JOURNAL OF CATALYSIS 48, 262–268 (1977)

Desorption Rate Isotherms in Flash Desorption Analysis

JOHN L. FALCONER

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309

AND

ROBERT J. MADIX

Department of Chemical Engineering, Stanford University, Stanford, California 94306

Received August 30, 1976; revised April 1, 1977

In most flash desorption and temperature programmed desorption experiments only a small fraction of the data obtained is used in the kinetic analysis. A technique which utilizes more of the desorption data from a series of desorption curves obtained at different initial surface coverages is discussed. A number of desorption rate isotherms can be obtained by measuring desorption rates and coverages at selected temperatures in the desorption range. Each isotherm is a plot of ln (rate) versus ln (coverage) measured at a given temperature and its slope corresponds to the order of the desorption. From a series of desorption rate isotherms, plots of ln (rate) against $1/T$ can be obtained; the activation energy as a function of coverage can be obtained from the slopes of these plots. The success of the method for assisting in distinguishing between simple first-order desorption, first-order desorption with a coverage dependent activation energy and second-order desorption is illustrated. Theoretical calculations show the technique is very sensitive for distinguishing desorptions with coverage dependent activation energy. Analysis by desorption rate isotherms requires few assumptions, is easy to apply and can be used to determine kinetic parameters for both unsupported and supported catalysis.

INTRODUCTION

Increasingly in recent years the flash desorption (or temperature programmed desorption) technique has been used to study desorption and/or reactions of adsorbed gases on metal surfaces and supported catalysts. The quality of recent experimental flash desorption data has improved so that more precise kinetic information can now be obtained. However, for most experiments only a fraction of the experimental data has been used in kinetic analysis of the desorption or reaction though a number of different analysis techniques have been employed. Many workers have used Redhead's (*1*) technique for analyzing desorption spectra. In Redhead's analysis, only the peak temperature (temperature at which the desorption rate reached a maximum) and the heating rate were used to determine the activation energy for first-order desorption; the preexponential factor was assumed. For second-order desorption the dependence of the peak temperature on the initial surface coverage was employed. Other more recent analysis techniques have used the peak temperature and the peak width at half maximum to determine the kinetic parameters so that assumptions about preexponential factors were unnecessary (*2*, *3*). All of these techniques required that the activation energy and preexponential factor be independent of

ISSN 0021-9517

both temperature and coverage. The variations in the peak temperature and the peak amplitude with heating rate have also been used to determine activation energies without assumptions about preexponential factors, reaction orders, or specific reaction mechanisms (*1, 4–7*). In another method activation energies, preexponential factors and initial surface coverages have been varied for computer-generated flash curves to obtain the best fit to the experimental curves (*8*). Other authors have employed the change in curve amplitude and coverage with temperature for the leading edge of a curve to calculate E and n (*9–12*). Detailed discussions of techniques for analyzing desorption spectra have been presented in reviews by King (*13*) and by Smutek *et al.* (*14*).

To varying degrees the above methods of obtaining kinetic parameters from flash desorption experiments make use of only a fraction of the available data. Ehrlich (*15*) was the first to suggest a technique for measuring the activation energy as a function of coverage which utilized more of the experimental data by measuring rates and coverages for a number of desorption curves corresponding to different initial coverages. Bauer *et al.* (*16, 17*) applied a similar technique to experimental data for measuring activation energies as a function of coverage. Also, Christman *et al.* (*18*) described such a technique for determining activation energies but they were unsuccessful in applying it to their data.

The technique of desorption rate isotherms (*18, 19*) will be presented as an easily applied method for obtaining both the reaction order n *and* the activation energy E from flash desorption curves by utilizing more of the data. In effect the method provides constant temperature kinetic information such as would be obtained from isothermal desorption.

THEORY

The rate of desorption of an adsorbate from a surface or the rate of decomposition of a gas adsorbed on the surface is usually expressed in the form,

$$\frac{dc}{dt} = N = \nu c^n \exp\left(-\frac{E(c)}{RT}\right), \qquad (1)$$

where

N	rate of desorption (or decomposition)
ν	preexponential factor
c	surface coverage per unit area
n	order of desorption (or decomposition)
$E(c)$	activation energy, which can be a function of coverage
T	surface temperature

