Determination of Catalyst Surface Area from Desorption Characteristics of Physisorbed Gases

A new experimental method for the measurement of catalyst surface area of supported catalysts has been developed using selective physisorption. The desorption characteristics of a gas are studied separately on the catalyst, the support, and the supported catalyst by carrying out thermal desorption experiments in a continuous flow sorptometer. Differences in the coverage vs. temperature curves, obtained from the thermal desorption experiments, are a measure of the selectivity of the physisorbing gas, and allow calculation of the fraction of total surface area occupied by the catalyst.

Two systems have been studied utilizing the thermal desorption with carbon dioxide as adsorbate: potassium carbonate/carbon black and silver/alumina. Supported catalyst surface area was determined for each system; the results were confirmed using physical mixtures of the two components (where the actual area of each component is known) and oxygen chemisorption for the silver/alumina system. The experimental technique allows for straightforward calculation of the catalyst area.

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SCOPE

The exposed surface area of a catalyst on a support is an important parameter in the characterization of catalytic behavior, particularly in sintering and dispersion studies. Several experimental methods of determining catalyst area have been developed, including chemisorption, electron microscopy, and X-ray techniques. The difficulties involved in applying electron microscopy to actual catalysts and the sophistication of small angle X-ray scattering prevent their practical application in many cases. Chemisorption techniques have met with success in several catalyst systems, but the chemisorption techniques are limited to well-defined metal catalysts and are not in general applicable to nonmetallic catalysts.

This paper presents a new method for determining catalyst area using physical adsorption. The method examines the adsorption characteristics of a gas separately on the catalyst (in powder or gauze form), the support, and the supported catalyst using a thermal desorption technique for the determination of the total exposed catalyst area as a fraction of the total catalyst and support area. This method has several advantages over other methods used in catalyst area measurements:

1) The physisorption experiments are easy to carry out and the equipment needed is low cost. The physisorption experiments show good reproducibility, and sample preparation is the same as in conventional physisorption.

2) The method can be applied to any catalyst system with the appropriate choice of adsorbing gas, since gases physisorb on all surfaces at low temperatures. This is in contrast to chemisorption, where the specific gas-solid interactions limit application to a few systems.

3) The total catalyst area is determined directly from the experiments. Unlike chemisorption, there is no need to know the adsorption stoichiometry to determine the total area.

CONCLUSIONS AND SIGNIFICANCE

The theoretical development for the experimental measurement of catalyst surface area has been presented. The method is based on the selective physisorption of gas onto both the catalyst and support surfaces. Examination of attractive forces of physisorption shows that the forces of physisorption, and hence the adsorption characteristics, of a gas will vary on various types of solids, giving rise to the selective adsorption necessary to determine supported catalyst area.

The specific desorption characteristics obtainable from thermal desorption are represented entirely by a unique curve of coverage vs. temperature. The difference in the dependence of coverage on temperature for the catalyst and support surfaces allows calculation of the catalyst area in the supported catalyst. The catalyst area is calculated by determining the coverage versus temperature curve for the supported catalyst which is then combined with the curves from the individual components; the lever rule is used to calculate the fraction of total surface area attributed to the catalyst.

The experimental method presented in this paper has been used to measure total catalyst surface area of two systems: potassium carbonate supported on carbon black and silver supported on alumina. The surface area measurements made using thermal desorption have been verified by repeating the experiments with physical mixtures of carbon black and potassium carbonate powders for which the surface areas are known, and qualitatively by the chemisorption of oxygen on silver catalyst. The results obtained by these two methods agree with the results obtained by thermal desorption.

The primary disadvantage of this method is the sensitivity of the experimental results to uncertainty in the raw data in systems where the desorption characteristics of a gas on two surfaces are nearly alike. This disadvantage can be overcome, however, by proper choice of a maximally selective adsorbate

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and precise experimental techniques.

This method is an important breakthrough in the area of total catalyst area measurement. The method is applicable to determination of catalyst area in nonmetallic catalyst systems where catalyst loadings are high and the catalyst covers a significant portion of the total surface area.

INTRODUCTION

The exposed catalyst surface area of a supported catalyst is an important quantity in catalytic research. Dispersion and specific activity derivable from this measurement are essential for characterization of catalytic reactions, as amply illustrated by Carberry (1976). This measurement also gives a measure of the efficiency of dispersion of a supported catalyst. Several methods are available for the measurement: electron microscopy, X-ray techniques including diffraction and scattering, and gas chemisorption. A review on surface area measurements by Farrauto (1974) gives details on the chemisorption method, and the article by Pulvermacher and Ruckenstein (1974) provides details on the other methods including magnetic measurements. Of these methods, gas chemisorption is perhaps the most accurate and certainly the easiest to implement, e.g., H_2 on Pt (Spenadel and Boudart, 1960; Adler and Kearney, 1960) and on Ni (Taylor, Yates and Sinfelt, 1964), CO on Pd (Scholten and Montfoort, 1962), and NO on oxides of Cu, N_i and Fe (Gandhi and Shelef, 1973). While the chemisorption method is a powerful tool for catalytic research, it has its limitations for the determination of active surface area. This is particularly so for catalysts of oxides or carbonates in which only a fraction of the exposed surface area is covered by chemisorbed gas molecules.

The very specific nature of interactions between surface atoms and chemisorbed gas, which allows determination of the active surface area, is the limiting factor for application of the chemisorption method to catalysts of metal compounds and metals of unknown stoichiometry. The nondiscriminatory nature of physisorption, on the other hand, makes it unsuitable for the active surface area measurement, yet it offers the advantage that the whole surface is covered by gas molecules regardless of the type of surface involved. It is, therefore, entirely possible to devise, based on physisorption, a universal method applicable to any surface for the determination of catalyst surface area provided that certain requirements are met. These requirements are: (1) monolayer coverage of catalyst surface by gas molecules, (2) a means by which the physisorption process can be made selective and specific. The first requirement is not difficult to meet since a proper selection of pressure for given adsorbate and temperature ensures monolayer coverage as the well-known BET equation amply demonstrates. The second requirement is much more difficult to meet. If, however, unique but different desorption characteristics can be found for catalyst and support, these can be utilized for the determination of the fraction of total surface area occupied by the catalyst. This is the essence of the new experimental method developed here.

