APPLICATION OF FLASH-DESORPTION METHOD TO CATALYST STUDIES. II.
trans-BUTENE-2-ALUMINA SYSTEM

By Y. Amenomiya and R. J. Cvetanović

The flash-desorption technique has been applied to the trans-butene-2–alumina system, and the results have been compared with those obtained previously with ethylene and alumina. The existence of two different types of sites for olefin chemisorption is confirmed by the good agreement between the results obtained in the two studies. The present results with butene-2 show that the total active sites occupy 2.9% of the total surface, 62% of which belong to site I, 38% to site II. This is in close agreement with the total active sites found previously for ethylene chemisorption (2.8% of the total surface, with 58% belonging to site I and 42% to site II). Activation energies of butene desorption of 12.1 and 16.2 kcal./mole have been obtained for sites I and II, respectively.

Introduction

It was reported in the previous paper[1] (part I) that flashing the adsorbed ethylene molecules from an alumina catalyst by raising the temperature uniformly (the flash-desorption method) showed two different kinds of sites on alumina surface for the chemisorption of ethylene. It was also found that these active sites occupied 2.8% of the total surface and that the activation energies of desorption from the two sites were 26.8 and 36.4 kcal./mole, respectively.

In the present paper the flash-desorption method has been applied to the trans-butene-2–alumina system in order to confirm the previous results with ethylene and compare them with those obtained with a larger olefin.

Experimental

Apparatus and the treatment of catalyst used in the present work were the same as described in part I.[1] Alumina was taken from the same batch of material as in part I, but in the present instance an amount of 0.130 g. was used and its total B.E.T. surface area was 21.4 m.². The experimental procedure was similar to the one employed previously except for the details of evacuation before flash-desorption. Adsorption of trans-butene-2 on the alumina was first measured. Pressure change in the gas phase was not observable by a cathetometer 5 min. after the gas was admitted to the catalyst. The adsorbed amounts reported in this paper are those measured 10 min. after gas admittance. Following these measurements, the catalyst was evacuated for various time intervals at various temperatures as will be described later. After the catalyst was cooled to room temperature, helium was admitted and the catalyst was then flashed by raising its temperature uniformly.

Phillips research grade trans-butene-2 (99.50%) was condensed twice in a liquid nitrogen trap followed by evacuation. It contained a trace of cis-butene, but no further purification was attempted.

Results and Discussion

Active Site Areas.—The adsorption isotherm at room temperature of trans-butene-2 on the alumina used in this work is shown in Fig. 1. After adsorption was measured, the catalyst was evacuated before flashing as mentioned above. Typical flash-desorption chromatograms are shown in Fig. 2. Figure 2a shows a chromatogram obtained after evacuation for 15 min. at room temperature, 2b a chromatogram obtained after evacuation for 120 min. at 80°, and 2c a chromatogram after evacuation for 95 min. at 160°. In all instances these evacuations were carried out subsequent to the adsorption measurements. In the case of ethylene (part I), weakly (physically) adsorbed ethylene was removed by evacuation for 10 min. at room temperature, and the strongly adsorbed (chemisorbed) ethylene

(1) Y. Amenomiya and R. J. Cvetanović, *J. Phys. Chem.*, **67**, 144 (1963).

was then removed by flash desorption giving a chromatogram similar to the one in Fig. 2b.[1] However, it was feared that physically adsorbed butene might be more difficult to remove than ethylene and that the chromatogram in Fig. 2a therefore might have been due to desorption of both physically adsorbed and chemisorbed butene. If the catalyst is evacuated at a suitable temperature for various time intervals, the amount of the gas remaining on the surface after this evacuation would decrease as the evacuation time is prolonged but would eventually reach a constant value because of the great difference in the activation energy of desorption of the physically and chemically adsorbed molecules. This is shown in Fig. 3 where the amount of gas flashed from the surface after previous evacuation at 80° is plotted against the evacuation time. The temperature at which the first peak maximum appeared is also indicated.

Table I gives examples of analyses of the gas recovered by flash desorption under these conditions as well as after evacuation at higher temperatures which

TABLE I
COMPOSITION OF THE FLASH-DESORBED GAS
(Flash-desorption at a rate of about 15°/min.)

