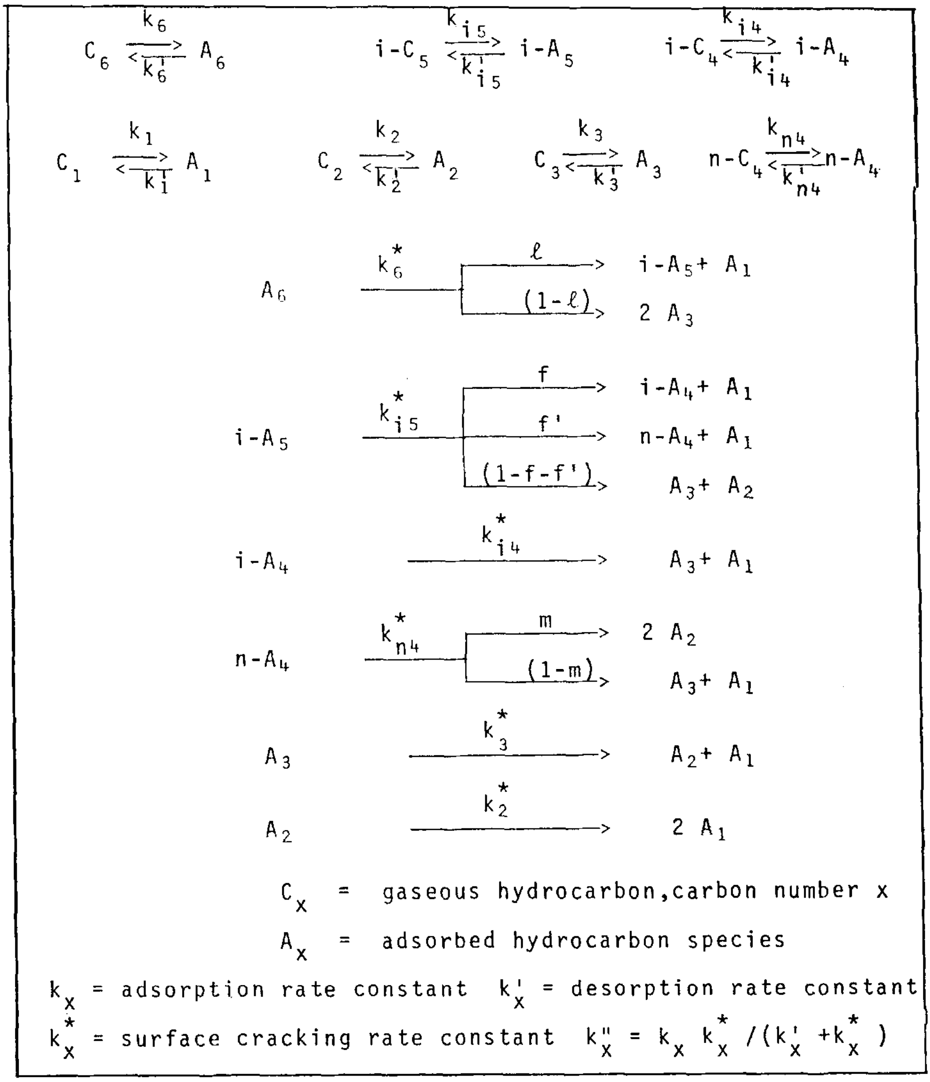

FIG. 1. Reaction network for the hydrogenolysis of 2,3-dimethylbutane.

RESULTS AND DISCUSSION

A reaction network is proposed for the hydrogenolysis of 2,3-dimethylbutane (Fig. 1) which includes all possible parallel and consecutive reactions. 2,3-Dimethylbutane has two types of carbon–carbon bonds, and its major product, isopentane, can split in three different ways. The other possible products are isobutane, *n*-butane, propane, ethane, and methane. Based on this network, selectivity equations were derived relating the selectivities of the various products to the conversion of the feed hydrocarbon. The following assumptions are made:

(a) All hydrocarbons adsorb and desorb reversibly.

