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Hydrogenolysis of 2,2-Dimethylbutane and *n*-Hexane over Supported Ruthenium, Nickel, Cobalt, and Iron

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Hydrogenolysis reactions of *n*-hexane and 2,2-dimethylbutane were studied in a differential reactor system over supported catalysts of ruthenium, nickel, cobalt, and iron, some containing a structural promoter. A wide range of conversions was covered, and the product distributions were fitted to equations that relate the selectivities to the conversion of the feed hydrocarbon. Quaternary carbon atoms are very stable on all catalysts. For *n*-hexane, nickel and cobalt selectively attack terminal carbon–carbon bonds while ruthenium cracks the different bonds with about equal probability. In the sequence—ruthenium, nickel, cobalt, iron—the product distributions shift toward smaller products. At the conditions used in these experiments, the surface cracking is the rate-limiting step on ruthenium only.

INTRODUCTION

Few kinetic studies have been made on the hydrogenolysis of higher hydrocarbons over transition metals (*1*), and they suggest mechanisms similar to those for ethane hydrogenolysis (*2*, *3*). Most of the studies with higher hydrocarbons have dealt with the product distributions (*4–10*). These selectivities are very dependent on the metal used, the reactant, and the temperature, and they yield information about the reaction mechanism. Nickel, rhodium, and palladium preferentially attack terminal carbon–carbon bonds causing successive demethylations of the carbon chains. Platinum and ruthenium were nonselective in cracking carbon–carbon bonds in straight chain hydrocarbons, but ruthenium showed preference in branched molecules for splitting bonds in the straight end of the chain. Platinum also caused isomerization and dehydrocyclization, and a carbonium ion mechanism has been proposed (*11*). On most metals, platinum being an exception, quaternary carbon atoms were much more stable than secondary or tertiary carbons, and the reactions usually stopped at quaternary carbon atoms. 2,2-Dimethylbutane yielded only methane and neopentane in almost equimolar amounts over a nickel catalyst (*5*, *8*). Experiments have also been reported for several cycloalkanes (*8*, *12*); pi-bonded species are suggested as intermediates on noble metals.

EXPERIMENTAL

The catalysts used in this study were prepared by impregnation, as described in previous papers (*4*, *13*): ruthenium on alumina, nickel on silicon carbide, and three catalysts with magnesia as a struc-

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tural promoter: nickel–magnesia on silicon carbide, cobalt–magnesia on silicon carbide, and iron–magnesia on silica. The reactor system was the same as the one described previously (*4, 13*). 2,2-Dimethylbutane was obtained from Phillips Petroleum Co. (pure grade, 99+%) and *n*-hexane from Fisher Scientific Co. (certified, 99+%); only traces of impurities were found by gas chromatography. The reactor system was differential, consisting of a fixed bed of catalyst and an external recycle pump. The system was shown (*14*) to behave as an ideally mixed one and external and internal temperature and concentration gradients were negligible. All the experi-