In this paper, we present the theoretical bases for and the rationale behind the new experimental method for the determination of catalyst surface area. We first provide a theoretical basis for the differences in physisorption forces, which are essential for the determination of individual surface areas of catalyst and support from their desorption characteristics. The choice of a suitable gas for the experiment also emerges from this. Given this basis, all that is required for the experimental method is to properly represent these characteristics. Experimental evidence from thermal desorption of physisorbed gas and the fact that individual rates of adsorption and desorption are very rapid do suggest that there exists a pseudoequilibrium between adsorption and desorption during transient desorption. While this is not a necessary condition for the method, it allows a means to characterize the desorption from an individual surface solely in terms of coverage vs. temperature. The sole dependence of the coverage on temperature during thermal desorption has been well documented (Miller, 1982) by our experiments, both by varying heating rates and by step changing and then holding the temperature at various levels. Finally, these theoretical bases lead to a method of determining the fraction of total surface area occupied by catalyst from the coverage vs. temperature data on catalyst, support and supported catalyst.

THEORY

Nature of Physisorption Forces

Thorough descriptions of physisorption forces are available in Brunauer (1943), Young and Crowell (1962), and Clark (1970), and will not be discussed here. However, the fact that different types of solid surfaces can give rise to different types of gas-solid interactions will be illustrated, for these differences will allow individual surface areas to be determined from their desorption characteristics.

An examination of physisorption forces leads to the conclusions that physisorption can be made selective by a proper choice of a gas and the choice of a gas can be made from knowledge of the various contributions of individual forces to the total physisorption force. For instance, the limited selectivity of physisorption was used by Huang and Emmett (1973) to study the effect of exchanged cations and heat treatment on the adsorption of various gases for cracking catalysts. Huang (1972) also studied the temperature dependence of heat of physisorption on the heterogeneous surface. Since the difference in interaction forces from one surface to another is responsible for the difference in physisorption characteristics, a gas that exhibits different interaction forces on two different solid surfaces will also exhibit different characteristics during transient desorption. The gas should be chosen so as to maximize the difference in the desorption characteristics of the gas on these two surfaces. While the choice of a suitable gas is often made on a trial-and-error basis, an idea of the types and magnitude of physisorption forces can eliminate some unnecessary experimentation and thus make the selection process more efficient.

As an example, the desorption characteristics of nitrogen, ethylene, and carbon dioxide on carbon black and potassium carbonate have been studied to identify differences in the adsorption characteristics of each of the gases on the two surfaces. The only significant difference in adsorption characteristics occurred with carbon dioxide, which exhibits two properties that nitrogen and ethylene do not: i) a large quadrupole moment, and ii) large asymmetry of the directional polarizabilities of the molecule. The directional polarizabilities of the three gases and several others are given by Ross and Olivier (1964) (Table 1). The directional polarizability of carbon dioxide along its principal axis is twice the magnitude of the polarizability along the other two axes, in contrast to nitrogen and ethylene which exhibit only mild asymmetry of the directional polarizabilities. In addition, nitrogen and ethylene have small quadrupole moments. We postulate that properties such as asymmetry of the polarizabilities and quadrupole moment are resonsible for the differences in adsorption characteristics of a gas on different solid surfaces. Extreme values of such properties will accentuate certain gas-solid interactive forces, thus magnifying any differences in properties of the solid surfaces being studied. For instance, nitrous oxide exhibits a large asymmetry in directional polarizabilities (Table 1) and would, therefore, be a possible adsorbate to be used in thermal desorption. It would be a more likely candidate than argon or ammonia which have nearly symmetric polarizabilities, although ammonia also has a significant dipole

TABLE 1. DIRECTIONAL POLARIZABILITIES OF MOLECULES

Gas	$\alpha_1^* \times 10^{18}$, m^3	$\alpha_2 \times 10^{18}$, m^3	$\alpha_3 \times 10^{18}$, m^3
Carbon Dioxide	4.01	1.97	1.97
Nitrogen	2.38	1.45	1.45
Ethylene	5.61	3.59	3.59
Argon	1.63	1.63	1.63
Ammonia	2.42	2.18	2.18
Nitrous Oxide	4.86	2.07	2.07
Sulfur Dioxide	3.49	2.72	5.49

* α_1 is along axis of highest symmetry.

moment which must be considered. Gas properties such as dipole moment, quadrupole moment, and polarizability are the primary information for the choice of an adsorbate which maximizes the differences in adsorption characteristics of the gas on the two solids during thermal desorption.

Pseudoequilibrium During Transient Desorption

For adsorption at coverages less than unity and constant adsorbate partial pressure, the change of the coverage with time during transient desorption can be expressed as

$$\frac{d\theta}{dt} = f_a(T,P,\theta) - f_d(T,\theta) \qquad (1)$$

where θ is coverage, and f_a and f_d are the rate of adsorption and the rate of desorption, respectively. For Langmuir kinetics, for instance, $f_a = pk_a(1-\theta)/v_m$ and $f_d = k_d\theta/v_m$ where v_m is the volume of gas occupying unit surface area at monolayer coverage, p is adsorbate partial pressure, and k_a and k_d are adsorption and desorption rate constants respectively.

In physisorption, the individual rates of adsorption and desorption are very rapid due to much smaller forces involved than in chemisorption and the greater mobility of adsorbed species. As a result, the transient term in Eq. 1 can be neglected in comparison with the individual adsorption and desorption rates. Thus, there exists at all temperatures during transient desorption a pseudo equilibrium between the free gas phase and the gas adsorbed on the solid surface. A direct consequence of this postulate is that the coverage θ will be dependent only on the system temperature for constant adsorbate partial pressure, as evident from Eq. 1. Our early experiments involving a continuous flow sorptometer verified the postulate: the coverage was dependent only on temperature and was independent of the heating rate dT/dt for experiments at constant partial pressure. Theoretical calculations of the individual rates in Eq. 1 using the Langmuir kinetics also verified the postulate (Miller, 1982). It should be recognized that the singular dependence of surface coverage on temperature is not dependent on any particular form of adsorption/desorption kinetics, as Eq. 1 indicates.

