Further Development of Selective Physisorption for Measuring Catalyst Surface Area

Platinum supported on silica is used as a model supported catalyst for the purpose of demonstrating that the selective physisorption method yields the fractional catalyst surface area of supported catalysts, including metal compounds catalysts for which the method is primarily intended. The selective physisorption results with nitrous oxide as adsorbate are compared with hydrogen chemisorption results for this purpose. Experimental and theoretical refinements of the method developed earlier in our laboratory are presented that allow rather accurate determination of the catalyst surface area. The refinements also make the method effective even when the catalyst covers a small portion of the total surface area. Because of the nature of physisorption, the method should be applicable to any supported catalyst including metal compounds catalysts, provided a suitable adsorbate is used. Adsorbates other than nitrous oxide and carbon dioxide which are suitable for selective physisorption, are suggested.

I. A. TOOR and H. H. LEE

Department of Chemical Engineering
University of Florida
Gainesville, FL 32611

SCOPE

An experimental method based on selective physisorption has been developed by Miller and Lee (1984) for determining the active catalyst surface area. While the method has been applied to several physical mixtures and supported silver catalysts with carbon dioxide as adsorbate, no definitive comparison has been made for the active surface area of a supported catalyst between the selective physisorption and an established alternate method of determining the catalyst surface area. Such a comparison based on a well-defined supported catalyst would open the way to the application of the method to those supported catalysts for which the traditional methods such as chemisorption fail to give the catalyst surface area. One drawback of the original work is that the method is efficient only when the catalyst covers a large portion of the total support surface. In order for the method to be more practical, a way has to be found to make it more sensitive to small catalyst surface area. This paper presents further development of the experimental method that deals with the two aspects of the method described above.

CONCLUSIONS AND SIGNIFICANCE

Experimental as well as theoretical refinements have been made in the original method of selective physisorption for determining the active surface area of supported catalysts. With the refinements, the effectiveness of the method has been tested on platinum catalysts supported on silica using nitrous oxide as adsorbate. The following conclusions can be drawn from the results:

1. Selective physisorption of nitrous oxide allows rather accurate determination of the fractional platinum surface area of the catalysts supported on silica. The results are in satisfactory agreement with those of hydrogen chemisorption.
2. The use of packing factor in place of the fraction of total volume adsorbed (coverage ϑ in Miller and Lee, 1984) results in a better sensitivity to small catalyst surface area and thus allows the fractional area to be determined even when the catalyst covers a small portion of the support surface.
3. An adsorbate exhibiting a large asymmetric directional polarizability is a good candidate for use in the selective physisorption technique.

INTRODUCTION

A new experimental method of measuring the active surface area of supported catalysts using selective physisorption of gases has been put forward recently by Miller and Lee (1984). The basic idea in the original development was that a mono- or submonolayer volume of a gas physisorbed on a two-component solid, as in supported catalysts, should distinguish between the

Correspondence concerning this paper should be addressed to H. H. Lee.

two different surfaces upon thermal desorption if the interactions between the gas and the surfaces are strong, say 3 to 6 kcal/mol in terms of the heat of adsorption. The desorption characteristics of gas coverage with temperature for the catalyst, the support, and the supported catalyst were used by Miller and Lee to calculate the fraction of the total surface area occupied by the catalyst. Because of the nature of physisorption, the selective physisorption method should be applicable to any supported catalyst, including oxides and metal compounds catalysts, provided a suitable adsorbate is used. This contrasts with the chemisorption method (Spenadel and Boudart, 1960; Adler and Kearney, 1960), which does not yield the catalyst surface area of some metal catalysts and the majority of metal compounds catalysts because of the specific nature of chemisorption, although it yields valuable information on the sites active to a chemisorbing gas. It should be noted in this regard that Parekh and Weller (1977) developed a method of determining catalyst surface area based on a low-temperature oxygen chemisorption for oxide catalysts.

In the original development (Miller and Lee, 1984), thermal desorption of physically adsorbed carbon dioxide on the surfaces of potassium carbonate-carbon black mixtures was used to determine the fractional surface area of each component in the physical mixtures. A qualitative comparison between selective physisorption and oxygen chemisorption results was also given for supported silver catalysts. Nevertheless, no conclusive evidence was presented as to the effectiveness of the selective physisorption method as applied to supported catalysts. Further, the thermal desorption experiments and the data analysis are such that the method was effective only when catalyst loadings are high and the catalyst covers a significant portion of the total surface area. In this paper, we present refinements of the original method that allow rather accurate determination of the catalyst surface area even when the catalyst covers a small portion of the total surface area. We also present evidence of the validity of the selective physisorption method as applied to a supported catalyst.

