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ADSORPTION EQUILIBRIUM AND THE RATES OF ADSORPTION AND DESORPTION^{*)}

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Abstract

The calculation of equilibrium pressure of adsorption from the rates of adsorption and desorption has been tried for ethylene on a silica-alumina catalyst. The rate of adsorption was measured by conventional methods, but the desorption rate and activation energy were measured with the temperature programmed desorption technique. Although the calculation was limited to low surface coverages, the equilibrium pressures calculated were in good agreement with those observed.

Adsorption equilibrium is, in principle, established by equalization of the rates of desorption and adsorption, so that the equilibrium pressure of adsorption of a gas can be calculated, if both rates are known as a function of pressure for the same surface condition. This calculation, when possible, is useful for the estimation of an adsorption equilibrium which cannot be measured directly. However, it has not been done successfully for adsorption on practical catalysts such as alumina and silica-alumina in particular, because of the experimental difficulties of measuring the rates, and because of the variation of activation energy with surface coverage.

The technique of temperature programmed desorption (T.P.D.) which has been developed recently by CVETANOVIC and the author, is sometimes useful for measurement of the rate of desorption under difficult conditions.¹⁾ This note reports the results of a comparison between the equilibrium pressure of ethylene adsorption on a silica-alumina catalyst as recorded by a manometer and that calculated from the rates of adsorption and desorption measured by the temperature programmed desorption technique.

The apparatus and the T.P.D. technique are described in detail elsewhere.¹⁾

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The catalyst used was Houdry M-46 silica-alumina, and was treated with air for 3 hr at 600°, followed by evacuation at the same temperature for more than 30 hr before use. The equilibrium pressure of adsorption was measured by a McLeod gauge in a constant volume.

The rate of adsorption was measured by two methods. In one, a conventional method, the adsorbed amount was plotted against time by following the pressure decrease during the measurement of adsorption equilibrium. Then $\Delta a/\Delta t/p$ (a is the adsorbed amount, t is the time and p the pressure in the gas phase) calculated from the graph was extrapolated to zero time. The initial rate of adsorption thus obtained (average of five experiments) was $4.3p$ cc/min·g (p in mmHg) at 24°C and the same value was obtained at -17°C within experimental error, suggesting a small activation energy of adsorption.