(b) The splitting steps are irreversible; no chain growth occurs.

(c) No isomerization takes place.

(d) Surface splitting and desorption are assumed to be first order in the adsorbed hydrocarbon species.

(e) Effects of the partial pressure of

hydrogen on splitting and desorption reactions are assumed to be the same for all species and are incorporated into the rate constants. The parameters evaluated from the reaction network occur only as ratios of rate constants. Common terms such as denominators of the Langmuir–Hinshelwood type, if present, would cancel.

(f) No rate-limiting step is assumed; overall material balances are used in the derivations.

(g) Splitting of carbon–carbon bonds occurs sequentially, one at a time. Splitting factors account for splitting of different bond types. These splitting factors are defined as the probability that a molecule will crack at a particular bond. These factors are assumed to be independent of conversion, but they may be dependent on temperature.

The selectivity equations for 2,3-dimethylbutane, based on the network of Fig. 1, are given in Fig. 2 (*12*). The experimental selectivities can be fitted to these equations directly. Three types of parameters can often be evaluated: the splitting factors of 2,3-dimethylbutane, isopentane, and n-butane and two groups of rate constants. The constant k''_x/k''_6 is the ratio of the overall rate of hydrogenolysis of hydrocarbon x to that of the feed hydrocarbon. The constant k''_x is defined as $k''_x = k_x k^*_x/(k'_x + k^*_x)$, and it is the overall first order rate constant for hydrocarbon x. The other parameter, $k'_x/(k'_x + k^*_x)$, is a measure of the relative

$$S_{i5} = j_{i5}\,\ell/(1 + (k''_{i5}/k''_6)\,Z)$$

$$S_{i4} = j_{i4}\,f(\ell - S_{i5})/(1 + (k''_{i4}/k''_6)\,Z)$$

$$S_{n4} = j_{n4}\,f'(\ell - S_{i5})/(1 + (k''_{n4}/k''_6)\,Z)$$

$$S_3 = \frac{j_3\,\{2 - \ell(1 + m\,f') - S_{i4} - S_{n4}(1 - m) - S_{i5}(1 - m\,f)\,\}}{1 + (k''_3/k''_6)\,Z}$$

$$S_2 = \frac{j_2\{\,2 - \ell(f + f' - m\,f') - S_3 - S_{i4} - S_{n4}(1+m) - S_{i5}(2 + m\,f - f - f')\,\}}{1 + (k''_2/k''_6)\,Z}$$

$$S_1 + 2S_2 + 3S_3 + 4(S_{i4} + S_{n4}) + 5S_{i5} = 6$$

where $Z = X/(1 - X)$, and X is the fractional conversion of 2,3-dimethylbutane.

S_x = selectivity of product x

$j_x = k'_x/(k'_x + k^*_x)$

rate constants are defined in Figure 1.