In order to provide a definitive comparison, a catalyst system was sought that is amenable to a well-established method of measuring the active surface area of the supported catalyst. Platinum supported on silica was chosen for the comparison since the hydrogen chemisorption has been well established as a reliable method of measuring the catalyst surface area. Although carbon dioxide was used as adsorbate in the original development, nitrous oxide was selected in this study in accordance with the recommendation made earlier (Miller and Lee, 1984) based on the directional polarizability data given by Ross and Oliver (1964). The criteria for the selection of adsorbate have been discussed in detail by Miller and Lee and will not be presented here. Experiments were also conducted using carbon dioxide.

We present the theoretical development first, which brings out the refinements of the original experimental procedures and the corresponding analysis method, before we proceed to the Experimental section.

THEORETICAL

The original method utilized the difference between gas coverage (ϑ) vs. temperature (T) relationships of the mono- or submonolayer of a physisorbed gas on the support and the catalyst to determine the fraction of the total surface area covered by the catalyst. It was assumed that a pseudosteady state exists during transient thermal desorption of the mono- or submonolayer of the physisorbed gas. Therefore, a single thermal desorption experiment was sufficient to obtain a ϑ–T relationship. The pseudo-steady-state assumption was avoided in this study. Instead, constant temperature baths were used to determine the amount of gas adsorbed at each temperature for the purpose of generating a more accurate ϑ–T relationship. The motivation is that the constant-temperature baths would provide more accurate adsorption isobars than the transient desorption could, and would thus enhance the accuracy with which the catalyst surface area can be determined since the accuracy is strongly dependent on that of the ϑ-T relationships.

Although the motivation for the use of equilibrium isobars was to obtain more accurate ϑ-T relationships, it was found in the course of the study that the use of "packing factor," which is the amount of gas adsorbed per unit surface area, in place of ϑ would allow more accurate determination of the fractional catalyst surface area. For instance, consider Figure 1, which compares the spread of the ϑ–T curves of the pure components of potassium carbonate and carbon black mixtures obtained by Miller and Lee with the spread of the γ (the packing factor expressed as volume of gas adsorbed per unit N_2 BET area) vs. T curves generated from the same data. It is clear that the spread of the γ–T curves is larger than that of the ϑ–T curves and therefore the γ–T curves will provide a better sensitivity. In the light of this development it was necessary to develop an expression for the determination of the fractional surface area based on the packing factor rather than ϑ in order to take advantage of the better sensitivity afforded by the packing factor.

If we let v_1 and v_2 be the volumes of the submonolayer of a gas adsorbed on the surfaces 1 (catalyst) and 2 (support) in the supported catalyst, the total volume of the gas adsorbed on the supported catalyst v_t is simply the sum of v_1 and v_2:

$$v_t(T) = v_1(T) + v_2(T) \tag{1}$$

Further if we let $\vartheta_i(T)$ be the fraction of the surface i which is covered by the adsorbate at temperature T, the total surface area of the supported catalyst, S_t, is given by

$$S_t = \frac{v_1}{\vartheta_1}\frac{1}{R_1} + \frac{v_2}{\vartheta_2}\frac{1}{R_2} \tag{2}$$

where the factor R_i is given by

$$R_i = \frac{\text{cm}^3 \text{ adsorbate on surface } i}{\text{m}^2 \text{ surface area of surface } i} \tag{3}$$

Since v_i cannot be measured but v_t can, we rearrange Eq. 2 with the aid of Eq. 1 to get

$$v_1(T) = \frac{S_t - v_t(T)/R_2\vartheta_2}{1/R_1\vartheta_1 - 1/R_2\vartheta_2} \tag{4}$$

Further, the fractional catalyst surface area S_1/S_t is given by

$$\frac{S_1}{S_t} = \frac{1 - \left(\frac{v_t}{S_t}\right)\left(\frac{1}{R_2\vartheta_2}\right)}{1 - \left(\frac{R_1\vartheta_1}{R_2\vartheta_2}\right)} \tag{5}$$

which follows from Eq. 4 and the relationship $S_1 = v_1/R_1\vartheta_1$. Since Eq. 5 yields a result at any temperature, the equation can be integrated over the temperture range of interest and still retain its validity. The integration cancels the scatter in the experimental data and gives a value averaged over the temperature range.