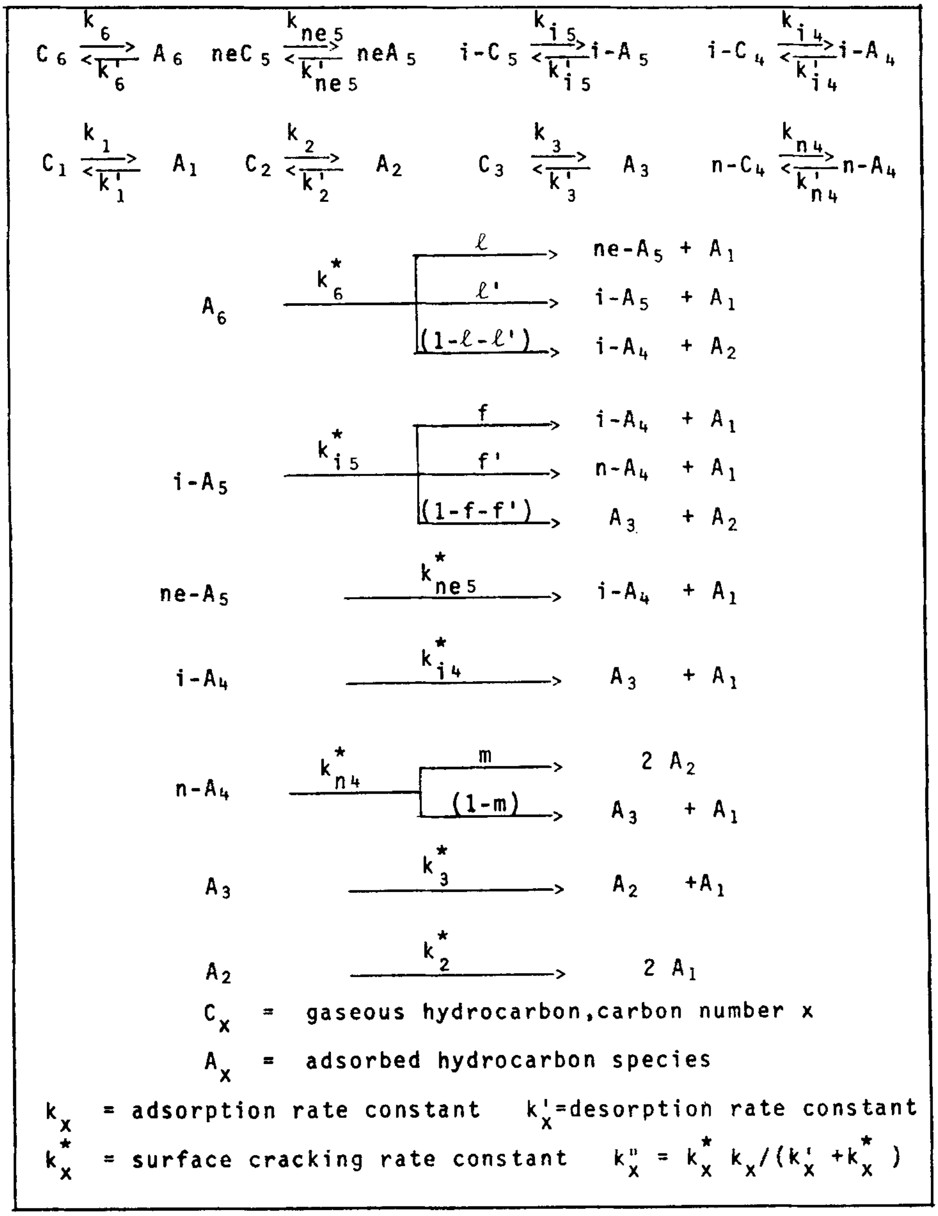

FIG. 1. Reaction network for hydrogenolysis of 2,2-DMB.

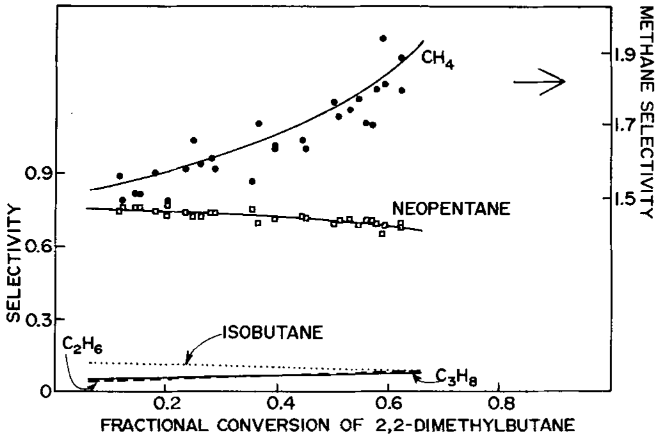

Fig. 2. Product distribution of hydrogenolysis of 2,2-dimethylbutane over Ni–Mg/SiC at 265°C and 1.2 atm.

