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Abstract

Full Text

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EFFECT OF THE STRUCTURE OF ALKYLAROMATIC HYDROCARBONS ON THE KINETICS OF THEIR DEHYDROGENATION

In previous works, the rate of dehydrogenation of alkylbenzenes was studied as a function of the structure of the alkyl radicals. In the present communication, the effect of replacing hydrogen in the ring by a CH_3 group on the rate of dehydrogenation of an alkyl radical was investigated. For this purpose the kinetics of dehydrogenation of the following hydrocarbons was studied: *m*-isopropyltoluene, symmetrical isopropylxylene, and symmetrical ethylxylene. The experiments were carried out in a flow system on the same oxide catalyst, with dilution of the hydrocarbons by steam in a ratio of 1 : 2–3 by weight. The apparatus and experimental procedure were the same as before ([1,2]).

The catalysts were analyzed by gas–liquid chromatography. Dinonyl sebacate deposited on fireclay brick served as the liquid phase. The contact gas was analyzed, as before, on an Orsa–Eger apparatus ([2]). The catalyst charge was 14.6 ml. After each experiment the catalyst was purged with a steam–air mixture and with air at the reaction temperature. The activity of the catalyst was monitored and remained constant during the experiments. In the experiments the catalyzate obtained was colorless and only at high temperatures became yellowish. According to combination-scattering spectra, the isopropyltoluene subjected to dehydrogenation consisted mainly of the *m*-isomer (90%); ethylxylene consisted of 1,3-dimethyl-5-ethylbenzene (85%) and 1,2-dimethyl-4-ethylbenzene (15%).

Table 1

Physical constants of the starting hydrocarbons *

Name of hydrocarbon	Starting hydrocarbon: b.p., °C	Starting hydrocarbon: d_4^{20}	Starting hydrocarbon: n_D^{20}	Literature data ([3]): b.p., °C	Literature data ([3]): d_4^{20}	Literature data ([3]): n_D^{20}
m-Isopropyltoluene	175–176	0.8610	1.4920	*o* 175.1*m* 175.6*n* 176.9	0.87520.8614[illegible]	[illegible]1.49221.4903
Symmetrical isopropylxylene	192–193	0.8600	1.4960	193	0.8620	1.4956

Name of hydrocarbon	Starting hydrocarbon: b.p., °C	Starting hydrocarbon: d_4^{20}	Starting hydrocarbon: n_D^{20}	Literature data (3): b.p., °C	Literature data (3): d_4^{20}	Literature data (3): n_D^{20}
Symmetrical ethylxylene	183–184	0.8640	1.4990	184.3	0.8644	1.4981

* Isopropyltoluene and isopropylxylene were kindly provided to us by staff members of the Institute of Petrochemical Processes, for which we express our gratitude.

Before the experiment, the starting hydrocarbons were distilled under vacuum on a column of 30 theoretical plates. The kinetics of hydrocarbon dehydrogenation was studied in the temperature range 490–550° and at a feed rate of 800–1000 ml per 1 l of catalyst per hour. The contact gas was evolved at a constant rate, uniformly. The evolved gas was measured every 3 min. As analysis showed, the exit gas consists mainly of hydrogen and a small amount of carbon dioxide (from 3.5 to 9%); no unsaturated hydrocarbons were detected in the gas. A close agreement was observed between the amounts of hydrogen and vinyl compounds formed. The data obtained are given in Table 2.

Table 2

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropylxylene. Feed rate 1000 ml/l· h	491	1.4990	13.0	12.0	91.0	13.3	1.2	–	98.8
Catalytic dehydrogenation of isopropylxylene. Feed rate 1000 ml/l· h	508	1.5008	18.7	17.0	91.0	19.0	2.8	–	97.7

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropylxylene. Feed rate 1000 ml/l• h	520	1.5030	26.1	23.0	91.0	24.5	5.0	–	95.0
Catalytic dehydrogenation of isopropylxylene. Feed rate 1000 ml/l• h	528	1.5048	31.7	29.0	91.0	31.1	5.2	–	94.5

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropylxylene. Feed rate 1000 ml/l•h	551	1.5125	54.5	50.0	91.0	54.0	5.8	0.1	93.8
Catalytic dehydrogenation of isopropylxylene. Feed rate 1000 ml/l•h	596	1.5150	90.0	82.6	91.0	89.0	7.0	1.0	91.0