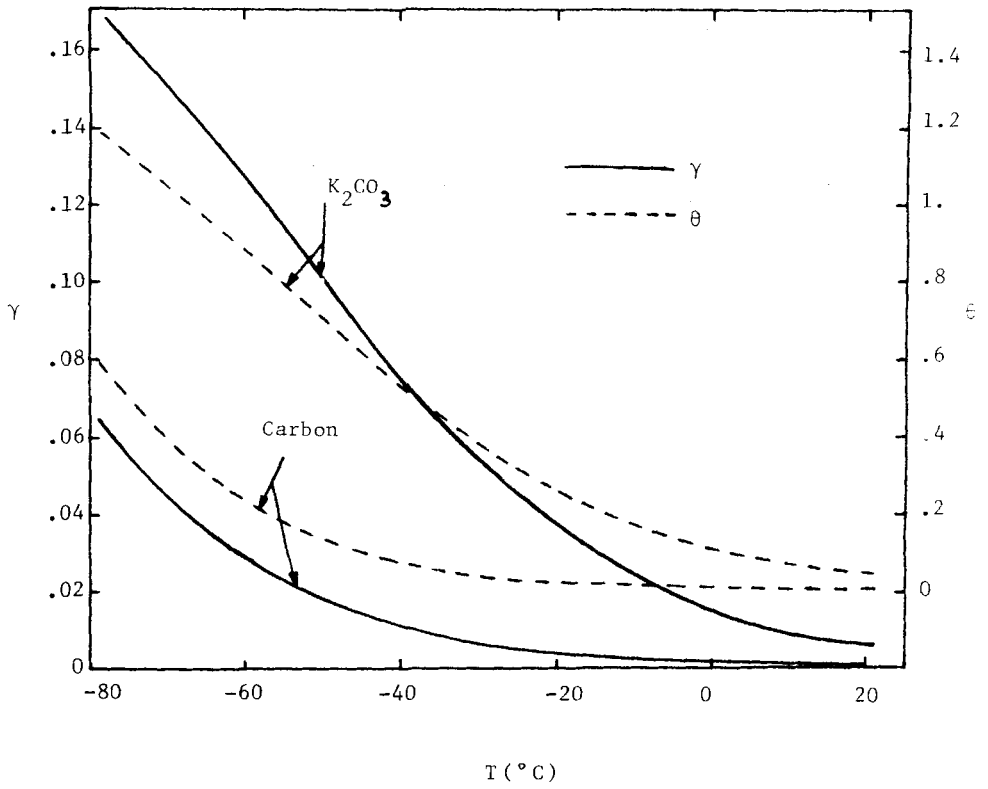

Figure 1. γ–T vs. ϑ–T curves of pure components for the mixtures of K_2CO_3 and carbon.

Multiplying S_1/S_t by the numerator of Eq. 5 integrating, and rearranging yields the following final result:

$$\frac{S_1}{S_t} = \frac{I_1}{I_t} \tag{6}$$

where

$$I_1 \equiv \int_{T_i}^{T_f} \left[1 - \left(\frac{v_t}{S_t}\right)\left(\frac{1}{R_2\vartheta_2}\right)\right] dT \tag{7}$$

$$I_t \equiv \int_{T_i}^{T_f} \left[1 - \frac{R_1\vartheta_1}{R_2\vartheta_2}\right] dT \tag{8}$$

Here T_i and T_f are the temperatures chosen for integration in the temperature range of interest.

The values of $R_i\vartheta_i$ can readily be obtained experimentally for the two pure components constituting the supported catalyst. The definitions of R_i and ϑ_i, where applied to the pure components, yield:

$$[R_i\vartheta_i(T)]_{\text{pure}} = \frac{U_i(T)}{(N_2 \text{ BET area})_{i,\text{pure}}} \equiv \gamma_i(T) \tag{9}$$

where U_i is the submonolayer volume of the gas adsorbed on pure catalyst ($i = 1$) and pure support ($i = 2$) surfaces at temperature T. It should be noted that U_i is different from v_i. For the platinum catalyst supported on silica, for example, the volume of gas adsorbed on pure platinum particles is U_1 whereas the volume of gas adsorbed on the platinum dispersed in the supported catalyst is v_1. If we assume that the quantity $R_i\vartheta_i$ for the surfaces in supported state is proportional to that for the surfaces in pure state, we have

$$R_i\vartheta_i(T) = b_i\gamma_i(T) \tag{10}$$

where b_i is the proportionality constant. However, if the adsorbate is indeed physisorbed it will not distinguish between pure and dispersed states of the catalyst and therefore constants b_i should assume a value of unity except in the case of strong metal-support interaction or very small crystallites. For such an adsorbate, $R_i\vartheta_i$ is equal to γ_i and all the quantities in Eqs. 7 and 8 can readily be obtained from experiments, thus allowing the calculation of the fractional catalyst surface area from Eq. 6 because Eqs. 7 and 8 reduce to:

$$I_1 = \int_{T_i}^{T_f} (1 - \gamma_t/\gamma_2)\, dT \tag{11}$$

$$I_t = \int_{T_i}^{T_f} (1 - \gamma_1/\gamma_2)\, dT \tag{12}$$

where $\gamma_t = v_t/S_t$.