ments were performed at a total pressure of 1.20 atm and with an excess of hydrogen. A wide range of conversions of the feed hydrocarbons was covered. Due to the deactivation of the catalyst (*4*), rate equations were not determined, but the selectivities were not affected by this deactivation. The products were analyzed by gas chromatography as described before (*4*, *13*). Results are expressed in terms of conversion of the feed hydrocarbon and selectivities for the various products (*4*). The selectivity of a product is defined as the moles of that product formed per mole of feed hydrocarbon reacted. Maximum values of selectivities in the hydrogenolysis of *n*-hexane are 1.0 for *n*-pentane and *n*-butane, 2.0 for propane, 3.0 for ethane, and 6.0 for methane. From 2,2-dimethylbutane, maximum values are 1.0 for neopentane, isopentane, isobutane, *n*-butane, and propane, 2.0 for ethane, and 6.0 for methane. Products of isomerization and/or of chain growth reactions were not observed in any of these experiments. Blank experiments with *n*-hexane on silicon carbide showed no reaction up to 400°C.

RESULTS AND DISCUSSION

Reaction networks, similar to the one for 2,3-dimethylbutane (*4*), are proposed. The network for 2,2-dimethylbutane is shown in Fig. 1; all the possible parallel and consecutive reactions are included. 2,2-Dimethylbutane has three different kinds of carbon–carbon bonds; isopentane, one of the possible products, also has three types of carbon–carbon bonds, and *n*-butane has two. Other products that can be expected are neopentane, isobutane, propane, ethane, and methane. The selectivity equations relate the selectivities to the conversion of 2,2-dimethylbutane; the assumptions made in their derivation were described in previous papers (*4*, *14*). In these derivations, no rate-limiting steps were assumed. The network for *n*-hexane is given in Fig. 4. *n*-Hexane has three types of carbon–carbon bonds and *n*-pentane has two. Other products are *n*-butane, propane, ethane, and methane.

The selectivity equations contain three types of parameters; one is the splitting factors defined as the probability that a particular type of bond will break. The splitting factors are assumed to be independent of the conversion, but they may be a function of temperature. The other two types of parameters occur in each of the equations and are groups of rate constants. k''_x/k''_6 is the ratio of the overall rates of hydrogenolysis of hydro-

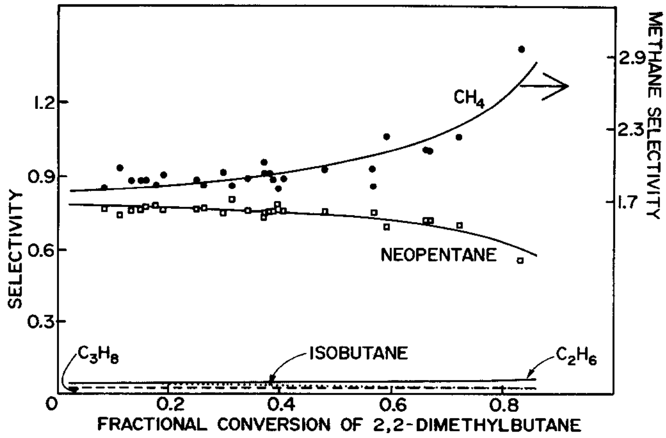

FIG. 3. Product distribution of hydrogenolysis of 2,2-dimethylbutane over Co–Mg/SiC at 245°C and 1.2 atm.

carbon x and the feed hydrocarbon. The parameter $k'_x/(k'_x + k^*_x)$ is indicative of the relative rates of cracking and desorption of the adsorbed species of hydrocarbon x. If the splitting reaction is rate controlling, this parameter will approach unity. The product distributions were fitted to these equations directly using nonlinear regression. In selectivity plots the solid lines are the calculated selectivities; the experimental data are shown as symbols. The experimental data could be fitted to the selectivity equations very well, within the experimental error, which was estimated to be 6 to 8%.