Expt. no.	Evacuation before flashing Temp. (°C.)	Time (min.)	Flash-desorbed gas (cc. NTP) C_2H_4	C_3H_6	$1\text{-}C_4H_8$	$cis\text{-}C_4H_8$	$trans\text{-}C_4H_8$
73	80	30	0.0051	0.0013	0.0060	0.0144	0.0259
74	80	60	.0042	.0011	.0057	.0131	.0235
75	80	120	.0048	.0013	.0055	.0127	.0219
98	152	73	.0040	.0011	.0027	.0051	.0081
85	160	60	.0052	.0014	.0024	.0045	.0072

will be discussed later. As evident from the table, the flash desorbed gas consisted mainly of n-butenes, although it contained a small amount of ethylene as well as a trace of propylene, indicating that not only isomerization but also some cracking occurred on the surface. However, the amount of ethylene formed corresponded to a butene conversion of only about 5% and this together with the trace of propylene was added to the amount of butene plotted in Fig. 3. The physically adsorbed butene was evidently removed at least within an evacuation interval of 70 min. at 80°. This is also supported by the fact that the temperature corresponding to the peak maximum also shifted with the removal of the physically adsorbed olefin and eventually became constant (157° at a rate of temperature increase of 15°/min. during flash-desorption). The results obtained with ethylene on the same catalyst are also
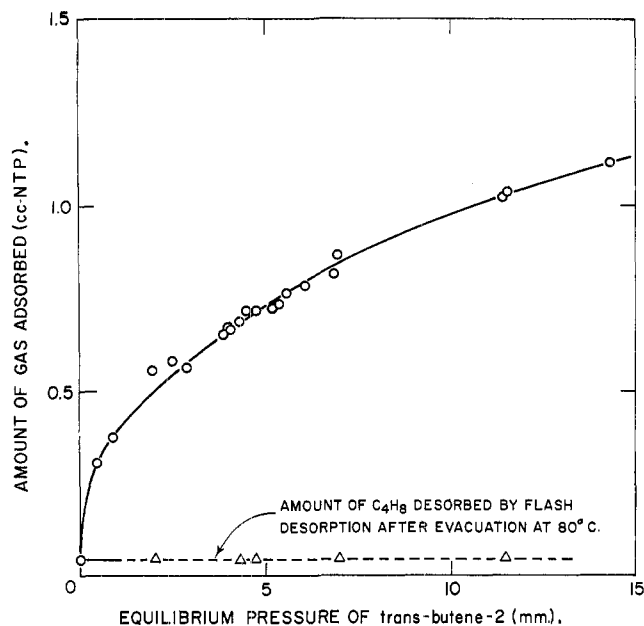
Fig. 1.—Isotherm of *trans*-butene-2 at room temperature. Catalyst weight 0.130 g.

shown in Fig. 3. The amount of the chemisorbed ethylene was 0.049 cc., which is close to 0.046 cc. of chemisorbed butene, as shown in the figure.

From the Langmuir plot of physically adsorbed butene at pressures from 5 to 15 mm., the amount of gas adsorbed (v_m) at complete surface coverage ($\theta = 1$) was found to be 1.56 cc./0.130 g. Combining this v_m with the B.E.T. area (21.4 m.^{2}), the cross-sectional area of an adsorbed butene molecule is found to be 51 Å.^{2}, which is of reasonable order of magnitude. With this v_m value, the active sites (0.046 cc.) correspond to 2.9% of the total surface area, which is in excellent agreement with 2.8% found in the case of ethylene.[1] Krylov and Fokina[2] reported that dehydration of isopropyl alcohol occurred on a small fraction (4–6%) of alumina surface. This is close to the active area for chemisorption obtained in the present study, although it is difficult to make a direct comparison since the type of alumina used by these authors is uncertain.