EXPERIMENTAL

Platinum/silica catalysts were prepared by impregnating silica (Alpha, 99.5% SiO_2 −400 mesh amorphous) with chloroplatinic acid solution. A stock solution was prepared by dissolving 5.1 g of chloroplatinic acid in 100 cm^3 of distilled water. 11.5, 24.5, and 36.0 cm^3 of this stock solution

TABLE 1. BET AND H_2 CHEMISORPTION RESULTS

Sample	N_2 Monolayer Vol. at STP cm^3/g	S_t BET area m^2/g	Amt. of H_2 Chemisorbed cm^3 H_2/g cat	Active Area* m^2 Pt/g cat
Pt particles	0.16	0.70	—	—
SiO_2	1.53	6.66	—	—
1 wt. % Pt on S_iO_2	1.22	5.79	67.6 (10^{-3})	0.324
5 wt. % Pt	1.19	5.66	7.7 (10^{-3})	0.037
10 wt. % Pt	1.11	5.26	59.0 (10^{-3})	0.283
15 wt. % Pt	0.96	4.57	54.7 (10^{-3})	0.262

* Area calculated from the amount of hydrogen chemisorbed.

were then added to three 5 g samples of sintered silica to prepare 5, 10, and 15 wt. % Pt catalysts, respectively. Each sample was heated to ~35°C until the water evaporated and a thick slurry was obtained. Each sample was allowed to stand for 24 h for impregnation. Intermittent stirring was continued during this 24 h period. The samples were then dried in an oven for 24 h at 120°C, followed by reduction in flowing H_2 for 17 h at 500°C.

Another catalyst sample with 1% loading of platinum on silica was prepared in the following manner. A calculated amount of chloroplatinic acid which gives 1% platinum loading on 10 g of silica was dissolved in 5 g of distilled water. The resulting solution was added to 10 g of amorphous silica (Alpha, 99.5% Si O_2-400 mesh amorphous) to obtain a thick slurry. This was allowed to stand for 24 h for impregnation. Intermittent stirring was continued during the 24 h period to maintain a uniform slurry. At the end of 24 h, the impregnated slurry was dried at 120°C for 24 h, followed by 16 h reduction at 500°C in a stream of flowing hydrogen. No pretreatment to improve the dispersion of platinum, was carried out for any of the catalysts.

In the BET and thermal desorption experiments, helium (Airco Grade 4.5, 99.995%) was used as the carrier gas with nitrogen (Line, Ultra-High Purity, 99.999%), carbon dioxide (Airco Grade 4, 99.99%) or nitrous oxide (Matheson, Ultra-High Purity, 99.999%) as the adsorbate. Each gas was purified by first passing through a 4 Å (0.4 μm) molecular sieve (Davison), followed by a cold trap. The cold trap consisted of a dry ice-acetone mixture when carbon dioxide or nitrous oxide was used as adsorbate and liquid nitrogen when nitrogen was used as adsorbate.

The experimental apparatus consisted of a Perkin Elmer continuous-flow sorptometer modified for thermal desorption studies. A detailed description of the apparatus has been given by Miller and Lee (1984) and will not be presented here.

The total surface area of each sample including pure platinum and pure silica was determined using nitrogen BET. Based on the BET results, the flow ratios of adsorbate to carrier gas were chosen for N_2O and CO_2 that correspond to a submonolayer coverage in the BET sense at −78°C, as detailed in the reference, for subsequent experiments for generating equilibrium isobars. Three constant-temperature cold baths made from acetone-dry ice, chloroform-dry ice, and chlorobenzene-dry ice mixtures were used to obtain constant temperatures of −78, −61, and −45°C (Phipps and Hume, 1968). The sample cell containing the catalyst sample was immersed in the cold bath and the system was allowed to equilibrate.

TABLE 2. SELECTIVE PHYSISORPTION AND HYDROGEN CHEMISORPTION FOR PLATINUM CATALYST SUPPORTED ON SILICA

Sample	% Platinum Area ($100 S_1/S_t$) H_2 Chemisorption	N_2O Physisorption
1 wt. % Pt	5.6	8.6
5 wt. % Pt	0.7	−0.9*
10 wt. % Pt	5.4	4.9
15 wt. % Pt	5.7	6.9

* This is the actual calculated value which is within the experimental error and should be considered as 0%.

Equilibrium was determined by a constant reading of the temperature recorder for a period of 4 to 5 min and a stable response from the thermal conductivity cell. After the equilibrium had been reached, the cold bath was removed instantaneously and the sample cell was heated to desorb the gas. The response of the thermal conductivity cell was recorded using an integrator recorder. A minimum of two readings were taken at each temperature. A 0.5 cm^3 pulse of adsorbate gas was used to calibrate the thermal conductivity cell response. The total amount of gas desorbed is v_t for the supported catalyst samples and U_i for pure platinum and pure silica samples.

All samples were processed one after another within a period of 24 h to insure minimal fluctuations in the gas flow rate. The gas flow rates were measured with a soap bubble meter after the last sample had been processed, as detailed in the reference.

A dynamic pulse method (Wanke et al., 1980) was used for the hydrogen chemisorption experiments. Nitrogen (Airco Grade 5, 99.999%) was used as the carrier gas. Pulses of 0.1 cm^3 of hydrogen (Airco, Grade 5.5, 99.9995%) were used for the chemisorption at 100°C. Each gas was purified by first passing through a bed of 4Å (0.4 mm) molecular sieve (Davison Chemical, Grade 513, 4–8 mesh beads) and then through a bed of copper.