The activity of the iron catalyst was very much lower than those of the other catalysts. With *n*-hexane, nearly all methane was obtained with only traces of ethane and propane. With 2,2-dimethylbutane the major product was again methane, but substantial amounts of neopentane were also present, the selectivity of neopentane being as high as 0.28.

Examples of the product distribution from 2,2-dimethylbutane are shown in Figs. 2 and 3 for the promoted nickel and the cobalt catalyst. Similar distributions were obtained on the ruthenium catalyst and on the unpromoted nickel. Neopentane

TABLE 1

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

	Ru/Al_2O_3	Ni/SiC	Ni–Mg/SiC	Co–Mg/SiC
Temperature (°C)	200	290	265	245
$k'_{ne5}l/(k'_{ne5} + k^*_{ne5})$	0.88	0.39	0.76	0.78
k''_{ne5}/k''_6	0.01	0.09	0.07	0.06
$k'_{i4}/(k'_{i4} + k^*_{i4})$	0.43	0.35	0.50	0.19
k''_{i4}/k''_6	0.19	1.2	0.62	0.64
k''_{n4}/k''_6	—	1.7	—	—
$k'_3/(k'_3 + k^*_3)$	—	0.48	0.35	0.14
k''_3/k''_6	—	0.25	0.04	0.30
$k'_2/(k'_2 + k^*_2)$	0.99	0.49	0.52	0.11
l	1.0	0.73	0.99	0.8
k''_2/k''_6	0.01	0.04	0.03	0.02

