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GAS CHROMATOGRAPHIC DETERMINATION OF EFFECTIVE DIFFUSIVITIES AND HEATS OF ADSORPTION OF C₅-C₈ HYDROCARBONS ON A COMMERCIAL PLATINUM-ALUMINA REFORMING CATALYST

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SUMMARY

The effective diffusivities of hydrocarbons (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, 2,2-dimethylbutane, 2,3-dimethylbutane, cyclopentane, methylcyclopentane, cyclohexane, benzene, toluene and xylenes) in commercial platinum-alumina reforming catalyst were measured using the chromatographic pulse-broadening unsteady-state technique in the temperature range 185-380°. The heats of adsorption of these hydrocarbons were estimated from the chromatographic data. The activation energy of pore diffusion and the heat of adsorption for the various hydrocarbons varied from 1.1 to 3.4 and from 5.2 to 18.5 kcal/mole, respectively.

INTRODUCTION

Early studies of diffusion in porous catalysts were mostly based on the well-known steady-state method, first developed by Wicke and Kallenbach¹ and later modified by Weisz². The use of this method is limited to a single catalyst pellet having a narrow pore size distribution and a continuous pore structure³. The other methods used were based on transient phenomena, such as measurement of the rate of sorption⁴⁻⁸ at constant volume, measurement of the rate of desorption of an adsorbed gas in a closed system at constant volume^{7,8} or at constant pressure⁹, release of adsorbed gas in a flow of inert gas¹⁰, and measurement of a transient flow of pure gas through a porous plug (time lag method)^{11,12}. These unsteady-state methods overcame most of the limitations of the steady-state method, but their use was restricted mostly to studying the diffusion of gases in molecular sieve solids (e.g., carbon and crystalline aluminosilicates) owing to certain practical difficulties. Recently, a number of gas chromatographic techniques, based on the pulse-broadening and moment and Fourier analysis of chromatographic peaks, have been applied to measuring the diffusivity of gases in porous solids. The methods have been reviewed by Choudhary¹³. These

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methods have the inherent advantage that measurements are made on a large and representative sample of the solid catalyst at temperatures that approach those used in commercial processes. Further, as it is an unsteady-state technique, the effective diffusivity would be expected to reflect the presence of small and "dead-end" pores as well as the continuous pore structure.

The use of gas chromatography in the measurement of the heats of adsorption of gases and vapours of volatile compounds by the eluted pulse and frontal analysis technique is well established. A critical review is available¹⁴.

The present investigation concerned the determination of the effective diffusivities and heats of adsorption of C_5 – C_8 *n*-alkanes, isoalkanes (2,2-dimethylbutane and 2,3-dimethylbutane), cycloparaffins (cyclopentane, methylcyclopentane and cyclohexane) and C_6 – C_8 aromatic hydrocarbons on the Engelhard RD-150 commercial reforming catalyst (platinum–alumina, containing 0.6% (w/w) of platinum) at 185–380° using the gas chromatographic pulse technique.

EXPERIMENTAL

A chromatographic column with a bed length of 100 cm was prepared by packing 16.8 g of Engelhard RD-150 catalyst (heated in air at 500° for 4 h before use) in the form of extrudates of 0.149-cm diameter (diameter based on the average size of extrudates calculated for spheres of equal volume) into 1/4-in. copper tubing.

The pore volume of the catalyst, p_v , was measured¹⁵ by the liquid penetration method using various solvents such as benzene, *n*-hexane, cyclohexane and carbon tetrachloride; the values of p_v obtained agreed within 5%. The particle density, ρ_p , was determined by the mercury displacement method¹⁵. The porosity of the extrudate and the void and solid fractions of the packed column were estimated from the knowledge of p_v , ρ_p and the density of the catalyst bed. The dispersion of platinum on the catalyst was measured by the gas chromatographic pulse technique¹⁶ based on the titration of chemisorbed oxygen with hydrogen. The data on the physical properties of the catalyst and packed column are summarized in Table I.

The aromatic hydrocarbons were obtained from BDH (Poole, Great Britain) (AnalaR grade), while the other hydrocarbons were Phillips (Bartlesville, Okla.,

TABLE I
PHYSICAL PROPERTIES OF CATALYST AND PACKED COLUMN

Property	Value
Catalyst	Engelhard RD-150 commercial reforming Pt–Al ₂ O ₃ [0.6% w/w, Pt]
Dispersion of Pt in the catalyst	43 ± 2%
Particle diameter (d_p)	0.149 cm
Particle density (ρ_p)	1.36 ± 0.01 g/cm ³
Particle pore volume (p_v)	0.360 = 0.018 cm ³ /g
Particle porosity (ϵ)	0.49
Density of catalyst bed (ρ_B)	0.771 g/cm ³
Void fraction of packed column (F_1)	0.434
Solid fraction of packed column (F_2)	0.566
Internal cross-sectional area of column	0.218 cm ²
Length of packed column (L)	100 cm