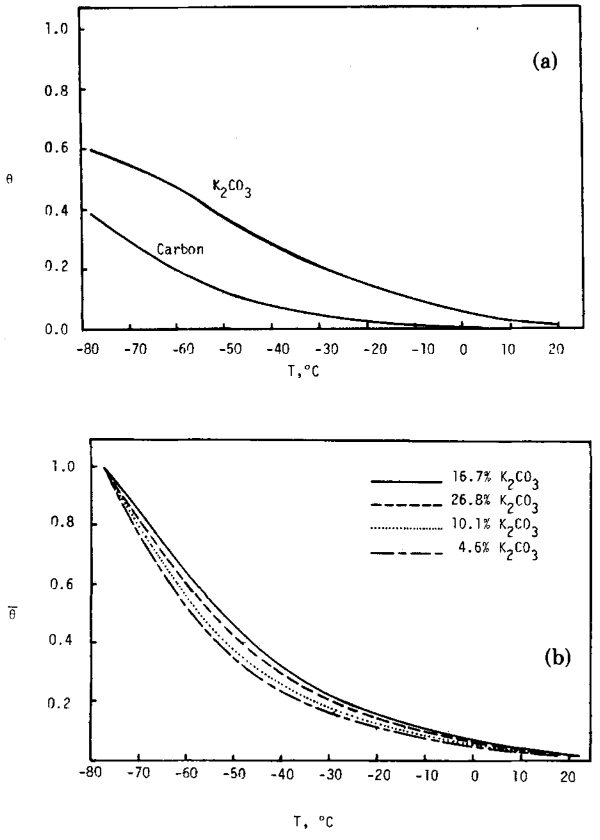

Figure 1. a) θ vs. T for K_2CO_3-carbon black. b) $\bar{\theta}$ vs. T for impregnated K_2CO_3-carbon black.

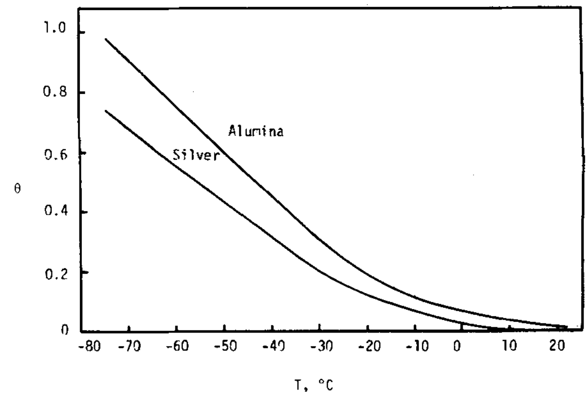

Figure 2. θ vs. T for silver alumina system.

Determination of Fraction of Catalyst Surface Area in a Supported Catalyst

If a singular relationship exists between coverage and temperature and these relationships are different for catalyst and support, the fraction of total surface area occupied by catalyst can readily be determined from these relationships. For the development to follow, it is assumed that the surface coverage on each component in the two component solid (supported catalyst) is the same as on each corresponding pure component (pure catalyst and pure support). This allows the desorption data collected for pure catalyst and support to be used in the analysis of the data on the supported catalyst.

The differences in the relationships between coverage and temperature can take two forms, Figures 1a and 2. Figure 2 represents the case where the initial values of coverage, θ, are different for each component, but the two curves are linearly dependent, differing only by a multiplicative constant. The second form is shown in Figure 1a where the initial values of θ are different and the curves are linearly independent. The methods of analysis can be different for the two forms. Expressions for calculating the catalyst surface area will be developed for the two cases.

To determine the catalyst surface area, the θ-T relationships must be obtained for the catalyst, support, and the supported catalyst from the thermal desorption experiment at constant partial pressure. Since there is a unique dependence of θ on temperature, the temperature during the thermal desorption experiment can be increased in any way provided the increase is monotonic. In addition, the volume of adsorbate occupying a monolayer coverage per gram of solid must be determined by a standard BET experiment for both pure catalyst and support to calculate the fractional coverages.

The following derivation applies to both forms and utilizes the concept of monolayer volume ratios R_1 and R_2 in the expression. These monolayer volume ratios are defined as

$$R_i = \frac{V_{m,i}}{V_{m,N_2}} \qquad i = 1,2 \quad (2)$$

where the monolayer volume of nitrogen per gram of solid, $V_{m,N2}$, must be determined experimentally for each of the pure components. The nitrogen monolayer volume is an effective measure of surface area, thus the relative volume ratio gives the area occupied by one molecule of adsorbate on each of the individual component surfaces. Our experimental results show that the relative volume ratios can differ by as much as 30% on different solid surfaces.

The volume adsorbed at any temperature on a two-component (supported catalyst) surface is given by

$$V_{\text{ads}}(T) = v_{m,1}S_1\theta_1(T) + v_{m,2}S_2\theta_2(T) \quad (3)$$

where $v_{m,1}$ and $v_{m,2}$ are the volumes of gas adsorbed at monolayer coverage on 1 m^2 of pure components 1 and 2. The packing factors R_i can be expressed as

$$R_i = \frac{v_{m,i}}{v_{m,N_2}} \qquad i = 1,2 \quad (4)$$

where v_{m,N_2} is the volume of nitrogen monolayer per unit area. Substituting R_1 and R_2 into Eq. 3 yields

$$V_{\text{ads}}(T) = V_{m,N_2}(R_1S_1\theta_1(T) + R_2S_2\theta_2(T)) \quad (5)$$

The total surface area of the supported catalyst is

$$S_t = S_1 + S_2 \quad (6)$$

from which it follows that

$$\frac{S_2}{S_t} = 1 - \frac{S_1}{S_t} \quad (7)$$

We now define $\bar{\theta}$ as the ratio of gas adsorbed on the supported catalyst at any temperature to that adsorbed at the initial temperature, T_a.

$$\bar{\theta}(T) = \frac{V_{\text{ads}}(T)}{V_{\text{ads}}(T_a)} \quad (8)$$

Substituting Eqs. 7 and 8 into Eq. 5 gives

$$\bar{\theta}(T)\, V_{\text{ads}}(T_a) = v_{m,N_2}S_t(R_1\theta_1(T)S_1/S_t + R_2\theta_2(T)(1 - S_1/S_t)) \quad (9)$$

This is the expression which can be rearranged to yield the fractional catalyst surface area S_1/S_t. Since this equation gives a result at any temperature, the equation can be integrated over the temperature range of desorption and retain its validity. The integration cancels the scatter in the experimental data and gives an average value of the catalyst surface area over the temperature range. Integrating and rearranging this equation gives the final result

$$\frac{S_1}{S_t} = \frac{\dfrac{V_{\text{ads}}(T_a)}{Vm,N_2}\bar{I} - R_2I_2}{R_1I_1 - R_2I_2} \quad (10)$$

where

$$I_1 = \int_{T_1}^{T_2} \theta_1(T)dT$$
$$I_2 = \int_{T_1}^{T_2} \theta_2(T)dT \quad (11)$$
$$\bar{I} = \int_{T_1}^{T_2} \bar{\theta}(T)dT$$

Here T_1 and T_2 are the temperatures chosen for integration in the range of the desorption temperatures, and can take values over any range where the pure component $\theta - T$ curves do not intersect. Thus the catalyst surface area S_1 can be calculated, since S_t is known from the nitrogen BET experiments.