RESULTS AND DISCUSSION

The BET and hydrogen chemisorption results are summarized in Table 1. The BET total surface area for each sample was determined using four data points at four different pressures. A one-to-one hydrogen to platinum correspondence was used to convert the amount of hydrogen chemisorbed on the active platinum surface area of the supported catalyst, using a value of 1.12 10^{19} Pt sites/m^2 (Spenadel and Boudart, (1960). It is interesting to note in Table 1 that the total BET surface area per gram of supported catalyst decreases with increasing platinum loading. This behavior could be due to the growing size of platinum crystallites as platinum loading increases. Large crystallites may block micropores and thereby cause a reduction in the total surface area of the supported catalyst.

The chemisorption results reported in Table 1 (equivalently in Table 2) need some comments. As indicated earlier, the impregnation procedures for the 1 wt. % Pt sample were different from those for the 5, 10, and 15 wt. % Pt samples. As apparent from the table, inefficient impregnation for higher-loading sample catalysts resulted in low platinum surface area. Because of the unusual behavior, the chemisorption experiments were repeated only to confirm the reported values in Table 2. This apparent drawback, however, was instrumental in demonstrating that selective physisorption can distinguish small differences in fairly small surface areas, which is an important feature because the technique was shown earlier (Miller and Lee, 1984) to be effective only for large surface areas. One can see for the higher-loading sample catalysts that the catalyst surface area increases as the loading increases from 5 to 10 wt. %. As the loading is further increased to 15 wt. %, the platinum surface area remains essen-

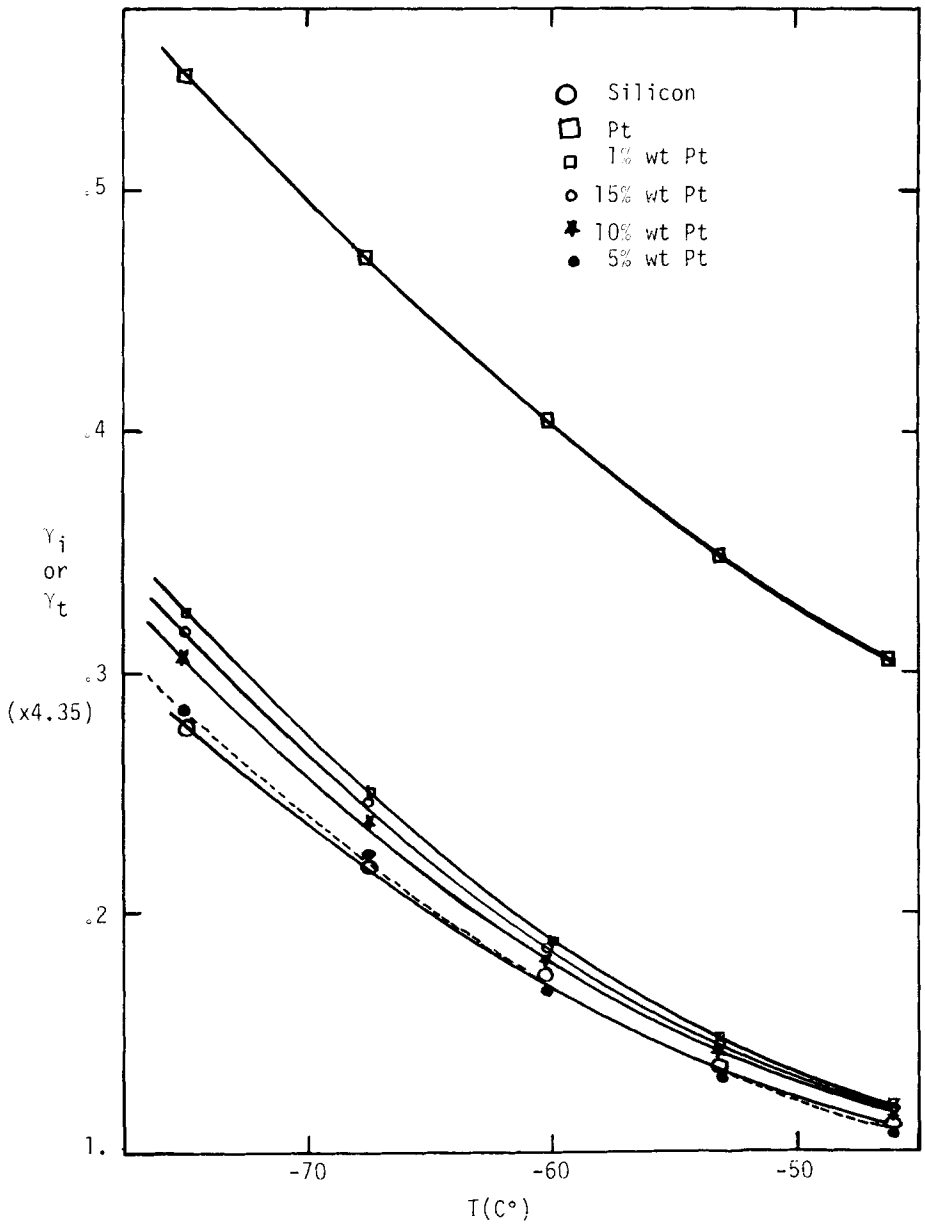

Figure 2. γ_i and γ_t for N_2O. N_2O adsorption on Pt-SiO_2 system (normalized curves). (P_{N_2O} = 0.101 bar)