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropylxylene. Feed rate 820 ml/l·h	528	1.5050	32.6	24.7	76.0	33.0	5.6	0.1	94.0
Catalytic dehydrogenation of isopropylxylene. Feed rate 820 ml/l·h	550	1.5120	52.0	40.5	76.0	53.0	6.4	0.2	93.2

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Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropylxylene. Feed rate 500 ml/l•h	528	1.5090	38.0	16.0	48.0	37.5	6.4	–	93.4
Catalytic dehydrogenation of isopropylxylene. Feed rate 500 ml/l•h	552	1.5140	63.0	32.0	–	65.4	7.0	–	93.0

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropylxylene. Feed rate 500 ml/l• h	500	1.5018	–	21.0	–	–	–	–	–
Catalytic dehydrogenation of isopropyl-toluene. Feed rate 1000 ml/l• h	516	1.4992	17.7	17.4	100	17.4	4.5	–	95.0

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Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropyl-l-toluene. Feed rate 1000 ml/l·h	518	1.4995	18.5	17.7	100	17.7	4.4	–	95.6
Catalytic dehydrogenation of isopropyl-l-toluene. Feed rate 1000 ml/l·h	528	1.5022	25.0	24.5	100	24.5	5.2	–	94.6

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropyl-l-toluene. Feed rate 1000 ml/l· h	538	1.5055	33.5	34.0	100	34.0	5.4	–	94.6
Catalytic dehydrogenation of isopropyl-l-toluene. Feed rate 1000 ml/l· h	557	1.5130	53.0	52.9	100	52.9	6.0	–	93.8

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of isopropyl-l-toluene. Feed rate 1000 ml/l· h	570	1.5182	65.5	66.3	100	66.3	6.0	–	93.8
Catalytic dehydrogenation of isopropyl-l-toluene. Feed rate 1000 ml/l· h	581	1.5222	75.0	73.5	100	73.5	5.6	–	94.0

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of symmetrical ethylxylene. Feed rate 1000 ml/l·h	519	1.5050	14.2	15.5	100.2	14.5	2.8	–	96.8
Catalytic dehydrogenation of symmetrical ethylxylene. Feed rate 1000 ml/l·h	525	1.5060	17.0	17.5	100.2	17.5	5.0	–	94.5

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Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of symmetrical ethylxylene. Feed rate 1000 ml/l·h	545	1.5095	27.0	26.5	100.2	26.5	9.0	–	91.0
Catalytic dehydrogenation of symmetrical ethylxylene. Feed rate 1000 ml/l·h	530	1.5078	19.5	19.0	100.2	19.0	9.8	–	90.0

Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of symmetrical ethylxylene. Feed rate 1000 ml/l·h	552	1.5100	31.5	–	–	–	–	–	–
Catalytic dehydrogenation of symmetrical ethylxylene. Feed rate 1000 ml/l·h	560	1.5120	37.0	37.5	100.2	37.5	11.2	–	87.5

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Process / feed rate	t, °C	n_D^{20} of catalyst	Formed, wt. %	Hydrogen evolved (N.T.P.) in 3 min, ml	Theor. amount of H_2 in 3 min, ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %: CO_2	Gas analysis, vol. %: C_nH_{2n}	Gas analysis, vol. %: H_2
Catalytic dehydrogenation of symmetrical ethylxylene. Feed rate 1000 ml/l·h	580	1.5135	48.0	48.4	100.2	48.4	10.4	–	86.9 + unsat. 1.8%

The experimental data are well described by the equation for monomolecular catalytic reactions in a flow system (^{4}):

$$\frac{dx}{dt} = k\frac{[A_1]}{[A_1] + Z_2[A_2] + Z_3[A_3]}. \tag{1}$$

The relative adsorption coefficients Z_2 and Z_3 of the reaction products entering into the equation were determined from experiments measuring the rates of dehydrogenation of the initial hydrocarbons with reaction products. Their numerical values were calculated by the formula (^{5}):

$$Z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1}. \tag{2}$$

It was found that the relative adsorption coefficient of hydrogen is equal to 0.7 and does not change with temperature. Isopropenyltoluene and isopropenylxylene have close values of the relative adsorption coefficients, varying from 3.8 at 520° to 0.9 at 560°. From Fig. 1 it is evident that between Z_2 and the reciprocal absolute temperature there is a logarithmic dependence. The points lie well on straight lines. The numerical values of the relative adsorption coefficients are given in Table 3.