FIG. 2. Selectivity equations for the hydrogenolysis of 2,3-dimethylbutane

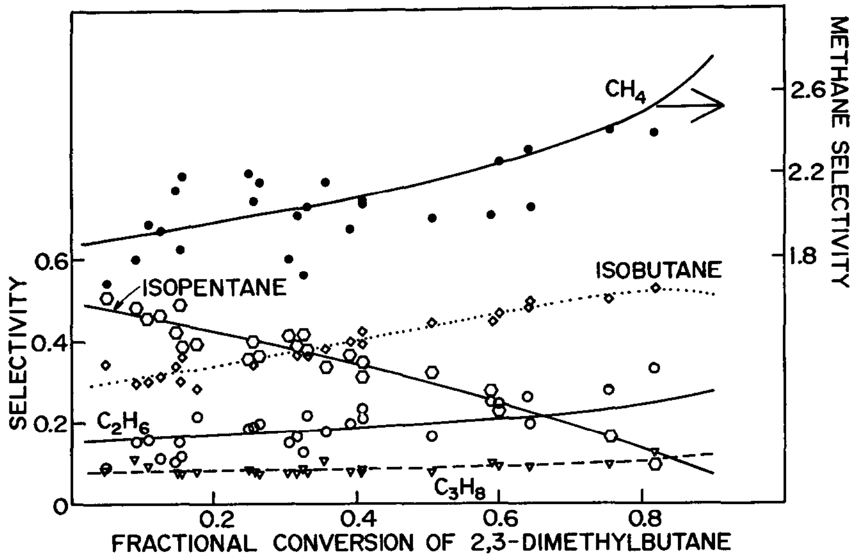

FIG. 3. Product distribution from the hydrogenolysis of 2,3-dimethylbutane over ruthenium on alumina at 200°C and 1.2 atm. Points represent experimental data; curves are theoretical.

rates of cracking and desorption of adsorbed species x. If the surface splitting reaction is rate controlling, as is often assumed in hydrogenolysis, this parameter will approach unity.

The product distributions for Ru, Ni, and Co catalysts were fitted to these equations using nonlinear regression analysis. In Figs. 3–6, the solid curves are the calculated selectivities while the experimental values are shown by symbols. In general the data fit the equations very

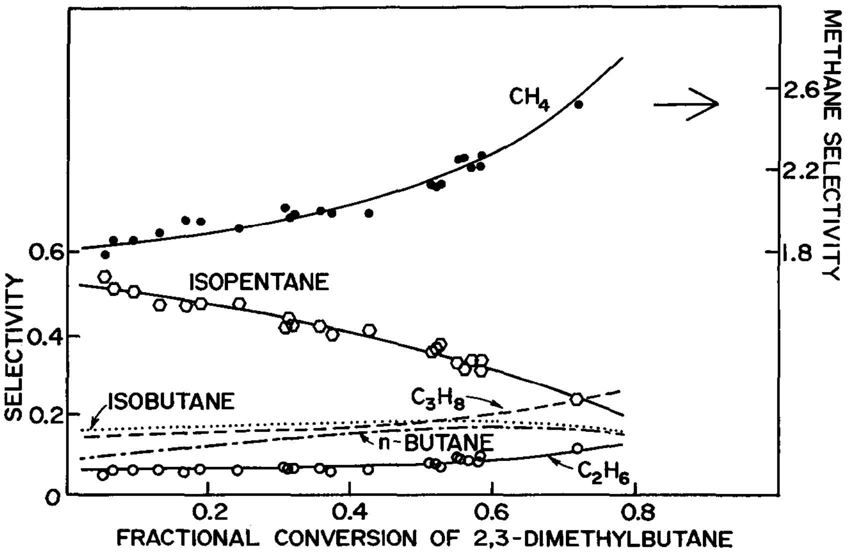

FIG. 4. Product distribution from the hydrogenolysis of 2,3-dimethylbutane over Ni–Mg on silicon carbide at 245°C and 1.2 atm. Points represent experimental data; curves are theoretical.