The above derivation applies to both functional forms, but requires that nitrogen BET experiments be performed on the catalyst, support, and the supported catalyst. These experiments are in addition to the thermal desorption and adsorbate BET experiments, and can be quite time consuming. The derivation that follows is a modification of the previous one and holds only when the $\theta - T$ curves are linearly independent, Figure 1a. The derived expression requires less BET experimentation than is necessary for Eq. 10, and hence can be more quickly implemented. If Eq. 3 is evaluated at the initial temperature of desorption, T_a, the definition of $\bar{\theta}(T)$ given in Eq. 8 can be written as

$$\bar{\theta}(T) = V_{\text{ads}}(T)/V_{\text{ads}}(T_a)$$
$$= (R_1S_1\theta_1(T) + R_2S_2\theta_2(T))/(R_1S_1\theta_1(T_a) + R_2S_2\theta_2(T_a)) \quad (12)$$

If the numerator and denominator are divided by S_t and Eq. 7 is substituted into Eq. 12, the result can be rearranged and integrated over the desired temperature to yield the desired expression for linearly independent $\theta - T$ curves:

$$\frac{S_1}{S_t} = \frac{R_2I_2 - R_2\theta_2^a\bar{I}}{(R_1\theta_1^a - R_2\theta_2^a)\bar{I} - R_1I_1 + R_2I_2}, \quad \theta_i^a = \theta_i(T_a) \quad (13)$$

This result applies to the linearly independent form as that in Figure 1a and does not require that the nitrogen BET experiment be performed on the supported catalyst to determine the quantity S_1/S_t. This is particularly advantageous in the characterization of several supported catalysts of the same catalyst and support but of different loadings or dispersion, where comparisons are of primary interest. However, to find the actual catalyst area S_1 the nitrogen BET experiment must be performed to obtain S_t, after which S_1 can be calculated. An extension of Eq. 13 to a multicomponent solid is given by Miller (1982).

In summary, Eqs. 10 and 13 essentially represent the lever rule for the fractional surface areas S_1/S_t and S_2/S_t. Equation 10 can be used for all two-component systems, once all the necessary experimental data have been obtained. Equation 13 can be used for the functional forms where the $\theta - T$ curves are linearly independent, with the advantage that relative information among the same types of catalysts can be obtained without the need for nitrogen BET experimentation on each sample. However, calculations using Eq. 13 rely on the linear independence of the $\theta - T$ curves, and become very sensitive to small changes in θ_1 or θ_2 as the difference in functional forms between θ_1 vs. T and θ_2 vs. T decreases. In all cases, the accuracy and reproducibility of the method increase as the differences in the $\theta - T$ curves increase.

EXPERIMENT

Apparatus

The entire experimental apparatus consists of a Perkin-Elmer continuous flow sorptometer which has been modified for the thermal desorption studies. The sorptometer, Figure 3, includes control valves and low-pressure regulators for exacting control of carrier gas and adsorbate, a sample cell for the catalyst samples being studied, and a thermal conductivity cell for detection of desorbed gases. The thermal conductivity cell is a four-element model which, when connected to an integrating recorder (1.0 mV full scale), can measure differences in composition as low as 200 ppm by volume.

The carrier gas used in the sorptometer is helium (Airco, Grade 5, 99.999%); the adsorbates are nitrogen (Airco, Grade 5, 99.999%) or carbon dioxide (Airco, Grade 4, 99.99%). These gases have been purified before entering the sorptometer by passage through 0.4 nm molecular sieves and a cold trap, which is liquid nitrogen or crushed dry ice-acetone mixture for nitrogen and carbon dioxide, respectively. The capillary tubing dampens any flow variations or irregularities; the regulator is used to control the individual gas flows in the range of 0–40 cm^3/60 s. The actual flow rates of the individual gases can be measured by a soap bubble meter connected to the instrument exhaust.

The sample cell consists of two vertical concentric Pyrex tubes of different lengths, Figure 4. The outer tube is sealed at the bottom; approximately 0.1 g of sample is placed in the tube to form a bed 1 cm in diameter and 0.3 cm in depth. Gas flows into the cell through the annulus between the tubes and exits through the center tube. Two microthermocouples are placed in the solid sample to monitor sample temperature and thermal gradients during the desorption experiments. To facilitate heating the

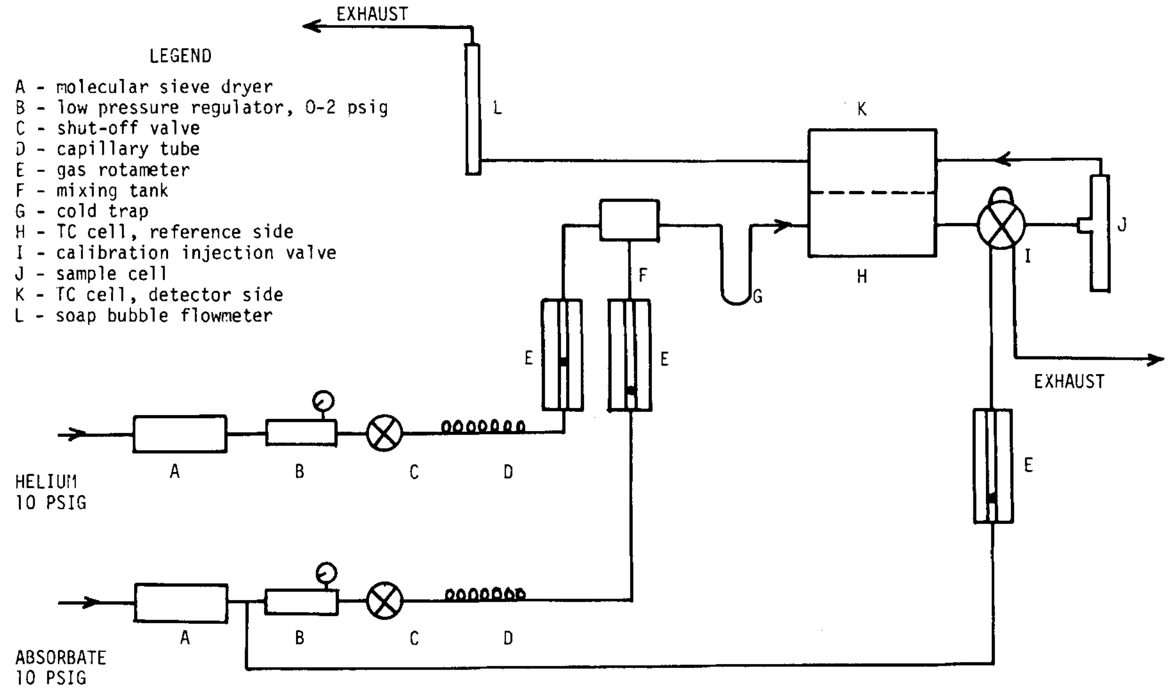

Figure 3. Sorptometer schematic.