[Fig. 1 and Fig. 2 graphs]

Fig. 1. Logarithmic relationship between the relative adsorption coefficients and the reciprocal absolute temperature: *a*—isopropenyltoluene, symmetrical isopropenylxylene, α-methylstyrene; *b*—symmetrical vinylxylene

Fig. 2. Logarithmic relationship between k_C and the reciprocal temperature: *a*—symmetrical isopropylxylene, *b*—*m*-isopropyltoluene, *v*—symmetrical ethylxylene

Table 3

Relative adsorption coefficients and thermodynamic functions of adsorption displacement

Hydrocarbon	t, °C	Z_2	$-\Delta F$, cal	$-\Delta H$, kcal/mol	$-\Delta S$, cal/deg · mol
Isopropenyltoluene	520	3.8	2102	–	74.3
Isopropenyltoluene	530	2.4	–	–	–
Isopropenyltoluene	540	1.5	654.2	61.1	74.2
Isopropenyltoluene	550	0.9	–	–	74.2
Isopropenylxylene	520	3.8	2102	–	74.3
Isopropenylxylene	530	2.4	–	–	–
Isopropenylxylene	540	1.5	654.2	61.1	–
Isopropenylxylene	550	0.9	–	–	–
Vinylxylene	520	5.1	2533	–	41.2
Vinylxylene	540	2.7	1651	35.2	41.2
Vinylxylene	550	2.3	–	–	–
Vinylxylene	560	1.6	960.5	–	41.1

The rate constants for dehydrogenation of the hydrocarbons studied, calculated from the experimental data by equation (1), are given in Table 4. It is evident from it that the introduction of CH_3 groups into the benzene ring increases the rate of dehydrogenation of alkyl radicals. Thus, the rate of dehydrogenation of *m*-isopropyltoluene is greater than that of isopropylbenzene. Introduction of a second methyl group into the ring promotes an increase in the dehydrogenation rate, and symmetrical isopropylxylene is dehydrogenated at an even higher rate. The same conclusion can be drawn when comparing the con-

Table 4

Rate constants and activation energies

Hydrocarbon	510	520	530	540	550	ε, kcal/mol	$\lg k_0$	$\varepsilon/\lg k_0$
	Rate constants, g/ml · 3 min; temperature, °C							
Isopropylxylene	1.27	1.83	2.21	2.97	–	26.3	5.5	4.78
Isopropyltoluene	0.76	1.26	1.62	2.1	–	32.7	7.1	4.6
Ethylxylene	–	0.91	1.18	1.49	1.94	32.2	6.85	4.72

···rate constants of dehydrogenation of the ethyl radical upon replacement of hydrogen in the ring by methyl groups. Figure 2 shows the logarithmic dependence of the rate constants on the reciprocal absolute temperature. The points fall on straight lines; the Arrhenius equation is obeyed. The activation energies calculated from the rate constants are equal to 32.7 kcal/mol for isopropyltoluene, 26.3 kcal/mol for isopropylxylene, and 32.2 kcal/mol for ethylxylene. It should be noted that dehydrogenation of these hydrocarbons under the conditions studied proceeds fairly smoothly, without noticeable formation of side decomposition products. The composition of the catalysts obtained is shown in the chromatograms in Fig. 3.

(Figure: Fig. 3. Chromatographic analysis of catalysts obtained in the dehydrogenation of symmetrical ethylxylene (a), *m*-isopropyltoluene (b), and symmetrical isopropylxylene (c))

Fig. 3. Chromatographic analysis of catalysts obtained in the dehydrogenation of symmetrical ethylxylene (*a*), *m*-isopropyltoluene (*b*), and symmetrical isopropylxylene (*c*).

From the values found for the relative adsorption coefficients, using known formulas, the changes in the free energy ΔF, heat content ΔH, and entropy ΔS of adsorption displacement were calculated (Table 3).

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