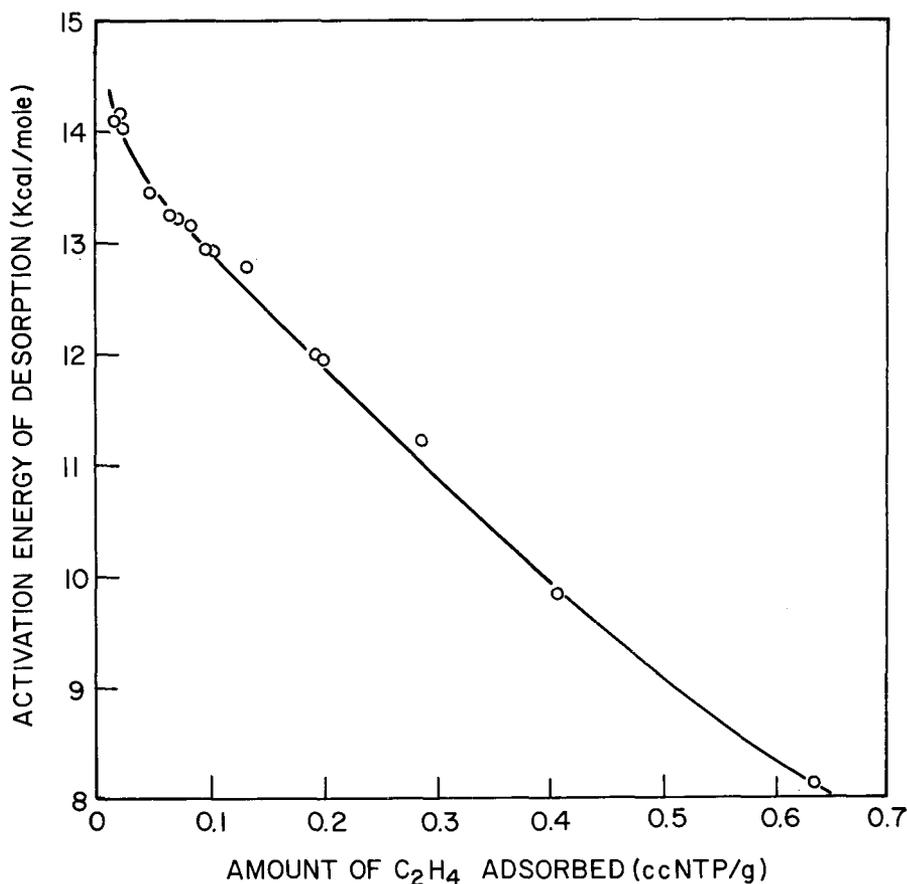


Fig. 1. Activation energy of desorption of ethylene on M-46.

Adsorption Equilibrium and the Rates of Adsorption and Desorption

In the other method, adsorption was permitted for 10 min at a constant, small pressure of ethylene by connecting the catalyst vessel with an ethylene reservoir kept at liquid nitrogen temperature. The pressure was constant at about 10^{-3} mmHg during the adsorption and the same as the vapour pressure before connecting to the catalyst vessel, indicating that the rate of evaporation of ethylene from the reservoir surpassed the rate of adsorption. The total amount adsorbed was measured by desorbing it in a helium stream by T.P.D. The desorption rate during the adsorption should be negligible at these small adsorbed amounts, as indeed verified by T.P.D. (no peak appeared up to 50°C). The average rate of adsorption at 24°C was $4.2p$ cc/min·g, in excellent agreement with the rate obtained by the first method. Pressure measurements in all the experiments reported here were made with the same McLeod gauge.

The rate of desorption was measured by the temperature programmed desorption technique. The plot of $2 \log T_M - \log \beta$ versus $1/T_M$ was made for a constant adsorbed amount but with different speed of increasing temperature, β , and the activation energy of desorption E_d , for this surface coverage and the temperature independent factor of rate constant divided by the saturated amount ($k_0/v_m = 1.03 \times 10^8 \text{ min}^{-1} \text{ g}^{-1}$) were determined. Then the T.P.D. chromatogram was taken with various adsorbed amounts, and the activation energy was calculated from the temperature of appearance of the peak maximum (T_M) by assuming that k_0/v_m was constant similarly to the case of propylene on alumina.²⁾ The activation energy thus obtained is shown in Fig. 1, where the adsorbed amount of ethylene was calculated from the peak area appearing after the peak maximum.

If it is assumed that with small amounts of adsorption, the surface coverage θ is so small that $1 - \theta \doteq 1$, we have the following equation at

TABLE 1. Comparison of observed and calculated pressure of adsorption equilibrium for ethylene on M-46.

Temp. ($^{\circ}\text{C}$)	Adsorbed amount (cc/g)	$p_{\text{obs.}}$ (mm/Hg)	$p_{\text{calc.}}$ (mm/Hg)
-17	0.100	$< 10^{-4}$	2.3×10^{-5}
	0.167	1×10^{-4}	1.4×10^{-4}
	0.246	1×10^{-3}	0.85×10^{-3}
	0.372	4×10^{-3}	7.1×10^{-3}
24	0.071	5×10^{-4}	2.8×10^{-4}
	0.139	1.5×10^{-3}	2.2×10^{-3}
	0.158	2×10^{-3}	3.5×10^{-3}

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equilibrium,

$$4.3p = k_0\theta \exp(-E_a/RT) = 1.03 \times 10^8 a_e \exp(-E_a/RT),$$

where a_e is the adsorbed amount at equilibrium ($a_e = v_m\theta$). Then p is calculated by putting E_a and a_e from Fig. 1 into the above equation. The results are shown in Table 1 in comparison with the observed pressures.

Bearing in mind the sharp change in E_a with surface coverage, the calculated results shown in Table 1 are in reasonable agreement with the observed pressures. Although application of the above equation is limited at present to small amounts of adsorption, it will be extended to cover a wider range when the value of v_m is known.

References

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