Chemistry

Corresponding Member of the Academy of Sciences of the USSR N. I. Shuikin, E. A. Timofeeva

1958

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR N. I. Shuikin, E. A. Timofeeva
and T. P. Dobrynina

DEHYDROGENATION OF *n*-PENTANE AND ISOPENTANE IN THE PRESENCE OF AN ALUMINA-CHROMIA-POTASSIUM CATALYST

We have previously shown that an alumina–chromia–potassium catalyst of composition
$Al_2O_3 + Cr_2O_2 + K_2O$ (90.7 : 5.6 : 3.7 mol. %) conducts well the dehydrogenation reaction of *n*-pentane and isopentane ([1–3]).

The use of mixed catalysts of this type for the dehydrogenation of lower alkanes is indicated in works by earlier authors ([4,5]). However, in a series of experiments we found: a) the most advantageous quantitative ratio of the catalyst components, and b) the conditions for its preliminary activation.

First the catalyst was heated in a stream of air to the required temperature. After displacement of the air by nitrogen, the catalyst was treated with hydrogen for 1.5 hr. Preliminary treatment of the catalyst with pentane or isopentane has the same activating effect. The amount of hydrocarbon required for this purpose depends on the experimental conditions, temperature, and space velocity. Activation of the catalyst is completed when, during passage of the hydrocarbon, the evolution of CO_2 and CO ceases. Regeneration of the spent catalyst was carried out by heating in a stream of air at 680–700°, as a rule for 5 hr. The reproducibility of the catalyst is good. Its activity, with periodic regenerations, remains at a high level for more than 200 hr.

In the present work, the effect of temperature, space velocity, and duration of the working cycles on the dehydrogenating ability of the alumina–chromia–potassium catalyst was studied. In all experiments the amount of catalyst was 30 ml, and the internal diameter of the catalytic tube was 18 mm. The catalyst grain size was approximately $3 \times 3 \times 3$ mm. After each regeneration, before the experiments, the catalyst was treated with hydrogen for 1.5 hr. The feed of hydro-

Table 1

Product balance of the reaction as a function of temperature

(in molar percent of the hydrocarbon passed)

Temp., °C	Unchanged hydrocarbon	Alkenes	Isoprene	Amount of hydrocarbon converted to "coke"	Amount of hydrocarbon converted to gas	Balance
n-Pentane	*n*-Pentane	*n*-Pentane	*n*-Pentane	*n*-Pentane	*n*-Pentane	*n*-Pentane
500	61	32	–	4	2	99
527	48	38	–	10	6	102
550	36	42	–	13	10	101
Isopentane	Isopentane	Isopentane	Isopentane	Isopentane	Isopentane	Isopentane
500	55	39	2	2	2	100
527	42	46	2	6	3	99
550	32	47	5	9	6	99

hydrocarbons was carried out automatically from a syringe burette. The temperature was measured with a thermocouple placed in the catalyst bed. The receiver was cooled with dry carbon dioxide. In each experiment 10 ml of hydrocarbon was taken. The olefin content in the catalyzates was determined by the bromometric method (6, 7), and the isoprene content by reaction with maleic anhydride by the gravimetric method.

Table 2

Dependence of the yields of pentenes and isopentenes on space velocity

Temp., °C	Space velocity, h^{-1}	Yield, mol. % based on hydrocarbon passed: pentenes	Yield, mol. % based on hydrocarbon passed: isopentenes
500	0.5	31	38
500	0.8	25	33
500	1.1	19	27
527	0.3	38	–
527	0.5	39	45
527	0.8	32	44
527	1.1	30	42
550	0.3	40	44
550	0.5	41	46

Figure 1. Dependence of isopentene yields on the duration of working cycles at different temperatures

Figure 1: Figure 1. Dependence of isopentene yields on the duration of working cycles at different temperatures

Temp., °C	Space velocity, h^{-1}	Yield, mol. % based on hydrocarbon passed: pentenes	Yield, mol. % based on hydrocarbon passed: isopentenes
550	0.8	–	45
550	1.1	39	45
575	0.3	–	35
575	0.5	–	37
575	1.1	–	37

Effect of temperature. The experiments were carried out at 450-575° with a space velocity of 0.5 h^{-1}. The catalyst conducted the reaction for one hour. The catalyzate and gas were collected during the last 43-44 min. Table 1 gives the results of experiments carried out at temperatures ensuring attainment of equilibrium yields of pentenes and isopentenes.

