Dehydrogenation and Hydrogenolysis of *n*-Pentane Over Ru–Al$_2$O$_3$ Catalysts

Group VIII supported metals, particularly Ru, possess a very high activity in paraffin hydrogenolysis. Among the studies of particular interest are those by Sinfelt (1) about ethane; Kempling and Anderson (2) about C$_4$; Kikuchi et al. about C$_5$ (3, 4) and Kochloefl and Bažant (5) about C$_8$ and higher paraffins. All these studies were conducted at relatively low temperatures (80–400°C), particularly when supported Ru was employed, and in every case only paraffins were found in the reaction products. The aim of the present work was to study the product selectivity of the *n*-pentane reaction over highly diluted (from 0.86 to 0.10 wt%) Ru on γ-Al$_2$O$_3$ at relatively high temperatures (450–490°C) and atmospheric pressure in the presence of hydrogen. Under these conditions it was found that olefins constitute by far the major reaction products, particularly at lower contact times.

The catalysts were prepared from Ru acetate, obtained from RuCl$_3 \cdot x$H$_2$O as suggested by Legzdins et al. (6), and adsorbed on 40–60 mesh F-110 Alcoa γ-alumina, by impregnation (24 hr) from aqueous solution. Great care was given to purifying the Ru acetate from chloride ions, since they have been found (7) to decrease the activity of Ru–Al$_2$O$_3$ in the analogous *n*-butane reaction at the same temperatures and pressure. Reduction of Ru was performed with hydrogen at 330°C in a tubular furnace and its concentration in the catalyst was determined both spectrophotometrically (8) and by X-ray fluorescence spectrometry. The total surface area of the catalysts and the surface area of the metal alone were determined, respectively, by the BET (nitrogen) method and by CO adsorption (9), with the assumption of 1:1 ratio between adsorbed CO and surface centers,

due to the high dispersion of the metal. For the 0.30 wt% Ru catalyst the results were 182 and 26.9 m^2/g of catalyst, respectively. The *n*-pentane used was a pure grade reagent (99.74 mol%), whose impurity was essentially isopentane. Hydrogen was essentially pure ($\geqslant$99.99 mol%). The reaction was performed in a Pyrex glass flow tubular microreactor (100 mm in height and 8 mm i.d.) and before each run the catalyst was activated at 500°C with hydrogen for 2 hr to remove all coke deposition from the preceding run and the catalyst activity was checked. Feed rates of *n*-pentane ranged from 1.65 × 10^{-3} to 115.25 × 10^{-3} mol/hr; the (hydrogen/*n*-pentane) molar ratio in the feed (FR) was varied from 5:1 to 12:1. In such conditions neither external nor internal diffusion were found to condition the kinetic results. Details of the reactor effluent analysis have been published elsewhere (10). An initial catalyst deactivation, probably due to coke deposition, was observed. The best way to preserve the catalyst surface from such a fouling was to operate with a sufficiently high value of FR. In this respect it was found that only with FR $\geqslant$ 5:1 could perfect steady state conditions extending for at least 7 hr be reached, after a small initial activity decay. Kinetic data were collected at 450, 470 and 490°C and the results are reported in Figs. 1–3. A comparison among the conversions given by our catalyst (0.30 Ru wt%) and an equal amount of pure alumina at the same operating conditions is given in Table 1. The total conversion C is defined as the molar ratio of converted *n*-pentane over fed *n*-pentane, i.e.:

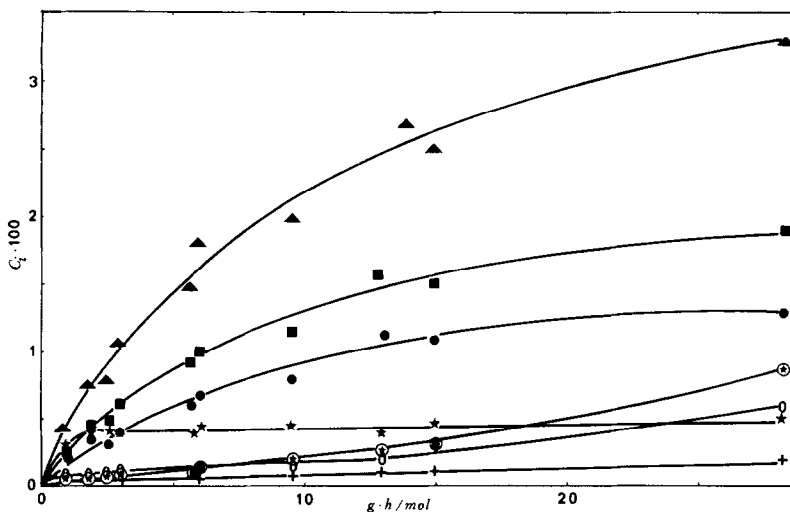$$C = \frac{(\Sigma N_j Y_j) - 5Y_{n-C_5}}{\Sigma N_j Y_j},$$

