Modeling of the Heat-Transfer Process in a Differential Scanning Calorimeter

B. Sen
Dept. of Chemical Engineering, Birla Institute of Technology and Science, Pilani, Rajastan, 333031, India

The model developed predicts a priori potential errors associated with the energy trace recorded by an isoperibol differential power scanning calorimeter in the measurement of heat of adsorption of H_2 on Pt and Pd catalysts. The uptake of H_2 by the catalyst sample was approximated by a diffusion-limited quasi-steady-state moving boundary model. This approximation is valid only if the parameter [(adsorption capacity of cat. sample)/(inlet conc. of H_2)] is extremely large (~24). The effect of flow rate, amount of H_2 adsorbed, sink temperature, and the thermal conductivity of the adsorbate mixture was examined. Model predictions indicate that the error in the energy trace recorded by the DSC is appreciable: if a large difference exists between the thermal conductivity of the inert carrier, Ar ($k = 0.017$ J/m·K·s), and the adsorbate, H_2 ($k = 0.174$ J/m·K·s); if the heat sink temperature is much lower (~90 K) than the measurement temperature. However, these errors can be eliminated by matching the thermal conductivity of the inert carrier and adsorbate, such as He ($k = 0.143$ J/m·K·s) and H_2 ($k = 0.174$ J/m·K·s). The results agree well with the experimental observations of Vannice et al. (1987) on high-purity Pt and Pd powder and supported Pt catalysts, if the H_2 uptake by the catalyst sample in the calorimeter is small (≤2 μmol).

Introduction

The application of differential scanning calorimetry (DSC) to catalytic research is relatively recent. Vannice et al. (1987), Chou and Vannice (1987), and Sen et al. (1986) have successfully used a modified commercial Perkin-Elmer DSC to measure accurate and reproducible values of isothermal, integral heats of adsorption of H_2, O_2 and CO on supported and unsupported platinum (Pt) and palladium (Pd) catalysts.

The inherent errors associated with the isothermal, integral heat of adsorption measurements, when a large difference exists in the thermal conductivity of the adsorbate and carrier gas, have been reported earlier by Vannice et al. (1987) and Sen et al. (1986). This falsification of the energy trace recorded by a DSC will necessarily be associated with any process that involves a change in the gas-phase composition accompanied by energy evolution/absorption in the sample cavity.

In this study, a model has been proposed for H_2 adsorption and the transient convective heat-transfer process occurring in a DSC and the effect these have on the energy trace recorded by the calorimeter. The adsorption of H_2 occurring in a slab of catalyst has been modeled by the moving boundary approximation. This process is accompanied by a depletion in the concentration of H_2 in the gas phase of the sample cavity, as compared to the reference cavity. This change in composition of the H_2/carrier gas mix alters the instantaneous sample-side heat-transfer coefficient (h_s) as compared to the instantaneous reference-side heat-transfer coefficient (h_r). Consequently, the energy measured is erroneous and further magnified if the surroundings (heat sink) temperature is much lower than the measurement temperature (300 K).

Theory of DSC

A differential power scanning calorimeter is an isoperibol instrument. Isoperibol operation requires that the surroundings or the heat sink be maintained at constant temperature (Hemminger and Hohne, 1984). Embedded in this sink are two cavities, each of which is equipped with a controlled heater and temperature sensor (Figure 1). The sample to be studied is placed in a holder in one of the cavities. The transient thermal behavior of the system is reflected in a perturbation of the

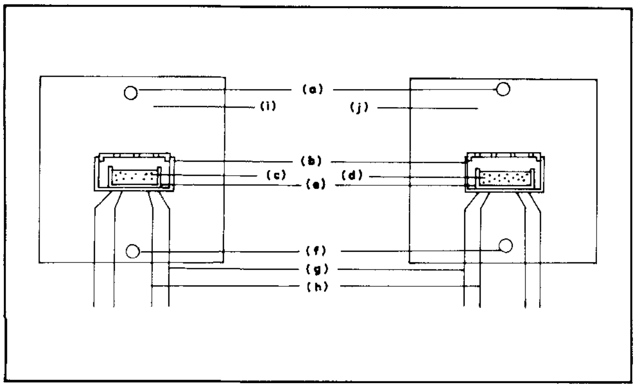

Figure 1. Sample and reference cavity of a differential scanning calorimeter.