tially the same (0.28 m^2 vs. 0.26 m^2). This is not very surprising at the high loading with inefficient impregnation. As the chemisorption result for the 1 wt. % sample, which was prepared differently, indicates, the impregnation procedures for the sample led to more efficient dispersion.

The equilibrium adsorption isobars obtained from experiments were normalized with respect to the total BET surface area. The results are shown in Figure 2 for the adsorbate nitrous oxide and in Figure 3 for the absorbate carbon dioxide. Given on the ordinate are $\gamma_i(T)$ for the pure platinum and silica and v_t/S_t for the supported catalyst samples. The fractional catalyst surface area, S_1/S_t, can readily be calculated from γ_t and v_t/S_t given in Figures 2 and 3 using Eqs. 6 and 10, provided b_i are known.

As indicated earlier, the values of b_i should be unity if the adsorbate is indeed physisorbed. For the results given in Figure 2, which is for the absorbate of nitrous oxide, the values of b_i were assumed to be unity. The fractional catalyst surface areas calculated from Eqs. 6 and 10 based on the experimental results in Figure 2 are given in Table 2. The integrals in Eqs. 7 and 8 were calculated using a four-point Simpson's rule in the temperature range of −78 to −45°C. The points used in the numerical integration are shown in Figures 2 and 3. The fractional catalyst surface areas determined from hydrogen chemisorption are also given in Table 2. The active surface area given in Table 1 was divided by