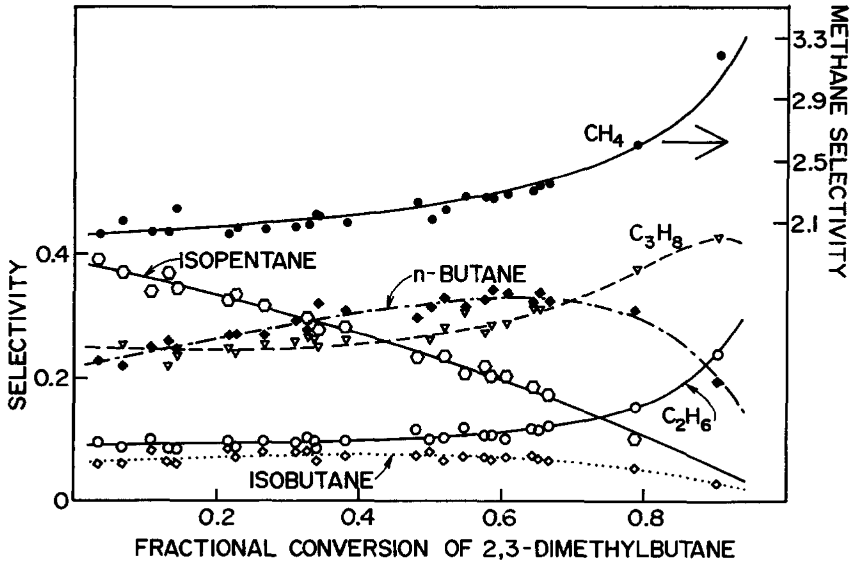

FIG. 5. Product distribution from the hydrogenolysis of 2,3-dimethylbutane over nickel on silicon carbide at 260°C and 1.2 atm. Points represent experimental data; curves are theoretical.

well, with average deviations between calculated and experimental selectivities being smaller than our estimates of experimental errors. The only exceptions were molecules present in very small amounts. The iron catalyst had a very low activity and temperatures of at least 300°C were required. The product was almost entirely methane; only traces of propane and some ethane were formed, and the equations could not be used. The large yield of methane on iron suggests that the adsorbed

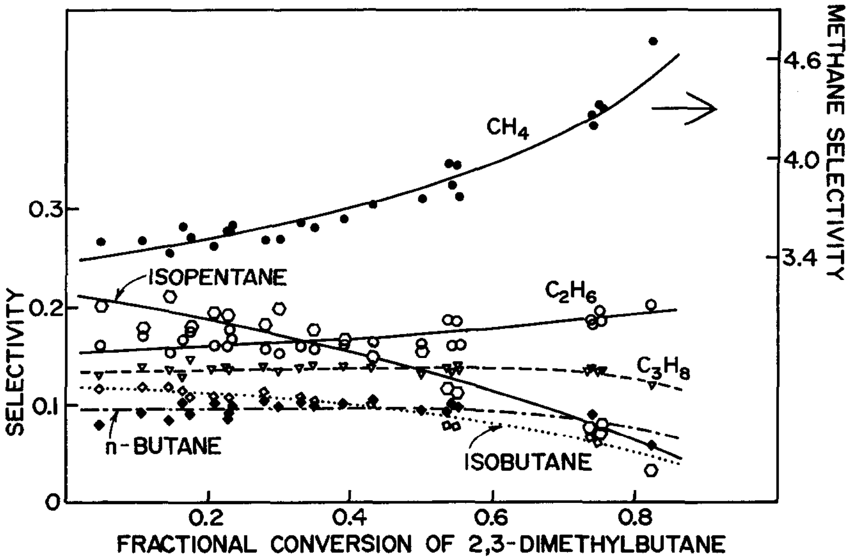

FIG. 6. Product distribution from the hydrogenolysis of 2,3-dimethylbutane over Co–Mg on silicon carbide at 227°C and 1.2 atm. Points represent experimental data; curves are theoretical.

TABLE 1

Estimated Parameter Values from the Selectivity Equations for 2,3-Dimethylbutane

	Ru/Al_2O_3	Ni/SiC	Ni–Mg/SiC	Co–Mg/SiC
Temperature (°C)	200	260	245	227
$k'_{i5}/(k'_{i5} + k^*_{i5})$	0.58	0.43	0.57	0.30
$k'_3/(k'_3 + k^*_3)$	0.22	0.55	0.50	0.15
$k'_2/(k'_2 + k^*_2)$	0.37	0.60	0.41	0.21
$fk'_{i4}/(k'_{i4} + k^*_{i4})$	0.79	0.13	0.39	0.24
$f'k'_{n4}/(k'_{n4} + k^*_{n4})$	—	0.50	0.79	0.19
k''_{i5}/k''_6	0.68	0.65	0.46	0.60
k''_{i4}/k''_6	0.03	0.23	0.23	0.50
k''_{n4}/k''_6	—	0.08	0.37	0.16
k''_3/k''_6	0.001	0.01	0.03	0.09
k''_2/k''_6	3×10^{-5}	0.001	0.005	0.02
l	0.85	0.90	0.93	0.75

species are very strongly bonded to the surface and crack very much faster than they desorb.