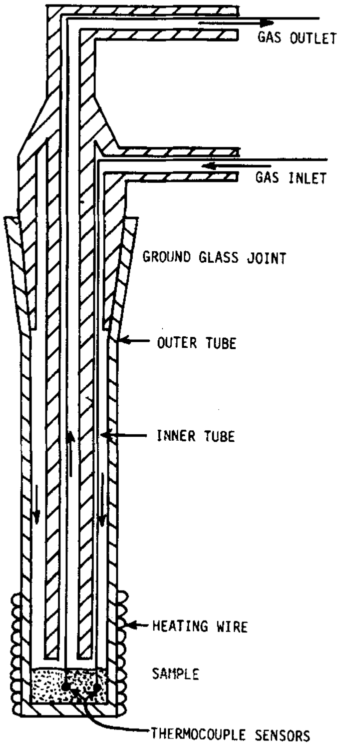

Figure 4. Sample cell schematic.

sample, a Chromel wire is wrapped around the outside of the sample cell and connected to a DC power supply. The heating rate can be changed by varying the DC voltage to the wire.

Procedure

Two types of experiments are performed in the continuous flow sorptometer; BET surface area measurements and thermal desorption experiments. The procedure for the BET experiment is well documented and will not be discussed. The following section describes the experimental procedure for the thermal desorption, used in the catalyst surface area measurement.

Warm-Up. At the start of an experiment, the individual carrier gas and adsorbate flows are set to give the desired composition corresponding to a coverage slightly less than monolayer, determined previously from BET experiment. With the flows set, the apparatus is allowed to stand for 15 minutes to flush all impurities from the system. The cold trap is then placed in the cooling fluid appropriate for the adsorbate used in the experiment. At this point the power to the conductivity cell can be turned on and the entire apparatus allowed to equilibrate for one or two hours for a steady recorder baseline. The sample is then degassed in situ by placing the heating wire around the cell and heating the sample to 150°C for 30 min.

Adsorption. With the heating wire in place and the instrument at steady state, the sample cell is immersed to a depth of about 1 in. (25 mm) into the cooling fluid appropriate for the adsorbate. The signal from the TC cell and the temperature are monitored to determine when the sample cell has reached a steady state at the adsorption temperature, T_a.

Thermal Desorption. To initiate thermal desorption, the power supply to the heating wire is turned on to give the desired heating rate, and the sample cell is immediately removed from the coolant. The sample cell is allowed to heat up to room temperature or above, until all gas has desorbed from the sample. For our experiments the maximum temperature reached was 40°C, at which point the power supply was shut off and the sample cell allowed to cool. This adsorption-desorption cycle is repeated several times for each solid sample.

Postexperimental Measurements. Three additional pieces of information are necessary for proper analysis of the thermal desorption data. The desorption peak is integrated by the recorder for the volume of adsorbate in the thermal desorption runs and the result given in arbitrary units. To convert these units to a volume of adsorbate, a known volume of adsorbate is injected into the gas stream via the sample injection valve for the calibration. This injection of adsorbate takes place with the sample cell at room temperature, immediately after the desorption runs.

There is a finite length of tubing between the sample and detector through which the gas must flow, resulting in a "lagging" of the TC cell output behind the temperature outputs. To measure this "lag" time, the tip of sample cell can be immersed in the

TABLE 2. RESULTS OF BET EXPERIMENTS FOR PURE COMPONENTS

Component	$V_{m,CO_2}\,\frac{\text{cm}^3\text{ (STP)}}{\text{g}}$	$V_{mN_2}\,\frac{\text{cm}^3\text{ (STP)}}{\text{g}}$	$S, \frac{\text{m}^2}{\text{g}}$	R	Source
Carbon Black	2.62	6.14	26.8	0.43	Fisher Scientific
Potassium Carbonate	0.113	0.183	0.80	0.62	Fisher Scientific
Alumina	0.069	0.179	0.78	0.38	Norton Co. #SA-5202
Silver	0.023	0.048	0.21	0.48	Alfa-Ventron 2.0–3.5

coolant for an instant and then removed. With the TC cell recorder chart drive on, the time it takes for the small adsorption peak to reach the TC detector is a measure of the lag time, which allows the temperature and volume curves to be brought together for simultaneous calculation.

The final piece of information is the gas-phase composition, which is measured by the soap bubble flowmeter. This measurement is always deferred until the thermal desorption runs for all samples in the system being studied have been completed, for it is necessary to shut off one of the gas flows to measure the other. Disturbing the gas flow rates is not recommended during the thermal desorption experiments. The adsorbate volume fraction is determined from the difference of carrier and total flow rates.

Analysis of Data

The thermal desorption data consist of the two temperature and the TC cell recorder outputs, the calibration peak, and a measurement of the lag time between the sample and the detector. Usually several thermal desorptions are run for each solid studied. Since the experimental accuracy is related to the instrument stability, two of these runs which exhibit the most stable baseline are analyzed individually in this section.

Figure 5 shows the data from an actual thermal desorption for carbon dioxide desorption from a physical mixture of silver and carbon black. Figure 5b shows the TC cell output and the integrator output over the run. The baseline shifted during the desorption, but it is assumed that the shift is linear with time during the run. Therefore, the value of the area under the baseline must be subtracted from the total area under the desorption curve for the entire run to correctly calculate the desorbed volume of gas.

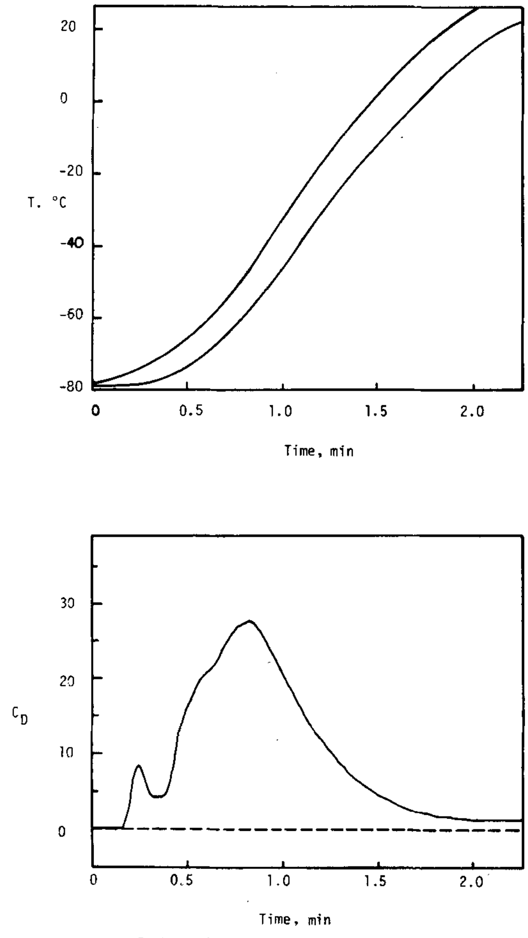

Figure 5. Raw data from thermal desorption.