In a flash desorption experiment the temperature is increased with time at a constant rate β, and the desorption rate is recorded as a function of temperature. Then, each point of a desorption curve corresponds to a measurement of the desorption rate at a given temperature, surface coverage and surface composition. By obtaining a series of desorption curves at initial coverages, c_0, from low coverage up to saturation, effective use can be made of the fact that each curve contains an infinite number of these measurements. At a selected temperature in the desorption range the desorption rate and the surface coverage can be measured for each desorption curve corresponding to a different initial coverage. The rate of desorption, N, is proportional to the curve amplitude at that temperature. The area under the portion of each curve to the right of that temperature is proportional to the surface coverage at that temperature. That is, the area which corresponds to the surface coverage at temperature T is equal to $\int_T^\infty N dT$. A plot of $\ln N$ versus $\ln c$ at constant temperature can then be made, and according to Eq. (1), this desorption rate isotherm should be a

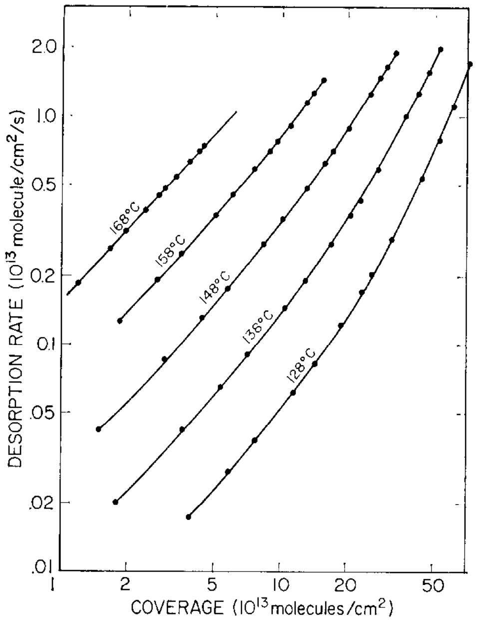

FIG. 1. Desorption rate isotherms from computer-generated first-order desorption curves with $\nu = 8.5 \times 10^{15}$ s^{-1}, $E = 32 - 2c/c_{sat}$ kcal/mole, and $c_{sat} = 10^{15}$ molecules/cm^2.

straight line with slope n *if* the activation energy is independent of coverage. A number of desorption rate isotherms can be plotted for temperatures over the desorption range. Then, *at a given coverage*, a number of measurements of desorption rates at different temperatures can be obtained from the desorption rate isotherms. A plot of ln N against $1/T$ at constant coverage can then be made and the activation energy is obtained from its slope. As long as consistent units are used for a set of experimental curves, it is not necessary to calibrate the amplitudes and areas to obtain reaction orders and activation energies. The accuracy of these measured kinetic parameters improves as the number of desorption curves obtained at different initial coverages increases, and as the number of temperatures selected for analysis increases. The preexponential factor can be obtained from equations relating ν to E, T_p, n, β, and c_0 for simple order desorption (*1*, *4*) or it can be obtained by computer generation of desorption curves with different ν until a good fit is obtained.

The activation energy, even if coverage dependent, can be obtained from the desorption rate isotherms. First-order flash desorption curves were computer generated for a linearly coverage dependent activation energy $E = 32 - 2c/c_{sat}$ kcal/mole with $\nu = 8.5 \times 10^{15}$ s^{-1} and c_{sat} equal to the saturation coverage. From the curves, generated at initial converges from 0.05 of saturation to saturation, desorption rate isotherms were obtained at five temperatures and are shown in Fig. 1. The desorption rate isotherm temperatures were chosen to cover the entire desorption range from the initial rise of the desorption curve to the low coverage tail.

At 168°C, which corresponded to low coverages for all curves (less than 5% of saturation coverage) a straight line was obtained corresponding to a slope $n = 1.04$. However, at lower temperatures (i.e.,

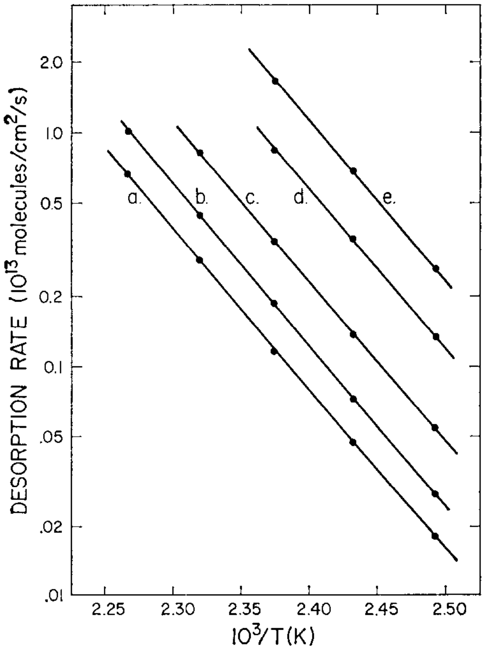

FIG. 2. Log N versus $1/T$ obtained from Fig. 1 for the following coverages (molecules/cm^2): (a) 4×10^{13}, (b) 6×10^{13}, (c) 1×10^{14}, (d) 2×10^{14}, (e) 3×10^{14}.