Examples of product distributions are shown in Figs. 3–6. The amount of smaller products increases in the sequence—Ru, Ni, Co, Fe—in the same way as observed for propane on some of the same catalysts (*11*). The amount of smaller products is also larger on the unpromoted nickel catalyst than on the promoted one, possibly due to the higher temperature required for the unpromoted catalyst. Addition of magnesia to nickel on low-area supports increased both activity and surface area about 10-fold (*11*).

An interesting observation was made on the ratio of *n*-butane to isobutane in the products. On ruthenium (Fig. 3) only traces of *n*-butane were observed, in agreement with Kempling and Anderson (*2*) who found that on this catalyst isopentane cracks perferably at the straight end of the chain to form isobutane. However, on nickel (Fig. 4) the ratio of *n*-butane to isobutane is about 1, and the ratio increases with increasing temperature. On the unpromoted nickel catalyst (Fig. 5) at higher temperature, the ratio of *n*-butane to isobutane varied from 4 to 7. This result agrees with observations on nickel that branched hydrocarbons are more reactive than the corresponding normal paraffins (*13*) in contrast to ruthenium; i.e., tertiary carbon atoms are relatively stable on ruthenium but not on nickel. Cobalt behaves like nickel in this respect (Fig. 6). A few experiments with isopentane on Ni–Mg/SiC verified these results: The product contained more *n*-butane than isobutane, the ratio increasing with increasing temperature (*14*).

Estimates of some of the parameters are tabulated in Table 1; some groups of parameters could not be separated. The values of the parameters are in most cases acceptable and consistent with observations on the product distributions as functions of conversion. The approximate confidence intervals of the parameters obtained from S_{i5}, S_{i4}, S_{n4}, and in some cases S_3 are satisfactory, but those from S_2 and sometimes from S_3 are large. This result is attributed mainly to the nature of the equations: For instance the parameter k''_2/k''_6, which has a value very much smaller than unity, can be estimated accurately only if experiments are carried out at very high conversions of 2,3-dimethylbutane (Fig. 2). The values of k^*_2/k'_2 are in agreement with similar results from propane (*11*): The rate of surface cracking is not slow compared to the rate of desorption of the adsorbed species. On ruthenium and on nickel these rates are about equal, while on cobalt the cracking is more rapid than the desorption. The temperatures used in these experiments were higher than those used in previous experiments in this laboratory (*1*, *2*). With increasing temperature, splitting rates usually increase more rapidly than rates of desorption; the activation energies for the splitting reactions are larger than those for desorption. The splitting constant, l, for 2,3-dimethylbutane is always close to unity; the center bond is not likely to break. The small amount of propane compared to isopentane also demonstrates this result. The product distributions suggest that on ruthenium the chemisorption of isopentane is principally at the straight section of the chain, while on nickel and cobalt the adsorption also occurs at the other end of the molecule. The values of k''_x/k''_6, relative rates of hydrogenolysis of hydrocarbon x and the feed hydrocarbon, indicate that the rate of hydrogenolysis decreases with decreasing carbon number. This decrease is rapid on ruthenium, but more gradual on nickel and cobalt. The strength of adsorption of the surface species increases in the sequence —ruthenium, nickel, cobalt, iron—causing an increase in the amount of smaller products. The sequence of activity of the metals is the same as found for the hydrogenolysis of propane: Ru > Co > Ni > Fe.

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