To convert the TC cell output to a volume desorbed vs. time curve, the peak is divided into ten or twelve intervals. In each, the area under the desorption curve is found, and the appropriate linear baseline is subtracted to give the net desorption during the time interval. The fractional coverage can be calculated by subtracting the desorbed volume curve from the total amount of gas desorbed during the run. The two temperature values are averaged at each point, after being corrected for lag time. It is now possible to plot the volume adsorbed (or fractional coverage) of adsorbate as a function of solid sample temperature, completing the analysis of the desorption data.

RESULTS

Thermal desorption of carbon dioxide has been used to determine the catalyst surface for several systems. Experimental results for the binary systems potassium carbonate-carbon black and silver-alumina will be presented in this section. Other experiments for the systems silver-carbon black and platinum-alumina are reported by Miller (1982).

The necessary information for the determination of catalyst surface area includes total surface area as measured by nitrogen BET experiment, monolayer volume of carbon dioxide measured by BET, and the thermal desorption fractional coverage versus temperature curves for the catalyst and support. Also required are the ϑ-T curves for the supported catalyst. The necessary information for the two binary systems being considered is summarized in Table 2, along with the relative volume ratio R defined as

$$R = V_{m,CO_2}/V_{m,N_2}$$

Carbon Black-Potassium Carbonate

Five samples of potassium carbonate impregnated on carbon black were prepared by first dissolving the desired quantity of K_2CO_3 into water, and then adding an equal amount of acetone to the solution. The prescribed amount of carbon black was then added to the solution to form a slurry. This slurry was stirred for 15 min and then dried for 24 hours under partial vacuum at 363 K. The addition of acetone was necessary for the carbon to be wetted. In addition to the slurries for the impregnated samples, potassium carbonate was prepared by crystallization from the acetone-water solution, and pure carbon black was also put through the impregnation procedure in a solution which had no K_2CO_3 added. Following preparation, part of each sample was heated in air at 973 K to oxidize all carbon. The residue was weighed to give the weight percent of potassium carbonate. The pure carbon black contained only 0.1% residue. The weight percent of potassium carbonate for the five samples from the pyrolysis is given in Table 3.

The thermal desorption experiments for the two components and the five impregnated samples were carried out in a single twelve hour period, to assure that the partial pressure was the same for each sample. In addition, a similar sample weight and experimental procedure was used for all samples to minimize any errors resulting from unforeseen effects not predicted by our theory.

TABLE 3. THERMAL DESORPTION RESULTS OF K_2CO_3 IMPREGNATED CARBON BLACK

Sample	wt. % K_2CO_3	V_{ads}, $\frac{cm^3\ (STP)}{g}$, CO_2	θ^a	$I_c, I_k, \bar{I}$	$\frac{S_k}{S_t}$
Carbon Black	0	1.013	0.387	8.47	—
1	1.4	1.125	—	22.3	0.013
2	4.6	1.110	—	22.3	0.013
3	10.1	1.035	—	24.2	0.078
4	16.7	0.966	—	27.7	0.230
5	26.8	0.885	—	25.7	0.138
K_2CO_3	100	0.0668	0.593	21.64	—

The plots of fractional coverage, ϑ, vs. temperature for carbon black and potassium carbonate are shown in Figure 1a, and the graphs of fraction adsorbed, ϑ, vs. temperature for four of the impregnated samples are shown in Figure 1b. The results in Figure 1b show that the catalyst loading does not necessarily represent dispersion. The ϑ-T curves for the pure components are seen to be linearly independent, allowing the fractional surface area of potassium carbonate on each of the impregnated samples to be calculated without determining the total surface area of each sample. The equation used to calculate the fractional area is

$$\frac{S_k}{S_t} = \frac{R_c I_c - R_c \vartheta_c^a \bar{I}}{(R_k \vartheta_k^a - R_c \vartheta_c^a)\bar{I} - R_k I_k + R_c I_c} \tag{14}$$

which in Eq. 13 with potassium carbonate (k) as the component 1 and carbon black (c) as the component 2. The integrals I_c, I_k, and $\bar{I}$ are determined numerically using the trapezoid rule with $\Delta T = 2.5$ K over the range 198 to 273 K. The values of ϑ_k^a and ϑ_c^a are determined from the total volume adsorbed on the pure components at the start of the thermal desorption. The data and results for the impregnated samples are given in Table 3.

Equation 14 is actually a special case of the more general derivation for catalyst surface area determination. The expression for the general case is

$$\frac{S_k}{S_t} = \frac{\frac{V_{ads,CO_2}}{V_{m,N_2}}\bar{I} - R_c I_c}{R_k I_k - R_c I_c} \tag{15}$$

which is Eq. 10 for the system under consideration. The disadvantage of using this expression is that the nitrogen monolayer volume V_{m,N_2} must be determined for the impregnated sample before the fractional area S_k/S_t can be determined. Thus the fractional area can be determined by Eq. 15 above without knowledge of the total supported catalyst surface area, but to determine S_k (catalyst area per gram) it is necessary to determine V_{m,N_2} and hence S_t. Of the five impregnated samples evaluated, the total surface area S_t was determined only for Sample 4, 16.7 wt. % K_2CO_3. For this sample, $V_{m,N_2} = 5.06$ cm^3 (STP)/g, giving a surface area $S_t = 22.1$ m^2/g. By Eq. 15, the resulting fractional area is $S_k/S_t = 0.17$, which is in fairly good agreement with the value obtained from Eq. 14. These results are determined independently of each other; Eq. 14 calculates the area based on the linear dependence of the ϑ-T curves for the pure components, and Eq. 15 is calculated based on differences in the value of ϑ for the two components. The result given shows the consistency of the data.