higher coverages) the points started to deviate from a straight line and the isotherm at 128°C showed significant curvature. Experimental data would not include the low coverage points for the lower temperature isotherms since these measurements are more difficult to make, and the resultant isotherms would be approximated as straight lines whose slope increased as the temperature decreased. From the desorption rate isotherms in Fig. 1 the activation energy can be determined as a function of coverage by obtaining rates and temperatures from the curves at a given coverage. Plots of ln N against $1/T$ are shown in Fig. 2. They are straight lines whose slopes, when multiplied by the negative of the gas constant, correspond to the activation energies expected at each coverage within 0.7%, the accuracy of least squares fit of the data points.

One of the important points to be noticed from these curves is that a relatively small dependence of activation energy on coverage (a 6% decrease in activation energy from zero coverage to saturation) caused a significant change in the desorption rate isotherms, i.e., the isotherms deviated significantly from straight lines with slopes of unity. Thus, plotting desorption rate isotherms for experimental data is a very sensitive technique for studying the desorption kinetics. It is also possible by the procedure described to obtain activation energies from desorption rate isotherms when the preexponential factor is a function of coverage.

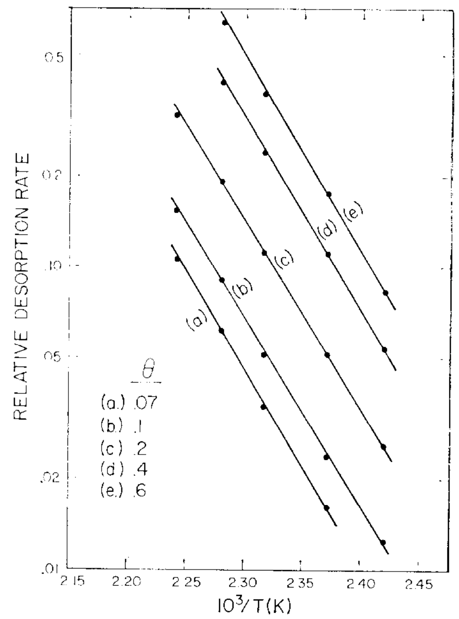

Fig. 4. Log N versus $1/T$ for CO desorption. Data points obtained from desorption rate isotherms in Fig. 3. Curves correspond to relative coverages in Fig. 3 of (a) 0.07, (b) 0.10, (c) 0.20, (d) 0.40, (e) 0.60.

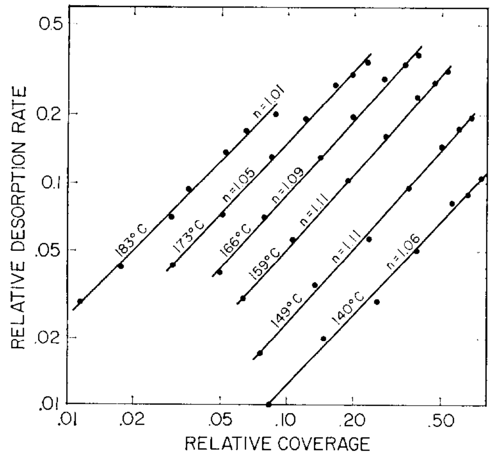

Fig. 3. Experimental desorption rate isotherms for CO desorption from clean Ni(110).

EXPERIMENTAL METHODS

Flash spectra obtained from the decomposition of deuterated formic acid on clean Ni(110) were analyzed by desorption rate isotherms. The data were obtained in an ultrahigh vacuum system described elsewhere (*11*, *12*) and the experimental results are discussed in detail in other publications (*4*, *11*, *20*). Flash spectra for hydrazine decomposition on supported iridium catalyst, which were obtained in a temperature programmed desorption apparatus described elsewhere (*21*), were also analyzed by desorption rate isotherms.

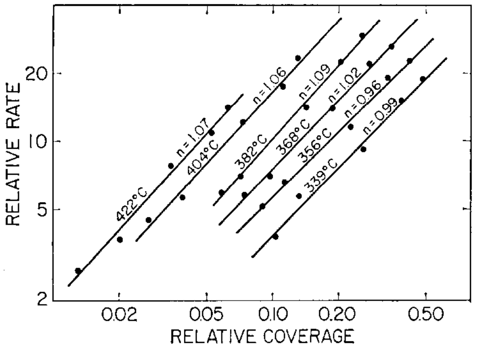

FIG. 5. Experimental desorption rate isotherms for nitrogen product from hydrazine decomposition on iridium-on-alumina catalyst.