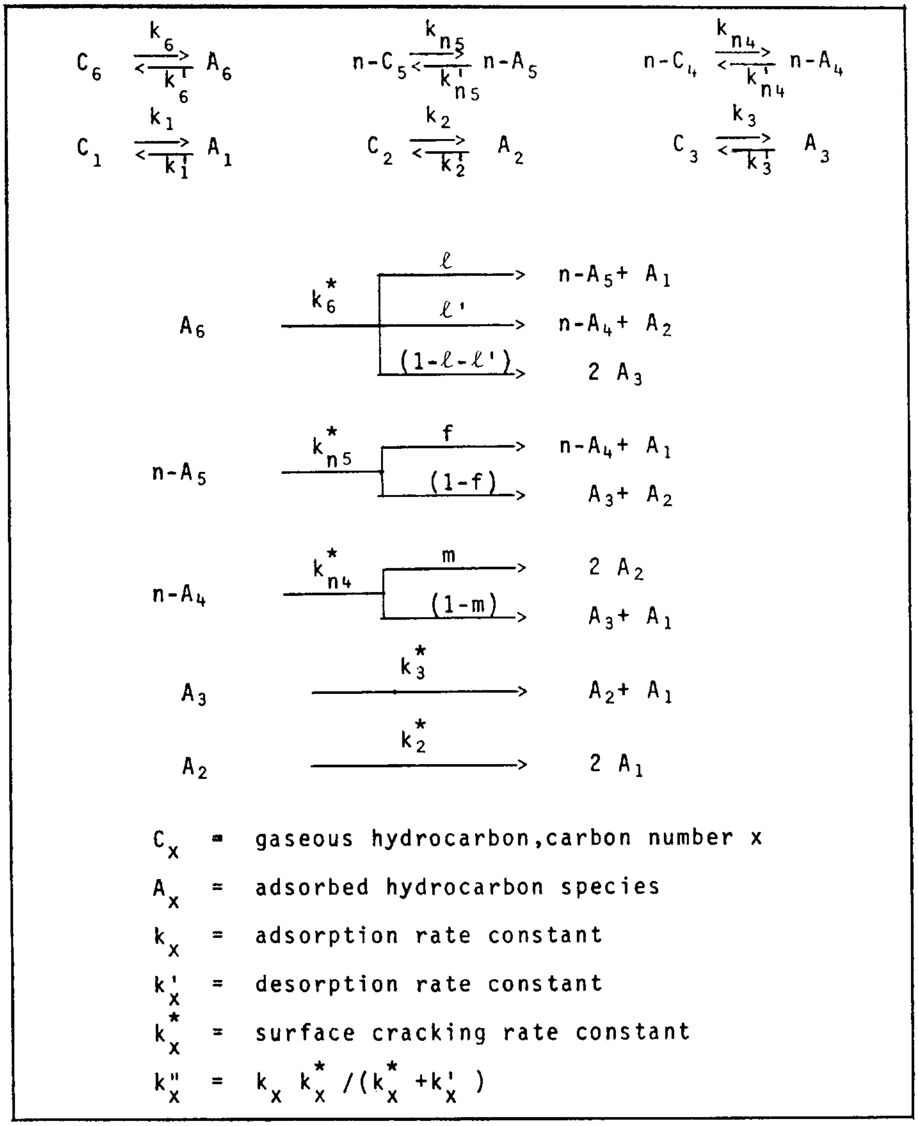

FIG. 4. Reaction network for hydrogenolysis of $n - C_6$.

is the main product on all catalysts, and the selectivity of neopentane does not change much with conversion. Isopentane and *n*-butane were detected only in trace amounts, if at all. The end carbon–carbon bond in the ethyl group is broken preferentially in all cases. Neopentane is very stable over all catalysts; the reaction almost stops at the quaternary carbon atom. Estimates of some parameters are tabulated in Table 1; in some cases groups of parameters could not be separated (*4*), but most of the parameter values seemed consistent with observations. The splitting constant for 2,2-dimethylbutane to neopentane is close to unity. The values of $k'_x/(k'_x + k^*_x)$ show that only on ruthenium is cracking of the adsorbed species slower than desorption, on nickel these rates are about equal, and on cobalt the

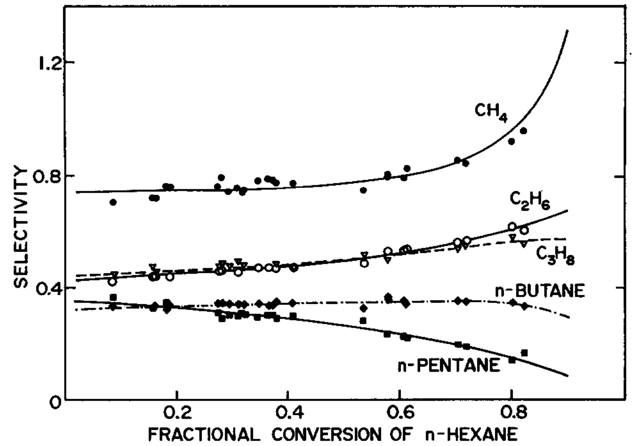

FIG. 5. Product distribution of hydrogenolysis of *n*-hexane over Ru/Al_2O_3 at 149°C and 1.2 atm.

desorption is slower than the cracking. Values of k''_x/k''_6 indicate that neopentane reacts slower than its products, as had been found previously (*1*).

Figures 5 and 6 give the product distributions from *n*-hexane on the ruthenium and the promoted nickel catalysts, respectively, and Table 2 shows the parameter values. The splitting constants could be separated only for ruthenium. The distributions indicate that the cracking is almost statistical on ruthenium; at low conversions all products are present in about equal amounts. The values of the splitting factors confirm this.