TABLE II
RESULTS OF DIFFUSION OF HYDROCARBONS IN PLATINUM-ALUMINA

Hydrocarbon	Temperature (°C)	C (sec)	K	$D_e \times 10^3$ (cm ² /sec)
<i>n</i> -Pentane	195	0.187	0.139	11.0
	250	0.153	0.264	11.4
	280	0.115	0.307	14.5
	345	0.089	0.452	15.6
<i>n</i> -Hexane	185	0.150	0.060	15.5
	195	0.147	0.069	15.8
	265	0.102	0.180	19.1
	345	0.067	0.420	21.5
<i>n</i> -Heptane	195	0.157	0.031	15.3
	250	0.130	0.080	17.3
	295	0.092	0.210	20.3
<i>n</i> -Octane	195	0.133	0.014	18.5
2,2-Dimethylbutane	200	0.141	0.078	16.0
	250	0.110	0.157	18.2
	300	0.084	0.262	20.8
	345	0.068	0.355	22.9
2,3-Dimethylbutane	200	0.136	0.071	16.7
	250	0.102	0.148	19.8
	300	0.077	0.253	22.9
	345	0.061	0.336	26.2
Cyclopentane	200	0.147	0.139	14.0
	250	0.113	0.246	15.8
	280	0.090	0.313	18.6
	345	0.066	0.438	21.4
Methylcyclopentane	200	0.170	0.074	13.3
	250	0.142	0.156	14.2
	280	0.114	0.217	16.3
	345	0.078	0.398	18.9
Cyclohexane	200	0.141	0.071	16.0
	250	0.113	0.149	18.6
Benzene	250	0.132	0.038	18.1
	295	0.086	0.108	24.0
	345	0.075	0.169	26.3
	380	0.061	0.188	31.5
Toluene	250	0.130	0.015	19.0
	300	0.100	0.051	23.3
	345	0.079	0.117	26.8
	380	0.063	0.144	32.5
<i>o</i> -Xylene	250	0.118	0.005	21.1
	300	0.097	0.022	23.2
	345	0.071	0.072	31.7
<i>m</i> -Xylene	250	0.117	0.006	21.4
	300	0.088	0.027	27.5
	345	0.071	0.086	31.5
<i>p</i> -Xylene	250	0.132	0.008	18.9
	300	0.098	0.031	24.5
	345	0.071	0.093	31.0

U.S.A.) Research Grade. Nitrogen was used as the carrier gas and was passed over copper heated at 400° and molecular sieve in order to remove trace amounts of oxygen and moisture.

The chromatographic data were obtained by using a Perkin-Elmer 900 chromatograph by injecting 0.1–0.5 μ l of hydrocarbon and measuring the retention time and the height equivalent to a theoretical plate (HETP) of the effluent pulse as a function of carrier gas velocity at different temperatures. The carrier gas velocity was varied from 5 to 50 cm/sec and the temperature from 185 to 380°.

RESULTS AND DISCUSSION

The effective diffusion coefficients of the hydrocarbons in the catalyst are obtained from the C term in the Van Deemter equation¹⁷ using the relationship^{18,19}

$$C = \frac{d_p^2}{\sqrt{2\pi^2}} \cdot \frac{F_1}{F_2} \cdot \frac{1}{\varepsilon D_e} \cdot \frac{1}{(1 + K F_1/F_2)^2} \quad (1)$$

where K is the distribution coefficient related²⁰ to the chromatographic parameters as follows:

$$K = 1/[\varepsilon + (t_m - t_0) v F_1/F_2 L], \quad (2)$$

The values of C are evaluated from the slopes of the linear plots of HETP *versus* interstitial velocity at high carrier gas flow-rates. The results of diffusion of the hydrocarbons in the catalyst at different temperatures are given in Table II. The apparent activation energies, ΔE , for diffusion are presented in Table III.

The heats of adsorption, ΔH , were estimated from the slopes of the linear plots of $\log V_R^0$ *versus* $1/T_c$ (slope = $-\Delta H/2.303 R$) and are included in Table III. The values of ΔH obtained are averaged over the temperature range as the heat of adsorption may change with temperature. A correlation between ΔH and the carbon number in the paraffinic and aromatic hydrocarbons is shown in Fig. 1. The values of

TABLE III
APPARENT ENERGY OF ACTIVATION FOR DIFFUSION AND HEATS OF ADSORPTION

<i>Hydrocarbon</i>	ΔE (kcal/mole)	ΔH (kcal/mole)
<i>n</i> -Pentane	1.14	5.2
<i>n</i> -Hexane	1.10	7.7
<i>n</i> -Heptane	1.50	10.8
2,2-Dimethylbutane	1.43	6.8
2,3-Dimethylbutane	1.80	6.8
Cyclopentane	1.72	5.4
Methylcyclopentane	1.56	7.7
Benzene	2.89	11.2
Toluene	2.91	14.4
<i>o</i> -Xylene	2.95	18.5
<i>m</i> -Xylene	2.68	18.0
<i>p</i> -Xylene	3.43	17.5