(*a*)	gas inlet	(*f*)	gas outlet
(*b*)	sample holder	(*g*)	thermocouple
(*c*)	catalyst sample	(*h*)	heater
(*d*)	pure support	(*i*)	sample cavity
(*e*)	sample pan	(*j*)	reference cavity (Chou, 1987)

sample holder temperature with respect to the reference side temperature (preset temperature = 300 K). This change is detected by a platinum resistance thermometer. As a consequence of this temperature change, the power input to the sample holder is altered to maintain it at the preset temperature. For all the catalyst samples studied (Chou and Vannice, 1987; Sen et al., 1986; Vannice et al., 1987), this change occurred very rapidly. Hence, isothermal conditions can be assumed to prevail in the sample and reference holder at all times. The time integral of the difference in the power input between sample and reference side during the adsorption process gives the desired energy change of the process. In this description, it has been implicitly assumed that the physical properties of the sample and reference cavities are identical, except for the thermal phenomenon occurring on the sample side.

To measure the heats of adsorption of various gases (H_2, O_2, CO) on supported catalysts, about 40-100 mg of the sample is placed in the sample cavity. An equivalent amount of the support is placed in the reference side. On introduction of the adsorbate/carrier gas mix into the calorimeter, an energy change is recorded owing to the exothermicity of the adsorption process. To summarize:

$$P_s = -Q + h_s A (T_s - T_{hs}) \tag{1}$$

$$P_r = h_r A (T_r - T_{hs}) \tag{2}$$

$$\dot{E} = P_s - P_r \tag{3}$$

$$E = \int_0^t \dot{E}\, dt \tag{4}$$

It is evident from Eq. 3 that the instantaneous DSC output will be a true reflection of the actual energy change, only if the heat-transfer losses from the sample and reference side are identical. This assumption implies the equality of the heat-transfer coefficients on the sample and reference side during the heat generation process. However, the energy released on adsorption of a gas by the catalyst is necessarily accompanied by a change in the gas-phase composition in the sample cavity, which does not occur on the reference side. Consequently, if the thermal conductivity of the adsorbate is very different from that of the carrier gas, the instantaneous heat-transfer coefficients, h_s and h_r, can be very widely different leading to an erroneous measurement. This error may be represented as:

$$Err = \int_0^t [h_s A (T_s - T_{hs}) - h_r A (T_r - T_{hs})] dt \tag{5}$$

In the following section, a mathematical model has been developed to estimate the magnitude of the error for the two cases: H_2/Ar mixture and H_2/He mixture.

Model Development

During an isothermal integral heat of adsorption measurement experiment in a DSC a flowing mixture of H_2/inert gas is introduced over the catalyst bed and over the pure support simultaneously, both of which are maintained at a constant preset temperature. Adsorption of H_2 on the catalyst surface releases heat and perturbs the temperature of the sample holder. The adsorption process on the sample side also alters the gas-phase concentration of H_2 with respect to the reference side. To obtain the transient gas-phase concentration of H_2, the following assumptions have been made:

- The packed bed of catalyst has been modeled as a slab of thickness, L.
- The gas phase in both of the cavities has been assumed to be well-mixed.
- Adsorption of H_2 has been neglected on the support, thereby specifying that the gas adsorbs solely on the exposed metal atoms.
- Isothermal conditions have been assumed to prevail in the catalyst bed.

With these underlying assumptions, the following conservation equations can be specified for the sample cavity. Material balance for H_2 in the gas phase yields,

$$\frac{dC'}{dt} = \frac{FI}{V_s} - \frac{FC'}{V_s} + \frac{BD}{V_s}\left(\frac{\partial C''}{\partial x}\right)_{0,t} \tag{6}$$

subject to the initial condition:

$$t = 0,\ C' = 0 \tag{7}$$

The variation of H_2 concentration in the catalyst bed is given by:

$$\frac{\partial C''}{\partial t} = D\frac{\partial^2 C''}{\partial x^2} - z\omega\rho (r_a - r_d) \tag{8}$$

where

$$r_a = \left(\frac{RT_s}{2\pi M}\right)^{1/2} \sigma C'' S (1-\theta)^2 \tag{9}$$

$$r_d = \kappa e^{-E_d/RT_s}\theta^2 \tag{10}$$

subject to the following initial and boundary conditions.