When the physically adsorbed olefin is removed by evacuating for more than 70 min. at 80°, the chromatogram (Fig. 2b) consists of two overlapping peaks similar to those observed with ethylene in part I. When the catalyst was evacuated at 160° instead of 80°, the first peak disappeared and only the second peak was left, as shown in Fig. 2c. However, the two peaks are too close to be completely separated by evacuation at a selected temperature. It was tried, therefore, to determine the area distribution between the two peaks roughly by drawing on the chromatogram a vertical line through the minimum between the two peaks, as is sometimes done in gas chromatographic analysis. It was found in this manner that 62% belonged to the first peak (site I) and 38% to the second peak (site II). The same method was also applied to the previous results with ethylene and gave an area distribution of 59 and 41%, respectively, which agreed well with 58 and 42% determined by evacuation at room temperature and 100°.[1]

The above results seem to indicate that the two types of active sites found on the alumina are responsible for
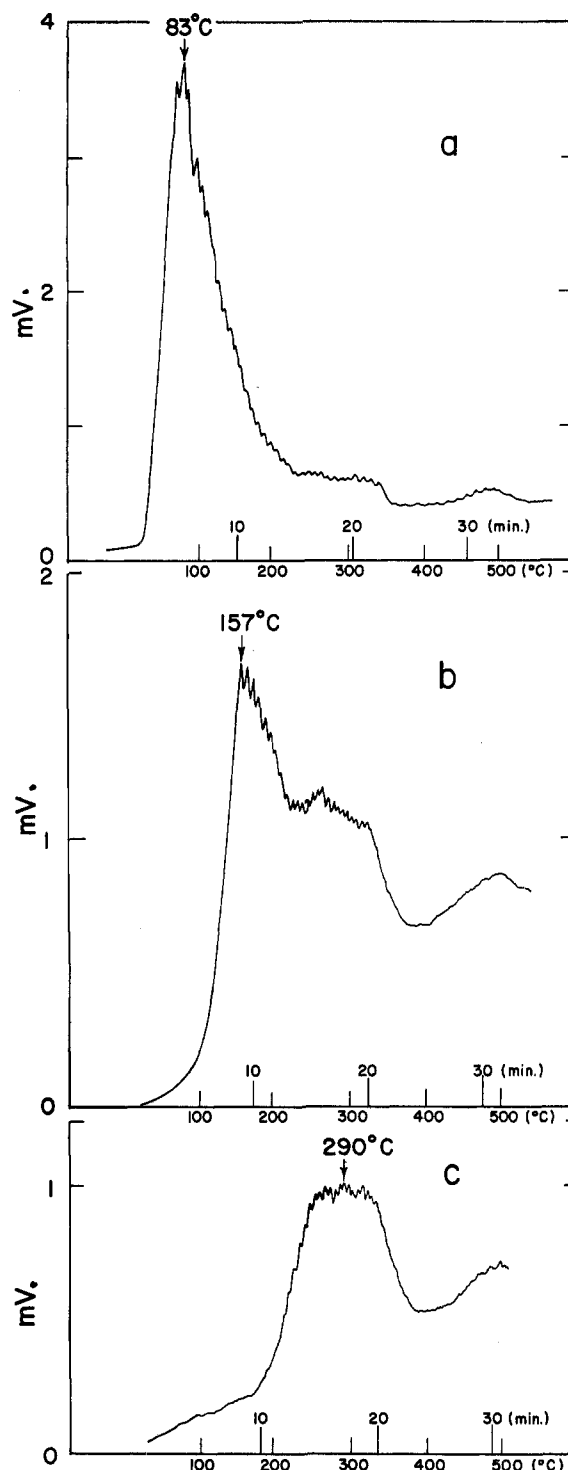
(2) O. V. Krylov and E. A. Fokina, *Kinetika i Kataliz*, **1**, 542 (1960).

Fig. 2.—Flash-desorption chromatograms: (a) expt. no. 68: evacuated before flashing 15 min. at room temperature; β = 15.5°/min.; (b) expt. no. 75: evacuated before flashing 120 min. at 80°; β = 15.3°/min.; (c) expt. no. 86: evacuated before flashing 95 min. at 160°; β = 15.3°/min.

the chemisorption of olefinic bonds in alkenes independently of which olefin is involved. The coincidence in the amounts of chemisorbed butene and ethylene suggests that the active sites on the surface are probably not dispersed patchwise or, at least, that the individual active sites are located far enough from each other so that butene molecules can be adsorbed as readily as molecules of ethylene. This supports the previous conclusion that the existence of two different values of the heat of adsorption, *i.e.*, of the activation energy of

desorption, was not due to the repulsive forces between adsorbed molecules.