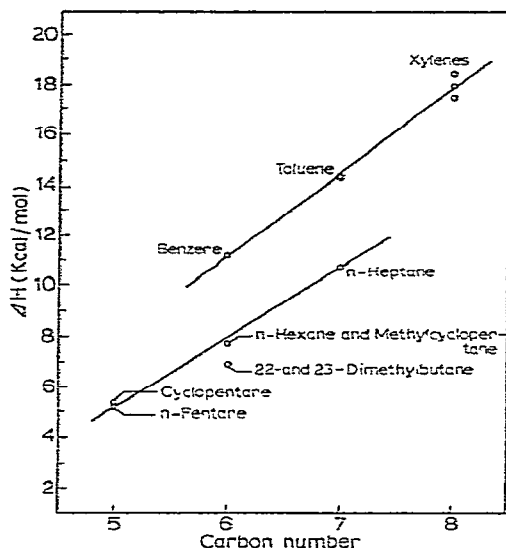


Fig. 1. Dependence of heat of adsorption on carbon number.

ΔH for the aromatic hydrocarbons are much higher than those of paraffinic hydrocarbons.

It can be seen from Table II that the distribution coefficient, K , decreases with the number of carbon atoms in the hydrocarbon and increases with temperature. The K values for the aromatic hydrocarbons are much lower and show a stronger dependence on temperature compared with those for the paraffinic hydrocarbons. This increased adsorption of the aromatic hydrocarbons is accompanied by higher heats of adsorption and activation energies for diffusion (Table III).

The diffusivity data could not be collected for some of the hydrocarbons at temperatures higher than those indicated in Table II because of the difficulties in the analysis of effluent pulse, either due to the peak asymmetry or because of the interference of the reactant (*i.e.*, the hydrocarbon under study) peak with that of product of the catalytic reaction. With cyclohexane, two distinct peaks were observed at temperatures above 280° , one for cyclohexane and the other for benzene, which is the product of the dehydrogenation of cyclohexane on platinum-alumina.

CONCLUSION

In a catalytic process, the total mass flux in the catalyst is due to the simultaneous occurrence of bulk and/or Knudsen diffusion in the pores, adsorption on the pore walls and surface diffusion. The relationship between the surface adsorption and diffusion is very complex and not completely established. The surface diffusion of a particular compound may be affected by the presence of other species in the adsorbed layer²¹. Hence, it is not possible to obtain a reliable value of the effective diffusivity of a catalyst for a particular compound by its prediction either from the available pore models²² or from the diffusivity of inert or other gases in the catalyst. In activated diffusion, even though the diffusion coefficient for the rare gases in well

defined pore systems can be calculated²³ theoretically, it is not possible to evaluate D_e for the species involved in the actual catalytic process. Hence, it is desirable to determine D_e , which is required in the design of catalytic reactors and for predicting the effects of intraparticle mass transfer on the reaction rate, experimentally under actual reaction conditions or even during catalysis.

The gas chromatographic pulse-broadening technique appears to be superior to the other unsteady-state techniques in that even a very small degree of adsorption, which is difficult to measure by the other techniques, can be taken into account²⁰. It can conveniently be used to determine the effective diffusivity of a catalyst under the actual reaction conditions provided that the catalytic reaction is negligibly small and also the reactant or product under study emerges from the column as a reasonably well defined peak. If reaction occurs, the product peak may interfere with that of reactant and the method fails to give reliable results, and so one must be very careful while using this technique for studying diffusion under reaction conditions and should confirm the extent to which the reaction occurs during the passage of a reactant pulse through the catalyst column for different flow-rates and temperatures. The method proposed by Kelly and Fuller²⁴, which is based on the passage of a pulse through a stirred reactor containing catalyst and analysis of the effluent pulse by using a more specific detector, overcomes this difficulty and appears to be of particular use in studying diffusion in catalysts under reaction conditions.

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LIST OF SYMBOLS

d_p	average particle diameter (cm).
D_e	effective diffusivity of catalyst (cm^2/sec).
ΔE	apparent activation energy for diffusion (kcal/mole).
F_1	void fraction in packing.
F_2	solid fraction in packing ($1 - F_1$).
ΔH	heat of adsorption (cal/mole).
K	distribution coefficient [ratio of concentration of adsorbate in the mobile phase (mole/ml) to that in the stationary phase (mole/ml)].
L	length of packed column (cm).
p_v	pore volume (ml/g).
R	gas constant (cal/°K/mole).
t_{rt}	retention time of adsorbate (sec).
t_0	retention time of non-adsorbate (sec).
T_c	column temperature (°K).
v	interstitial carrier gas velocity (cm/sec).
V_R^0	corrected specific retention volume (ml/g).
ϵ	particle porosity.

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