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FIG. 1. n-C_5 percentage molar conversion to the various reaction products vs time factor. Catalyst: 0.30 Ru wt% on γ-Al$_2$O$_3$; $P = 1$ atm; $T = 490°C$; (H$_2$/n-C$_5$) molar ratio in the feed: 5:1; (▲) t-2-pentene, (■) c-2-pentene, (●) 1-pentene, (★) pentadienes, (⊛) ($\neq$ n-C$_5$) paraffins, (○) methylbutenes, (+) light olefins.

Y_j is the molar fractions of the various hydrocarbons in the reactor effluent and N_j the number of carbon atoms in each hydrocarbon. The time factor is defined as $\tau = W/F$, W being the catalyst (Ru + alumina) weight (g) and F the n-pentane feed rate (mol/hr). The selectivity S_i is defined as percentage molar conversion of n-pentane

FIG. 2. Selectivities of reaction products vs time factor. (▲) t-2-pentene, (★) c-2-pentene, (●) 1-pentene, (○) pentadienes, (▲) iso-pentane, (+) methylbutenes. Reaction parameters as for Fig. 1.

to the i-th product over total conversion, i.e., $S_i = (C_i/C) \times 100$, where $C_i = N_i Y_i / \Sigma N_j Y_j$. As a consequence, the maximum possible selectivity S_i is given by: $[(N_i/5) \cdot (5/N_i)_{\text{integer}}] \times 100$.

It can be seen that, over such highly diluted Ru and at the reported temperatures, the most rapid reaction taking place is the n-pentane dehydrogenation to 1-pentene, while 2-pentenes form in a second stage by isomerization of 1-pentene (see Fig. 3). Analogous behavior was also observed for the reaction of n-butane and hydrogen over a similar catalyst at 490°C (11). The formation of pentadienes starts quite rapidly (Fig. 1). At first sight this could signify that pentadienes are primary products. However, from Fig. 3 it can be observed that the (1,4-pentadiene/1-pentene) ratio goes through a maximum and decreases when τ tends to zero. This fact, if considered together with the quite improbable simultaneous abstraction of four hydrogen atoms from the same C$_5$ chain, leads to the conclusion that dienes should form from 1-pentene. From Fig. 3 it can also be noted that 1,3-pentadienes should form from 1,4-pentadiene, probably by
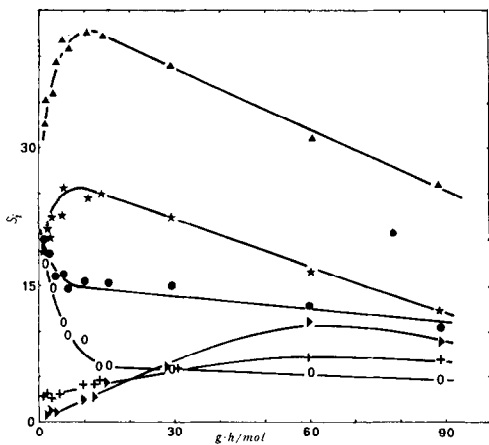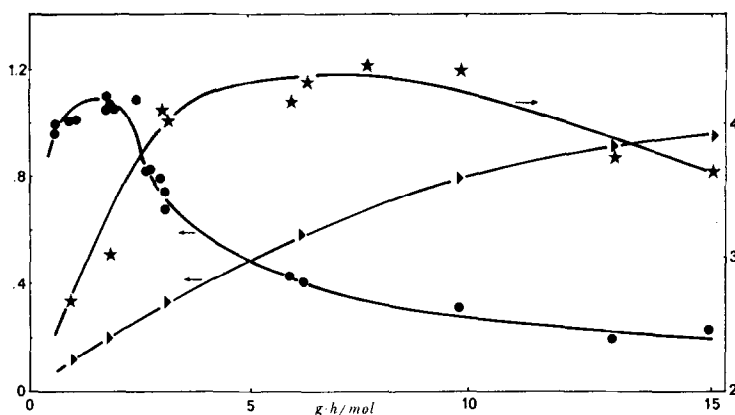
FIG. 3. Selectivity ratios vs time factor. (★) 2-pentenes/1-pentene, (▶) 1,3-pentadienes/1,4-pentadiene, (●) 1,4-pentadiene/1-pentene. Reaction parameters as for Fig. 1.