Effect of space velocity. The results obtained, given in Table 2, showed that at space velocities within the range from 0.3 to 1.1 h^{-1}, the yields of pentenes and isopentenes depend on temperature, and the lower it is, the more pronounced this effect.

Thus, changing the space velocity from 0.5 to 1.1 h^{-1} at 500° leads to a decrease in the yields of isopentenes from 38 to 27%, and for pentenes from 31 to 19%. The same change in space velocity at 527° leads to a decrease in the yields of isopentenes from 45 to 42%, and for pentenes from 39 to 30%. An increase in the space velocity at 550 and 575° within the range from 0.3 to 1.1 h^{-1} practically no longer affects the yields of pentenes and isopentenes. The yields of isoprene depend almost not at all on space velocity and range from 1-2% at 500° to 5-6% at 550°.

Effect of the duration of working cycles without regeneration of the catalyst. In this series of experiments, the reaction of dehydrogenation of isopentane at 500, 527, and 550° was studied at a space velocity of 1.1 h^{-1}. At each of these temperatures 28 experiments were carried out without regeneration of the catalyst. It turned out that the higher the temperature, the faster the catalyst activity decreases with time, as is seen from Fig. 1. The content of isopentenes in the catalyzates obtained over a working cycle of 18 min increases with increasing temperature from 25 wt. % to

Fig. 1. Dependence of isopentene yields on the duration of working cycles at different temperatures

the isopentane passed through, from 45 wt. % at 500° to 55° [sic] at 550°. However, the yields of isopentenes over a working cycle of 3 hr 18 min at 527° are somewhat higher than at 550°, namely 39.6 against 37.1%. The yields of isopentenes in the catalyzates obtained over a working cycle of 8 hr 24 min at 527° (30%) are also higher than at 550° (26%). Thus, at 550° it is advisable to carry out the reaction in short cycles, not more than 1 hour, at high space velocities. This requires frequent regeneration of the catalyst. At 527°, dehydrogenation of isopentane can be carried out in longer cycles, of more than 3 hours. Carrying out the reaction at 500° is apparently less advisable, owing to the comparatively low yields of isopentenes in the initial period. However, at this temperature the reaction can be conducted in longer working cycles.

As an example, we cite the principal indices of the process obtained at 527° and a space velocity of 1.1 hr^{-1}, with a working-cycle duration of 3 hr 18 min. Under these conditions a catalyzate is obtained containing 44 wt. % isopentenes and 2.6 wt. % isoprene. Calculated on the isopentane passed through, this amounts to 40 and 2%, respectively, and on the decomposed isopentane, 78 and 5%. The productivity of the catalyst in the production of isopentenes is 274 g/l · hr, and for isoprene, 16 g/l · hr.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
4 I 1958

CITED LITERATURE

1. N. I. Shuikin, T. P. Dobrynina, E. A. Timofeeva, Yu. P. Egorov, *Izv. AN SSSR, OKhN*, 1955, 952.

2. N. I. Chouikine, T. P. Dobrynina, E. A. Timofeeva, *Rev. Inst. Franç. du Pétrole*, **11**, 1185 (1956).

3. N. I. Shuikin, E. A. Timofeeva, V. M. Kleimenova, *Izv. AN SSSR, OKhN*, 1957, 875.

4. J. Burgin, H. Groll, R. M. Roberts, *Nat. Petrol News*, **30**, R-432 (1938).

5. A. V. Grosse, V. N. Ipatieff, *Ind. and Eng. Chem.*, **32**, 268 (1940).

6. G. D. Gal' pern, *Tr. Inst. nefti AN SSSR*, **4** (1954).

7. E. A. Timofeeva, V. M. Kleimenova, T. P. Dobrynina, *Izv. AN SSSR, OKhN*, 1957, 122.

Note: Figure translations are in progress. See original paper for figures.