RESULTS

Several sets of experimental data were analyzed by desorption rate isotherms and some of them are presented here. Results of analysis of other data will be published elsewhere (*11*).

Carbon Monoxide Desorption

Following DCOOH adsorption on clean Ni(110) at 37°C, CO was one of the products observed during the flash. This CO product corresponded to CO desorption (*12*, *22*) and exhibited first-order desorption with an activation energy which decreased slightly as the coverage increased. The activation energy was determined by the heating rate variation technique (*4*). Desorption rate isotherms were obtained for these CO desorption curves, corresponding to seven different initial coverages, at selected temperatures both above and below the peak temperature. As shown in Fig. 3 the data for the isotherms were well fit by straight lines. The slopes of these lines, which corresponded to the order of the desorption, were calculated by least squares fits, and they varied from 1.01 to 1.11. The deviations from unity were statistically significant (for 95% confidence limits) for the isotherms at 166, 159 and 149°C. Thus the desorption of CO appeared to be very close to first order and the change in slope with isotherm temperature was that expected for a first-order desorption with a very slightly coverage dependent activation energy, as discussed above.

Plots of ln N against $1/T$ were obtained at selected coverages from the isotherms in Fig. 3. As shown in Fig. 4, at each coverage the data points were well fit by straight lines whose slope was proportional to the activation energy of desorption. From a least squares fit the average activation energy was 29.2 ± 1.7 kcal/mole; this was close to the values calculated by heating rate variation and by other experimental techniques (*4*). The scatter was such that the small change in activation energy with coverage of 1.2 kcal/mole could not be accurately measured.

Nitrogen from Hydrazine Decomposition

Hydrazine was adsorbed from the gas phase onto an iridium-on-alumina catalyst in a helium flow stream at atmospheric pressure and the products of decomposition were observed by mass spectrometer during temperature programmed desorption. Since nitrogen did not adsorb on the iridium surface any nitrogen product was due to decomposition and not desorption (*21*). Figure 5 shows desorption rate isotherms obtained at temperatures both above and below the peak maximum for the nitrogen product peak. For each isotherm the slope was obtained by a least squares fit. Because only five desorption curves, corresponding to five different initial coverages, were obtained experimentally the slopes calculated for the nitrogen product from hydrazine decomposition were not as accurate as those calculated for CO desorption. Within 95% confidence limits, the deviations of the slopes from unity were not significant. Thus, the decomposition was first order with an activation energy independent of coverage.

Data points for plots of ln N against $1/T$

were obtained from the isotherms in Fig. 5 and are plotted in Fig. 6 for five different coverages. Least squares fits of these points were used to determine the slopes, which were proportional to the activation energies. The activation energies varies from 17.8 to 19.4 kcal/mole, but within 95% confidence limits these differences were not significant, and an average value of 18.3 ± 1.1 kcal/mole was calculated.

Other Systems

Desorption rate isotherms were also used to analyze the D_2 desorption observed following HCOOD adsorption on Ni(110) C(4 × 5) at −60°C (*20*). The average slopes obtained from the least squares fit of the isotherm data were found to be 1.95 and all values were within 8% of this value. This was consistent with the second-order behavior indicated by the shift in peak temperature with initial coverage. An activation energy of 12.1 kcal/mole was then calculated from the ln N versus $1/T$ plots and was within 5% of the value of E obtained from the heating rate variation technique. The results of this analysis will be published in detail elsewhere (*20*).

Desorption rate isotherms were also used to analyze water desorption from clean Ni(110) following adsorption of water at −60°C. The slope of the isotherm was 1.00 at high temperatures and it increased to 1.26 at lower temperatures. However, the ln N versus $1/T$ plots were not linear at constant coverage, indicating the desorption was not simply first order with a coverage dependent activation energy. The desorption was attributed to two first-order desorptions with different activation energies and is discussed in detail elsewhere (*11*). Similarly, desorption rate isotherms were used to analyze other desorptions and decompositions (*11*).

Besides indicating the order of desorption and the activation energies for simple desorptions, the desorption rate isotherm can be used as a guide to distinguish between first-order desorption with coverage dependent activation energy, simultaneous, overlapping first-order desorptions and second-order desorption. It can also distinguish between second-order desorption and second-order desorption with coverage dependent activation energy. Thus the method is quite sensitive to the desorption order as well as the activation energy as a function of coverage.