Several analytical methods have been attempted to obtain an independent measure of potassium carbonate surface area and thus verify the results obtained by thermal desorption. Two X-ray studies and transmission and scanning electron microscopy revealed no useful information. X-ray line broadening for Sample 4 and Sample 5 yielded only a crystallite size of 14 nm for both samples. From the data reported for the surface area of Sample 4, the spherical particle size estimated from the weight percent of K_2CO_3 and the fractional surface area is of the range of 0.1 μ. Thus the line broadening gives a crystallite size smaller than the calculated particle size. Small angle X-ray scattering on Sample 4 also gave no useful information. Since the maximum particle size measurable using small angle scattering is approximately 50 nm, the particles in the sample may have been too large for analysis. Scanning and transmission electron microscopy similarly yielded no useful information about potassium carbonate area, since it was impossible to distinguish between K_2CO_3 and carbon particles when the samples were examined in the microscopes. Thus none of the analytical methods tried gave positive verification of the results obtained by the thermal desorption experiment.

TABLE 4. THERMAL DESORPTION OF PHYSICALLY MIXED CARBON BLACK—K_2CO_3

Sample	$W_{K_2CO_3}$	$(S_k/S_t)_{calc}$	θ^a	$\bar{I}, I_c, I_k$	$(S_k/S_t)_{exp}$
Carbon	0.0	0	0.714	11.66	—
1	0.888	0.192	—	21.6	0.15
2	0.969	0.484	—	26.9	0.37
3	0.980	0.589	—	28.9	0.49
4	0.987	0.692	—	31.5	0.69
5	0.992	0.794	—	33.5	0.88
K_2CO_3	1.0	1.0	1.189	41.0	—

To obtain partial verification of the method, five samples of physically mixed powders of carbon black and potassium carbonate were prepared for analysis by thermal desorption. Weighed amounts of the two components were placed together and mixed, so that the surface area of each component was known. The K_2CO_3 surface areas can be calculated from

$$\frac{S_k}{S_t} = \frac{\bar{S}_K W_K}{\bar{S}_K W_K + \bar{S}_c(1 - W_K)} \tag{16}$$

where W_K is the weight fraction of K_2CO_3 in the physically mixed sample and $\bar{S}_K$ and $\bar{S}_c$ are the total surface areas per gram of K_2CO_3 and carbon black respectively. The physically mixed samples were analyzed by thermal desorption in the same manner as the impregnated samples. The fractional areas calculated from Eq. 16 and the fractional areas determined by thermal desorption are given in Table 4. A plot of the experimentally determined areas vs. the calculated values is given in Figure 6.

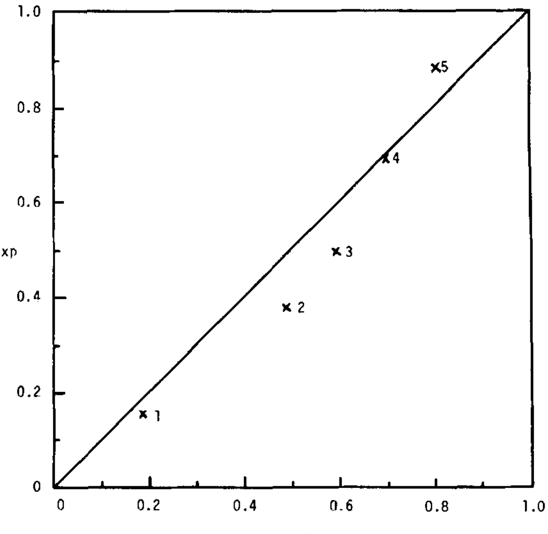

Figure 6. $(S_K/S_T)_{calc}$ vs. $(S_k/S_T)_{exp}$ for physically mixed K_2CO_3-carbon.

TABLE 5. THERMAL DESORPTION OF Ag-Al_2O_3

Sample	wt. % Ag	S_T, m²/g	$V_{m,N_2} \frac{\text{cm}^3\ \text{(STP)}}{\text{g}}$	S_A/S_T	S_A
Ag	—	0.21	0.048	—	—
1	4.7	1.04	0.239	0.48	0.50
2	3.6	1.06	0.243	0.52	0.55
3	6.4	1.17	0.268	0.59	0.69
Al_2O_3	—	0.78	0.179	—	—

TABLE 6. O_2 CHEMISORPTION ON Ag-Al_2O_3

Sample	Vol. O_2 Chemisorbed $\frac{\text{cm}^3\ \text{(STP)}}{\text{g}}$	Thermal Desorption Silver Area S_A, m²/g
1	0.022	0.50
2	0.037	0.55
3	0.046	0.69

The use of physical mixtures is only a partial verification of the thermal desorption method. Nevertheless, the results obtained show that fractional areas can be calculated for distinct components.

Silver-Alumina

To gain a positive verification of the surface area measurement by thermal desorption, it was necessary to choose a catalyst system for which the catalyst surface area could be measured by an independent method. Silver catalyst supported on alumina was chosen with the expectation of obtaining the silver surface area by oxygen chemisorption or scanning electron microscopy. A further objective was to demonstrate the application of thermal desorption method to metallic as well as nonmetallic catalysts.

Three samples of silver impregnated on alumina were prepared by chemical deposition of silver. The method for chemical deposition was described in detail by Forzatti et al. (1973). The loading of silver was varied by exposing one catalyst to single impregnation, the second to double impregnation, and the third to triple impregnation. The weight percent silver on each sample was determined by Volhard's method, described by Christian (1980).

The alumina support consisted of fused alumina pellets about 1 cm in diameter, made from 1 to 3 μ nonporous alumina spheres bonded to each other by heat and pressure. The pellets were crushed and sieved to retain particles of size 0.074–0.5 mm (−32 + 200 mesh). Attempts to procure pure silver powder by the chemical deposition method were unsuccessful, so a silver powder of 2.0–3.5 μ diameter particles was used as the silver pure component. This silver powder was reduced along with the impregnated samples to obtain as much similarity between pure and supported silver surfaces as possible.

The thermal desorption experiments for silver and alumina showed that the ϑ-T curves for the two components are not linearly independent but instead differ only by a multiplicative constant. This restricts the analysis to the use of Eq. 15, using the proper parameters for silver and alumina. The silver and alumina ϑ-T curves are given in Figure 2, and the experimental results of the thermal desorption are given in Table 5 for the three samples studied. Since the integrals I_{A1}/ϑ^a_{A1}, I_A/ϑ^a_A and $\bar{I}$ for the three samples were identical, the calculation of fractional surface area could be carried out by the following simplified formula

$$\frac{S_1}{S_t} = \frac{\dfrac{V_{\text{ads},CO_2}}{V_{m,N_2}} - R_{A1}\vartheta^a_{A1}}{R_A\vartheta^a_A - R_{A1}\vartheta^a_{A1}}$$

which is obtained by dividing through by the value of $\bar{I}$. This formula requires only the initial conditions of adsorption for calculating fractional area, and is useful for estimation in cases where the ϑ-T curves for the two components are linearly dependent.