Activation Energy of Desorption.—Table II shows the results of experiments carried out with varying equilibrium pressures of adsorption and the rates of temperature increase in the flash-desorption. In these experiments the catalyst was evacuated for more than 80 min. at 80° before flashing, because this evacuation time was found to be sufficient to remove the physically adsorbed olefin as mentioned before. The amounts of gas recovered by flashing listed in the table have also been plotted in Fig. 1, and it is evident that the amount of gas remaining on the surface after the evacuation is independent of the amount of gas adsorbed initially. This is in agreement with the conclusion that the flash-desorption chromatogram does not involve physically adsorbed olefin.

TABLE II

ADSORPTION AND FLASH-DESORPTION OF trans-BUTENE-2

(Flow-rate of helium in flash-desorption 45.0 cc./min.)

	Adsorption		Evacuation time before flashing (min.)	Flash-desorption data		
Expt. no.	Pressure (mm.)	Amount (cc. NTP)		β (°C./min.)	T_M (°C.)	Amt. of gas desorbed (cc. NTP)
75	4.72	0.718	120	15.3	157	0.0462
78	2.49	.580	84	19.2	165	...
79	1.95	.553	85	9.66	145	0.0445
80	6.96	.868	85	30.9	175	.0492
81	11.44	1.021	89	38.6	183	.0470

The equation

$$2 \log T_{M1} - \log \beta = E_d/2.303RT_{M1} + \log E_d v_m/Rk_0 \quad (1)$$

was used in Fig. 4 to plot the results from Table II as was done previously[1] in the case of ethylene. Here T_{M1} is the temperature corresponding to the first peak maximum (°K.), β is the speed of raising temperature (°C./min.), E_d is the activation energy, and k_0 is the temperature-independent factor of the rate constant of desorption. As shown in Fig. 4, a good linear plot is obtained and from its slope and intercept E_d and k_0/v_m were found to be 12.1 kcal./mole and 7.33×10^5 min.$^{-1}$, respectively. The activation energy should be approximately equal to the heat of adsorption since the adsorption equilibrium was attained very quickly.

Unfortunately, the second peak is too broad for accurate determination of the maximum peak temperature, as is evident from the chromatogram in Fig. 2c. However, taking in this case for k_0/v_m the value of 7.33 $\times 10^5$ min.$^{-1}$ obtained for the first peak and an average T_{M2} of 290° at $\beta = 15.3°$/min., the activation energy of desorption for the second peak is calculated as 16.2 kcal./mole. On the other hand, when the catalyst was evacuated in turn at 150 and 160°, the amount of gas recovered by flashing after the evacuation (the gas remaining on the surface) varied with the evacuation time, as shown in Fig. 5. From the slope of the straight line plots in Fig. 5, k_0/v_m and E_d were found to be, respectively, 1.59×10^5 min.$^{-1}$ and 15.2 kcal./mole, assuming that the rate of desorption was of the first order. These values are in reasonable agreement with those calculated above.

The intercept of the plots in Fig. 5 should represent v_m for site II. However, no quantitative conclusions
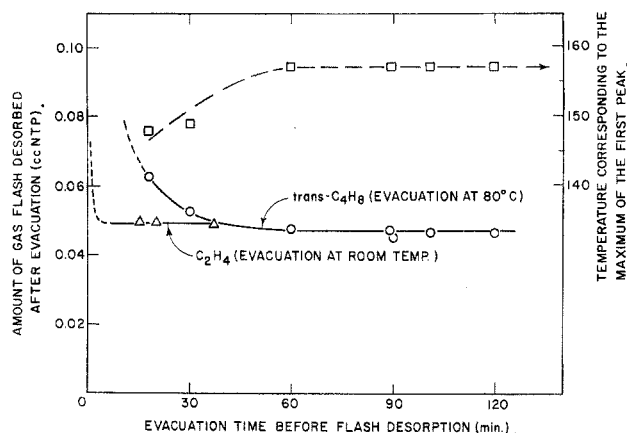