isomerization. The cracking of the C–C bond may be observed mainly at higher values of τ. As a consequence of the relative bond strengths [see, for example, Refs. (12, 13)] such a cracking probably takes place preferably on olefins rather than paraffins, and at different points along the chain, according to the different positions of the double bond. Skeletal isomeric C_5 olefins might form either by dehydrogenation of the isopentane, present as impurity in the fed n-pentane, or to skeletal isomerization of 1-pentene, via the intermediate formation of a carbonium ion (14, 15) on the acid centers of the catalyst. They could also form from n-pentane by catalytic isomerization action of the metal itself (4, 16–18), via the formation of a

TABLE 1

PRODUCT DISTRIBUTION ON 0.30 wt% Ru ON γ-Al$_2$O$_3$ (A) AND ON PURE γ-Al$_2$O$_3$ (B) AT 490°C[a]

| Product | τ(ghr/mol) | Conversion ($C_i \times 100$) | | | | | |
| | | 5.71 | | 9.52 | | 28.57 | |
		A	B	A	B	A	B
Methane		0.01	Tr[b]	0.03	0.01	0.09	0.04
Ethane		0.02	0.01	0.04	0.03	0.12	0.10
Ethylene		0.01	Tr	0.01	0.01	0.01	0.01
Propane		0.01	—	0.03	—	0.11	—
Propylene		0.04	0.02	0.04	0.04	0.12	0.15
n-Butane (+ isobutane)		Tr	—	0.07	—	0.09	—
Butenes		0.02	—	0.05	—	0.06	0.03
Isopentane		0.02	—	0.16	—	0.29	—
1-Pentene		0.57	—	0.66	—	1.29	—
t-2-Pentene		1.45	—	1.85	—	3.30	—
c-2-Pentene		0.90	—	1.00	—	1.89	—
Methylbutenes		0.07	—	0.16	—	0.52	—
Pentadienes		0.40	—	0.43	—	0.50	—
Total conversion		3.52	0.04	4.53	0.09	8.39	0.33

[a] Total pressure, 1 atm (H$_2$/n-pentane) molar ratio in the feed: 5:1.
[b] Tr = less than 0.01%.

1,3-diadsorbed partially ionic intermediate and successive dehydrogenation. Since no data are available in the literature on our range of experimental conditions, it would be useful to perform some experiments on pure Ru, in order to establish the relative importance of such three possible ways. The formation of isopentane in quantities higher than those present as impurity in the feed (Fig. 2) may be due either to the hydrogenation of isopentenes, formed as previously reported, or to the direct isomerization of n-pentane, as suggested also by others (4, 16–18). As to the influence of reactant partial pressure on product selectivity, some runs made at 470°C, with $\tau = 2.96$ (g hr/mol) and at n-pentane partial pressure in the feed ranging from 0.091 to 0.167 atm, showed that the selectivity ratios of the main olefins with respect to 1-pentene remain quite constant. However, due to the narrowness of the explored range of reactant partial pressure, such data are not sufficient for conclusions of general validity about the last mentioned effect. Finally, it was observed by some authors that, over Pt, the selectivities of skeletal isomerization (19) and hydrogenolysis (20) reactions of some C_5 paraffins are affected by the metal crystallite size. A dependence of the selectivity on Ru surface concentration was observed also in our case. At 490°C, FR = 5:1 and $\tau = 3.1$ (g hr/mol), for catalysts of 0.86, 0.52, 0.33, 0.22 and 0.10 Ru wt%, heat treated all together in the same furnace, the following values for the selectivity S of the dehydrogenation reaction were obtained, respectively: 62.9, 66.7, 71.7, 83.3 and 96.3. According to the Kobozev theory (21), for catalyst prepared at equal conditions of heat treatment, the number of metallic atoms present in each crystallite grows with the surface concentration of the metal. Our results seem then to indicate that the dehydrogenation is preferentially promoted by the smaller crystallites.

ACKNOWLEDGMENTS

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