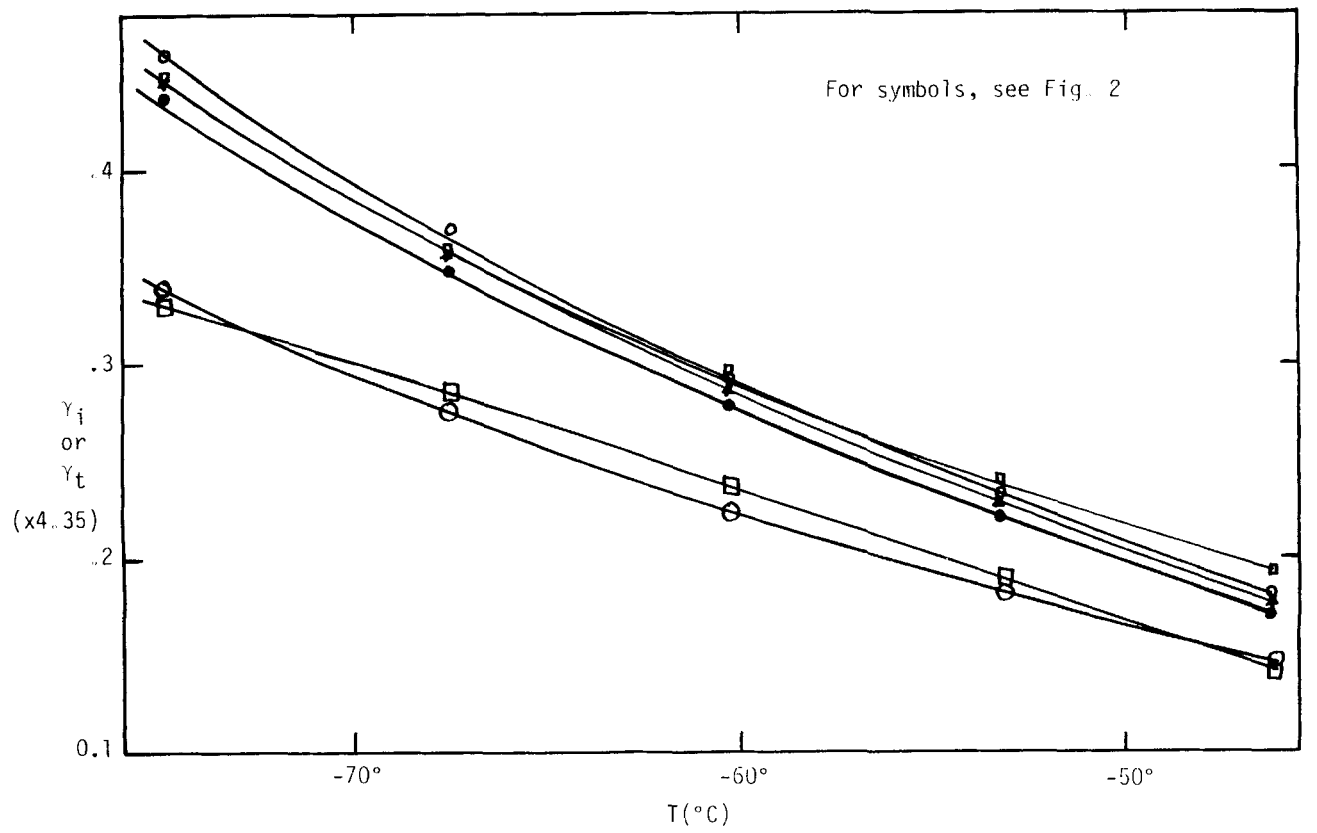

Figure 3. γ_i and γ_t for CO_2. CO_2 adsorption on Pt-SiO_2 system (normalized curves). (P_{CO_2} = 0.081 bar)

the total BET surface area to obtain the percent platinum area given in Table 2 under the heading H_2 chemisorption.

The comparison made in Table 2 between chemisorption and selective physisorption shows that for the higher loading samples (5, 10, and 15 wt. % Pt), the selective physisorption results for the percent platinum area compare well with the chemisorption results, i.e., −0.9% (0) vs. 0.7%, 4.9 vs. 5.4%, and 6.9 vs. 5.7% for 5, 10 and 15 wt. % Pt catalysts respectively. The comparison for the 1 wt. % Pt catalyst (8.6 vs. 5.6%) in not, however, as good as for the higher-loading samples. The crucial test for the selective physisorption method was whether it can distinguish between 0.7 and 5.7% platinum surface area in a reproducible manner, especially when the total platinum surface areas are as small as 0.037 and 0.324 m^2/g cat, respectively. While the selective physisorption results are not as accurate as hydrogen chemisorption is for platinum-silica catalysts, the comparison shows that it can still distinguish the difference between small variations of active catalyst surface areas. This finding is significant in light of the fact that there are at present no other experimental methods that can give such an accuracy for supported metal base oxide catalysts, for which the selective physisorption is intended, and even for some supported metal catalysts, as indicated by our previous attempts with x-ray diffraction/small-angle scattering and SEM/TEM techniques for the surface areas of potassium carbonate supported on carbon and silver supported on fused alumina (Miller and Lee, 1984).

If an independent method is available for comparison, as in the supported platinum catalyst, it is easy to determine whether the chosen adsorbate is indeed inert enough to set b_i equal to unity, since the comparison would allow this determination. For the supported catalysts for which an independent method is not available, the definition of b_i can be used to determine whether the chosen adsorbate is suitable for the selective physisorption method, i.e., whether the adsorbate is inert such that $b_i = 1$. According to the definition of b_i (Eq. 10), the adsorbate should not distinguish between pure and dispersed solids when $b_i = 1$. Thus, v_t/S_t should be the same if $b_i = 1$ whether it is for a physical mixture or a supported catalyst as long as S_1/S_t is the same for both. For the chosen adsorbate for a given catalyst, therefore, one can first assume that $b_i = 1$ and calculate (S_1/S_t) from Eqs. 6, 11, and 12. Using this calculated value of S_1/S_t, a physical mixture of the two components constituting the supported catalyst can then be prepared and v_t/S_t obtained experimentally. A comparison between (v_t/S_t) thus determined and (v_t/S_t) obtained for the supported catalyst should reveal whether the chosen adsorbate is suitable for the supported catalyst. The better sensitivity afforded by the use of γ–T relationship rather than ϑ–T relationship is illustrated in Figure 4 for the platinum catalyst being considered. As was the case in Figure 1, the use of the packing factor leads to a spread between the pure components larger than that for the ϑ–T relationships and thus allows a more accurate determination.

The results shown in Figure 3 for the adsorbate carbon dioxide immediately reveal that carbon dioxide is not a suitable adsorbate for the supported platinum catalyst. The results also reveal that b_i cannot be unity since γ_t curves do not lie between γ_1 and γ_2 curves. Nevertheless, the results are quite intriguing in that car-