Fig. 3.—Variation of the amount of gas remaining on the surface with evacuation time. Flash-desorption at about 15°/min. Evacuation temperature 80° for butene, room temp. for ethylene.
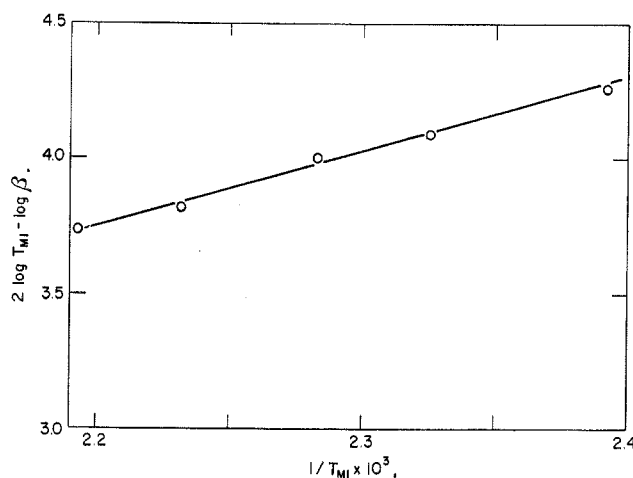

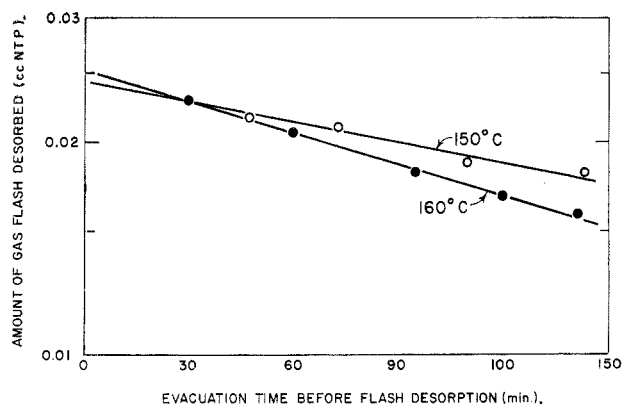Fig. 4.—Plot of eq. 1 for the first peak.

Fig. 5.—First-order plot of desorption.

should be drawn from this, since the gas removed by flashing contained a considerable amount of cracked products besides the butenes, as was shown in Table I. (This was much more pronounced at still higher evacuation temperatures and the plots in Fig. 5 have therefore been limited to 150 and 160°.) In addition, a constant activation energy would have to be implied while in fact there may be a range of values as a result of heterogeneity of the adsorption sites. The results of the present work do not lend themselves to a discussion of the potential existence of such a heterogeneity and the data presented in Fig. 5 are therefore considered as suitable only for a rough comparison of k_0/v_m and E_d values with the estimates given above.

DISCUSSION

H. W. HABGOOD (Research Council of Alberta).—I was wondering about the values you have obtained for the heats of desorption of ethylene and butene. The butene value is lower than that for ethylene; would you not expect it to be at least as large? The butene value is only relatively little higher than is normally found for physically adsorbed butene on most adsorbents even though the butene resists pumping at room temperature.

R. CVETANOVIĆ.—It would be difficult to predict in general the relative values of heats of adsorption for 2-butene and ethylene on particular adsorption sites. It is known, for example, that the trend in the stability of the complexes formed between olefins and electron acceptors may be strongly affected by a superposition of adverse steric effects and the purely polar effects responsible for complex formation. We should like to point out, at the same time, that the quoted values of the activation energies of desorption and the frequency factors obtained by the flash-desorption technique are strictly valid only for homogeneous surfaces and a lack of diffusion control. For sites I there is indication that the effect of the heterogeneity is relatively small. We are in the process of investigating the effect of a possible diffusion control. For Knudsen diffusion, as would be expected for our conditions, the effective diffusion coefficient may be written as $D = D_0 T^{1/2}$, and eq. 1 then reduces to a good approximation to

$$2.5 \log T_M - \log \beta = \Delta H/2.303\ RT_M + \log (2\nu_m l^2 \Delta H/rD_0 A \pi^2 R)$$

where ΔH is the heat of adsorption, l and r are the mean length and radius of the cylindrical pores, and A is related to the entropy of adsorption. Plots of this equation give for ΔH very similar values to those obtained for E_d by plotting eq. 1. The "frequency factors," however, will have a different significance in this interpretation.