In order to verify the surface areas determined by thermal desorption, oxygen pulse chemisorption (Akella, 1983) was carried out. The experimental results from the oxygen chemisorption are given in Table 6. Oxygen adsorption on silver is not fully understood: the unknown stoichiometry of the adsorption and the fact that the quantity adsorbed goes through a maximum at 433–473 K are two major uncertainties in the process. Nevertheless, the results given in Table 6 show that the silver areas determined from thermal desorption and the volumes of oxygen chemisorbed are in qualitative agreement, both increasing with the sample number.

To further study the silver surface, scanning electron microscopy of the three samples was done. Twelve photographs of each sample were taken at ×48,000, giving about six hundred particles for each sample. The particles have been counted and weight-averaged to determine an average particle size. The results obtained are inconclusive for the determination of silver catalyst area. The only information obtained was by visual examination of the pictures, which showed that the area of silver was of the order of 20 to 50% of the total area. The uncertainty in measuring particle diameter is larger than the differences in silver area for the three samples, so that all micrographs appear to be from a single sample and are indistinguishable. This is a general difficulty with the use of microscopy for determining supported catalyst surface areas. Factors such as particle shape and catalyst heterogeneities from one position on the surface to another prevent practical use of microscopy for area measurements.

The silver-alumina system studied here has provided a partial verification of the thermal desorption method. The use of oxygen chemisorption has provided qualitative verification of the relative values of catalyst surface area determined by thermal desorption, but lack of information on the oxygen-silver stoichiometry has prevented a comparison of absolute surface areas. Most importantly, however, the success of the thermal desorption method on this system shows applicability in general to metallic catalysts, even for cases where the difference in the ϑ-T curves for the two components do not differ greatly.

DISCUSSION

The determination of the relative surface areas of two components of a solid (a supported catalyst) depends on several assumptions. The first is that the fractional coverage of each component depends only on temperature during rapid thermal desorption even though it is also a function of adsorbate partial pressure. This has been well documented (Miller, 1982) by our experiments, both by recording the ϑ versus temperature curves at various heating rates, and by step changing and then holding the temperature at various levels while recording the differential volumes of gas desorbed. These results give strong evidence as to the sole dependence of coverage on temperature. The second assumption is that the fractional coverage versus temperature curves obtained for the pure components can be used for the two component solid area determination. This is strictly true only if each of the two components has the same surface structure as in its pure state. However, unless a catalyst forms very small crystals or forms a thin layer on the support surface, it can be assumed that the surface structures will not differ greatly for a given catalyst, regardless of whether it is pure or in a supported state. To assure this, the pure components used in the experiments were prepared in exactly the same manner as the supported catalyst. The third assumption is that of submonolayer coverage for all surfaces. If a surface is non-porous and energetically homogeneous, the adsorbent will form a well-defined statistical monolayer which can easily be determined by a BET experiment. If, however, the surface is irregular, the volume at monolayer coverage is not well defined, and at high partial pressures multiple layers of adsorbate could form at some points on the surface. For irregular surfaces, the values of the partial pressure should be adjusted so that the initial fractional coverages are in the range $0 < \vartheta \leq 0.7$. This will assure that there is no multilayer formation.

Perhaps the most important fact to recognize for the experimental method is that it utilizes the difference in desorption characteristics of two components in a binary system as characterized by the ϑ-T curves. The method does not necessarily require information on desorption kinetics provided that, at an adsorbate partial pressure corresponding to a sub-monolayer coverage, a unique value of coverage exists for a given temperature, thus allowing the generation of a unique ϑ vs. T curve. Thus, static experimental method can be used to generate such adsorption isobars. The dynamic method was used in our experiments to generate the adsorption isobars because it is much faster than collecting a series of static points, and further is easier and just as accurate, as our extensive calculations and experimental results (Miller, 1982) attest.

As for the reproducibility of ϑ-T curves, we have found in our experiments that the ϑ-T curves for each of the runs are within ± 0.01 the average value of ϑ for all runs, at a given temperature. Thus the maximum deviation for any two runs is $\Delta\vartheta = 0.02$ at a given temperature, for a given sample. Detailed analysis (Miller, 1982) of the sensitivity involved in calculating the frictional surface area showed that the maximum possible deviation in calculating S_1/S_t for silver and alumina, for which the difference in the desorption characteristics is relatively small, is 26%. This leads us to conclude that the separation of the ϑ-T curves for this system is near the minimum required separation for successful application of the thermal desorption method.

One limitation of the experimental method is in the choice of an adsorbate that will give the necessary separation in the ϑ-T curves. For instance, the characterization of platinum-alumina system using carbon dioxide as adsorbate failed because the ϑ-T curves are too close together to allow analysis of supported platinum catalysts. However, the fact that this method can be used for systems where chemisorption, X-ray line broadening, small angle X-ray scattering, and electron microscopy methods fail, as was the case for silver/alumina and potassium carbonate/carbon black, amply demonstrates the usefulness of the new experimental method. Nevertheless, further refinements of the method are required to make the method more practical.

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NOTATION

f_a = rate of absorption
f_d = rate of desorption
I_1,I_2 = integral of pure component ϑ vs. T curve for components 1 and 2
$\bar{I}$ = integral of supported catalyst or physically mixed sample $\bar{\vartheta}$ vs. T curve
k_a = adsorption rate constant
k_d = desorption rate constant
p = adsorbate partial pressure
R_1,R_2 = molar volume ratios of adsorbate on components 1 and 2
S_o = total surface area of solid
S_1,S_2 = surface area of components 1 and 2 in two component solid
S_t = total surface area of two component solid
T = temperature of sample
T_a = minimum temperature of adsorption, usually liquefaction temperature of adsorbate
v_m = volume of gas occupying monolayer coverage per unit area of solid
$v_{m,1},v_{m,2}$ = monolayer volume of adsorbate per unit area of components 1 and 2
v_{m,N_2} = monolayer volume of nitrogen per unit area
$V_{ads}(T)$ = volume of gas adsorbed on a solid at T
$V_{m,1},V_{m,2}$ = monolayer volume of adsorbate per gram of pure components 1 and 2
V_{m,N_2} = monolayer volume of nitrogen per gram

Greek Letters

ϑ = fractional surface coverage of solid
ϑ_1,ϑ_2 = fractional coverage of components 1 and 2 in two component solid
$\vartheta_1^a,\vartheta_2^a$ = initial fractional coverage of components 1 and 2 at initial temperature T_a
$\bar{\vartheta}$ = fraction of gas adsorbed on two component solid

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