On the nickel catalyst successive demethylation occurs; the major initial product is *n*-pentane, and the next most abundant species are *n*-butane, propane, and ethane. The unpromoted nickel catalyst and the cobalt catalyst have similar patterns but with more extensive cracking than is shown in Fig. 6. The unpromoted nickel operated at a higher temperature than the promoted catalyst. Cobalt catalysts rather generally crack hydrocarbons

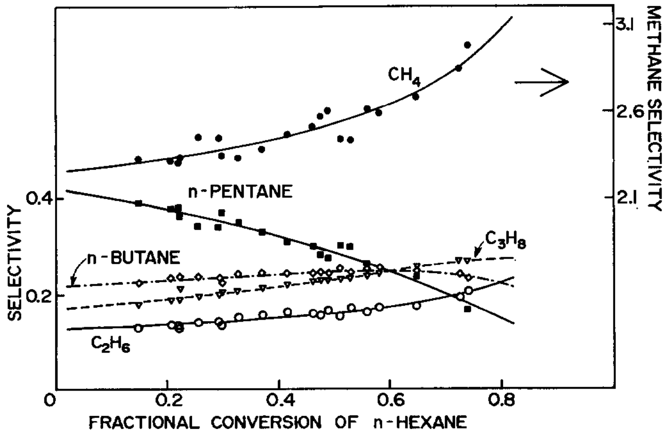

FIG. 6. Product distribution of hydrogenolysis of *n*-hexane over Ni–Mg/SiC at 255°C and 1.2 atm.

TABLE 2

Estimated Parameter Values from the Selectivity Equations for *n*-hexane

	Ru/Al_2O_3	Ni/SiC	Ni–Mg/SiC	Co–Mg/SiC
Temperature (°C)	149	285	255	219
$k'_{n5}l/(k'_{n5} + k^*_{n5})$	0.36	0.28	0.42	0.16
k''_{n5}/k''_6	0.34	0.63	0.46	0.39
$k'_{n4}f/(k'_{n4} + k^*_{n4})$	0.47	0.49	0.55	0.14
k''_{n4}/k''_6	0.06	0.32	0.16	0.14
$k'_3/(k'_3 + k^*_3)$	0.97	0.9	0.54	0.14
k''_3/k''_6	0.03	0.15	0.09	0.09
$k'_2/(k'_2 + k^*_2)$	0.96	0.71	0.33	0.21
k''_2/k''_6	0.03	0.01	0.01	0.04
l	0.35	—	—	—
l'	0.43	—	—	—
f	0.62	—	—	—

more extensively than nickel; the intermediates have been postulated to be more strongly adsorbed on cobalt (*4*, *13*). The values of $k'_x/(k'_x + k^*_x)$ again show that surface cracking is the rate-determining step on ruthenium only; on nickel cracking and desorption rates are about equal and on cobalt cracking is faster. Because on nickel cracking and desorption rates are about equal, appreciable amounts of *n*-butane and smaller products are formed at low conversions of *n*-hexane. The rates of hydrogenolysis, as shown by the k''_x/k''_6 values, decrease as the carbon number decreases; this effect is most pronounced on ruthenium but more gradual on nickel and cobalt.

In the sequence, ruthenium–nickel–cobalt–iron, the amount of smaller molecules in the product increases, as was observed with propane (*13*) and 2,3-dimethylbutane (*4*). This result may be explained in terms of the values of $k'_x/(k'_x + k^*_x)$. In the sequence above the strength of adsorption of intermediates increases, so that the adsorbed species are more likely to react further rather than to desorb. Tertiary carbon atoms were relatively stable on ruthenium, but not on cobalt and nickel (*4*). The present paper shows that quaternary carbon atoms are very stable on all the metals. The sequence of activity of the catalysts can be roughly estimated from the temperatures required in the experiments reported. The sequence of activity of the metals was the same for the reactions of *n*-hexane, 2,2-dimethylbutane, 2,3-dimethylbutane (*4*), and propane (*13*): Ru > Co > Ni > Fe. The promoted nickel catalyst always was more active than the unpromoted one. On ruthenium *n*-hexane was much more reactive than the other three feed molecules, which agrees with previous results (*1*) that normal hydrocarbons react faster than branched isomers of the same carbon number. On nickel (*8*) branched isomers are more reactive as long as they do not contain quaternary carbon atoms. Indeed, *n*-hexane was found to be less reactive than 2,3-dimethylbutane.

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