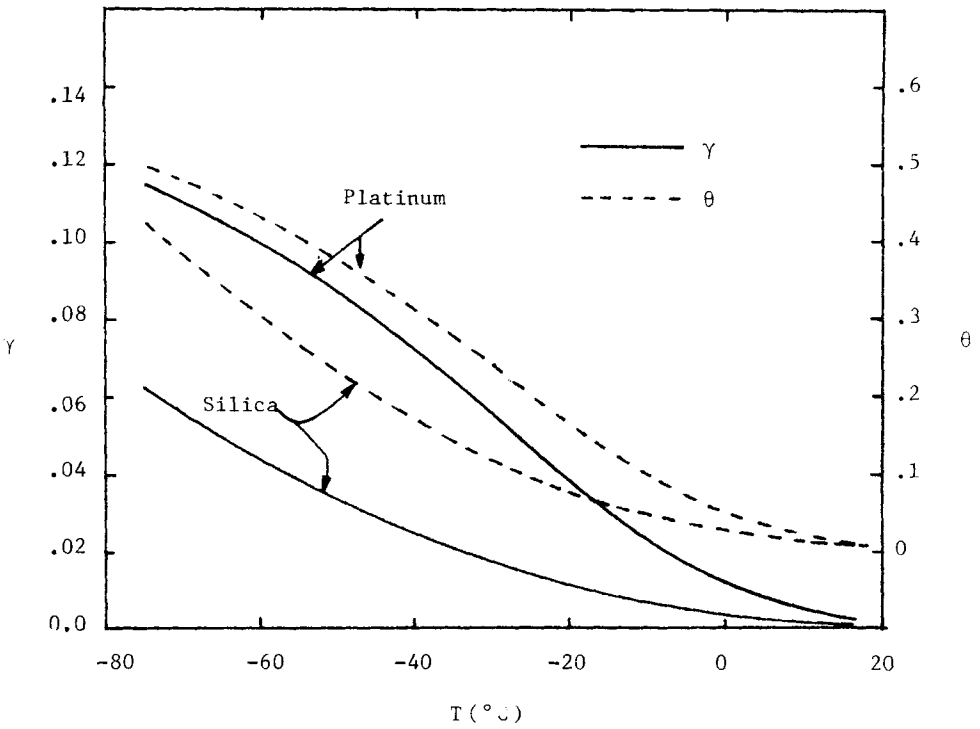

Figure 4. γ-T vs. ϑ-T curves of pure components for Pt/SiO_2 catalysts.

bon dioxide does not distinguish pure platinum from pure silica and yet it does distinguish between supported catalysts of different loadings as evident from different γ_t curves shown in Figure 2. This finding suggests that the selective physisorption of carbon dioxide could be used as a probe for studying the platinum catalyst since the amount of chemisorbed hydrogen per unit surface area of the catalyst is the same regardless of dispersion, whereas the amount of selectively physisorbed carbon dioxide per unit surface area of the catalyst depends on dispersion.

Earlier work (Miller and Lee, 1984) with carbon dioxide and the results presented here with nitrous oxide fortify the earlier contention that an adsorbate exhibiting a large asymmetric direction polarizability is a good candidate for the selective physisorption method. According to the directional polarizabilities tabulated by Ross and Oliver (1964), carbon disulfide, acetylene, and benzene should also be good candidates for the selective physisorption method in addition to nitrous oxide and carbon dioxide.

SUMMARY

It has been shown that the selective physisorption method yields the catalyst surface area of supported catalysts based on the model system of a Pt/SiO_2 catalyst for which a reliable, independent method of measuring the catalyst area is available. Experimental and theoretical refinements of the original development have been made, involving the use of equilibrium isobars and in particular a data analysis method which is effective for supported catalysts. These refinements allow more accurate determination of the catalyst surface area and make the method effective even when the catalyst covers a small portion of the total surface area.

A comparison between selective physisorption and hydrogen chemisorption has been made for the well-defined system of Pt/SiO_2 to show that the selective physisorption method can yield rather accurately the catalyst surface area of metal compound supported catalyst, since by the nature of physisorption, the method would be applicable to metal compound catalyst if it is applicable to metal catalyst. Further, the Pt/SiO_2 system was chosen in place of a metal compound catalyst since standard methods such as chemisorption, x-ray, and electron microscopy techniques cannot yield the surface area in sufficient accuracy for such a comparison, as our previous attempts with potassium carbonate on carbon and silver on fused alumina indicate (Miller and Lee, 1984). The comparison shows that the selective physisorption method cannot distinguish a few percent difference in the catalyst surface area normalized with respect to total BET area but it can distinguish a difference larger than several percent even for small catalyst surface area. Such an accuracy cannot be attained with the standard techniques except for some well-defined supported catalysts such as platinum, nickel, and palladium.

NOTATION

b_i = proportionality constant in Eq. 10
I_1 = integral defined by Eq. 7 or Eq. 11
I_t = integral defined by Eq. 8 or Eq. 12
R_1 = volume of gas absorbed on catalyst per unit surface area of the catalyst in the supported state
R_2 = volume of gas adsorbed on support per unit surface area of the support in the supported state
S_1 = catalyst surface area
S_2 = support surface area
S_t = total surface area ($S_1 + S_2$)
T = temperature
T_t = lower limit for integration with respect to temperature

T_f = upper limit for integration with respect to temperature
U_i = volume of gas adsorbed on pure catalyst ($i = 1$) or pure support ($i = 2$)
v_1 = volume of gas adsorbed on the catalyst in the supported state
v_2 = volume of gas adsorbed on the support in the supported state
v_t = $v_1 + v_2$

Greek Letters

γ_1 = U_1/S_1
γ_2 = U_2/S_2
γ_t = v_t/S_t
ϑ_i = coverage by an adsorbate on i surface

Subscript

i = $i = 1$ for catalyst and $i = 2$ for support

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