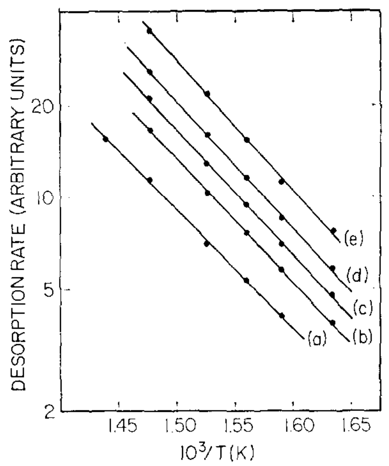

FIG. 6. Log N versus $1/T$ for nitrogen product from hydrazine decomposition. Data points obtained from desorption rate isotherms in Fig. 5. Curves correspond to relative coverages in Fig. 5 of (a) 0.07, (b) 0.10, (c) 0.125, (d) 0.15, (e) 0.20.

There are, however, some important experimental considerations to be aware of before analyzing flash desorption curves by desorption rate isotherms. It is important that the spectra are obtained with a flat baseline for accurate measurement of coverage. In an ultrahigh vacuum system the pumping speed must be large enough so that the partial pressure change is proportional to the desorption rate from the surface. It may be necessary to calibrate the system using a well-studied desorption, such as CO from nickel, to be certain this is the case. It is also very desirable to obtain a large number of spectra over a coverage range from saturation down to low coverage. In particular, it is important by expanding recorder scales or detection sensitivity to obtain a number of desorption curves at low coverage. Because the analysis plots are log–log, the low coverage curves make a disproportionately large contribution to the slope of the lines. Also, it must be noted that the technique of desorption rate isotherms may not work well for determining kinetic parameters for complicated desorption kinetics or for two or more surface states whose spectra overlap significantly.

CONCLUSIONS

Analysis of flash desorption or flash decomposition spectra by desorption rate isotherms can be a powerful technique for obtaining kinetic information about both desorption and decomposition of adsorbed molecules. Experimentally, only the measurement of desorption curves for different exposures is required and the subsequent analysis is very easy to apply. Most importantly, analysis by desorption rate isotherms utilizes much more of the data obtained than other techniques so that more extensive kinetic information can be obtained. Also, this method appears to be sensitive to the desorption kinetics and easily distinguishes desorptions with coverage dependent activation energies. In addition, it does not assume a reaction order and works equally well for zero-order, first-order, second-order or fractional order desorptions or reactions.

REFERENCES

1. Redhead, P. A., *Vacuum* **12**, 203 (1962).
2. Schmidt, L. D., *Cat. Rev.-Sci. Eng.* **9**, 115 (1974).
3. Edwards, D., Jr., *Surface Sci.* **54**, 1 (1975).
4. Falconer, J. L., and Madix, R. J., *Surface Sci.* **48**, 393 (1975).
5. Ehrlich, G., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 14, p. 255. Academic Press, New York, 1963.
6. Edwards, D., Jr., *J. Appl. Phys.* **46**, 1444 (1975).
7. Lord, F. M., and Kittelberger, J. S., *Surface Sci.* **43**, 173 (1974).
8. Winterbottom, W. L., *J. Vac. Sci. Technol.* **9**, 936 (1972).
9. Arthur, J. R., and Cho, A. Y., *Surface Sci.* **36**, 641 (1973).
10. McCarty, J. G., and Madix, R. J., *Surface Sci.* **54**, 210 (1976).
11. Falconer, J. L., and Madix, R. J., *J. Catal.*, in press.
12. McCarty, J. G., Falconer, J. L., and Madix, R. J., *J. Catal.* **30**, 235 (1973).
13. King, D. A., *Surface Sci.* **47**, 384 (1975).
14. Smutek, M., Cerny, S., and Buzek, F., in "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 24, p. 343. Academic Press, New York, 1975.
15. Ehrlich, G., *J. Appl. Phys.* **32**, 4 (1961).
16. Bauer, E., Bonczek, F., Poppa, H., and Todd, G., *Surface Sci.* **53**, 87 (1975).
17. Bauer, E., Poppa, H., Todd, G., and Bonczek, F., *J. Appl. Phys.* **45**, 5164 (1974).
18. Christmann, K., Ertl, G., and Pignet, T., *Surface Sci.* **54**, 365 (1976).
19. Falconer, J. L., and Madix, R. J., *Bull. Amer. Phy. Soc.* **21**, 935 (1976).
20. Abbas, N., and Madix, R. J., to be published.
21. Falconer, J. L., and Wise, H., *J. Catal.* **43**, 220 (1976).
22. Falconer, J. L., and Madix, R. J., *Surface Sci.* 473 (1974).