Table 1. Parameter Values Used in Simulation

Parameter	Magnitude
A	1.0×10^{-4} m^2
B	3.9×10^{-5} m^2
d	1.5×10^{-2} m
D	5.6×10^{-6} m^2/s*
E_d	75.2 kJ/mol
F	Varied**
I	Varied**
l	1.5×10^{-2} m
L	Varied**
S	0.5
T_{hs}	Varied**
T_r	300 K
T_s	300 K
V_r	2.65×10^{-6} m^3
V_s	2.65×10^{-6} m^3
z	0.8
α	Varied**
κ	1×10^{13} s^{-1}
σ	4.03×10^{7} m^2/kmol

*$D=97\times$(mean pore radius)$\times(T/M)^{0.5}$; mean pore radius $=4.7\times10^{-9}$ m (Smith, 1981).

**Appropriate magnitudes are given in the figure captions.

Table 2. Comparison of the Characteristic Time Constants

Time Parameter	Physical Significance	Est. Magnitude(s)
$\eta=\frac{L^2}{D}$	Mass diffusion time	$\sim 1.8\times10^{-1}$
$\tau=\frac{V}{F}$	Average residence time in sample/reference cavity	~ 8
$\tau_a=\left[\left(\frac{RT_s}{2\pi M}\right)^{0.5}\sigma C_s'' S\right]^{-1}$	Inverse of pseudo first-order rate constant for H_2 adsorption	$\sim 10^{-8}$
$\tau_e=[ke^{-E_d/RT_s}]^{-1}$	Inverse of first-order rate coefficient for H_2 desorption	~ 1

Initially, the catalyst surface is clean: that is, no H_2 is present in the catalyst bed,

$$t=0,\ C''=0 \tag{11}$$

The concentration of H_2 is assumed to be equal at the gas and sample "slab" interface in the sample cavity,

$$x=0,\ C'=C'' \tag{12}$$

Since, the sample holder is impermeable to H_2, Eq. 13 naturally suggests itself.

$$x=L,\ \frac{\partial C''}{\partial x}=0 \tag{13}$$

Finally, the surface coverage of the adsorbed species is specified by the following equation:

$$\frac{d\theta}{dt}=r_a-r_d \tag{14}$$

with the initial condition,

$$t=0,\ \theta=0 \tag{15}$$

The above set of equations (Eqs. 6-15) comprise an exact description of the physical phenomenon. However, the solution of these coupled nonlinear differential equations is not trivial. By retaining the essential features of the physical process, certain simplifying assumptions can be made, thereby greatly reducing the computational effort. This has been done by comparing the relative rates of various processes occurring in the sample cavity. The magnitude of the characteristic time constants of various processes are listed in Table 2 using values from Table 1. The rate parameters used to describe the dissociative adsorption and molecular desorption of H_2 are representative of the values reported in the surface science literature for Gr. VIII metals (Somorjai, 1981). The effective Knudsen diffusivity was estimated by the method indicated by Froment and Bischoff (1979).

It is apparent (Table 2) that the time constant for the dissociative adsorption of H_2 (τ_a) differs from the remaining processes by several orders of magnitude. Since the rate of adsorption is much faster than any other physical process, we can conceive of the adsorption process as a moving boundary problem, where the adsorbate gas is captured and immobilized by the metal atoms. This is similar to the shrinking-core assumption employed in the modeling of noncatalytic gas-solid reactions (Froment and Bischoff, 1979). Hence, we can model the chemisorption of H_2 in the catalyst bed as a moving adsorption front with the boundary demarcating the region of saturated surface metal atoms from a region where the catalyst is completely devoid of any adsorbate (Eq. 19). In other words, it is the diffusion of the gas through the porous catalyst bed which limits the adsorption. The simplified model equation for the concentration dependence of H_2 in the pore volume of the catalyst bed behind the moving adsorption front will then be given by:

$$\frac{\partial C''}{\partial t}=\frac{D\partial^2 C''}{\partial x^2} \tag{16}$$

with the following initial and boundary conditions:

$$t=0,\ C''=0 \tag{17}$$

$$x=0,\ C'=C'' \tag{18}$$

$$x=y,\ C''=0 \tag{19}$$

Finally, the relationship for describing the movement of the adsorption front:

$$\alpha\nu\frac{dy}{dt}=-D\left(\frac{\partial C''}{\partial x}\right)_{x=y} \tag{20}$$

where α is the adsorptive capacity of the catalyst, and ν has been assumed to be 1 for H_2 adsorption, that is, one H atom adsorbs on one surface metal atom.

The model equations can be nondimensionalized by setting:

$$\hat{t}=\frac{Dt}{\gamma L^2},\ \hat{x}=\frac{x}{L},\ \hat{C}'=\frac{C'}{I},\ \hat{C}''=\frac{C''}{I},\ \text{and}\ \hat{y}=\frac{y}{L}$$

Hence, the mass balance for the adsorbate in the cavity volume reduces to:

$$\frac{d\hat{C}'}{d\hat{t}}=\frac{\eta\gamma}{\tau}(1-\hat{C}')+\beta\gamma\left(\frac{\partial\hat{C}''}{\partial\hat{x}}\right)_{0,\hat{t}} \tag{21}$$

with the initial condition,

$$\hat{t}=0,\ \hat{C}'=0 \tag{22}$$

Concentration of the adsorbate in the sample "slab" behind the moving adsorption front is described by:

$$\frac{1}{\gamma}\frac{\partial\hat{C}''}{\partial\hat{t}}=\frac{\partial^2\hat{C}''}{\partial\hat{x}^2} \tag{23}$$

with the associated conditions,

$$\hat{t}=0,\ \hat{C}''=0 \tag{24}$$

$$\hat{x}=0,\ \hat{C}''=\hat{C}' \tag{25}$$

$$\hat{x}=\hat{y},\ \hat{C}''=0 \tag{26}$$

The equation for the moving adsorption front reads:

$$\frac{d\hat{y}}{d\hat{t}}=-\left(\frac{\partial\hat{C}''}{\partial\hat{x}}\right)_{\hat{x}=\hat{y}} \tag{27}$$

Using the additional transformation,

$$\xi=\frac{1-\hat{x}}{1-\hat{y}} \tag{28}$$

It is possible to "freeze" the moving boundary, where the position of the boundary, at all times, is given by $\xi=1$. Hence, Eqs. 23 reads:

$$\frac{\partial^2\hat{C}''}{\partial\xi^2}=\frac{(1-\hat{y})^2}{\gamma}\frac{\partial\hat{C}''}{\partial\hat{t}} \tag{29}$$

$$\hat{t}=0,\ \hat{C}''=0 \tag{30}$$

$$\xi=\frac{1}{1-\hat{y}},\ \hat{C}''=\hat{C}' \tag{31}$$

$$\xi=1,\ \hat{C}''=0 \tag{32}$$

The parameter γ is the ratio of the adsorption capacity of the catalyst to the inlet concentration of the adsorbate. The solution is developed for a catalyst having a high adsorptive capacity (or the inlet concentration being low). Since γ does not multiply the highest order derivative in Eq. 29, this gives rise to a regular perturbation problem and the zero-order solution to this problem has been obtained.

Solution of Eq. 29 gives:

$$\hat{C}''=\left(\frac{1-\hat{y}}{\hat{y}}\right)\hat{C}'(\xi-1) \tag{33}$$

Equations 21 and 27 reduce to:

$$\frac{d\hat{C}'}{d\hat{t}}=\frac{\eta\gamma}{\tau}(1-\hat{C}')-\beta\gamma\frac{\hat{C}'}{\hat{y}} \tag{34}$$

$$\frac{d\hat{y}}{d\hat{t}}=\frac{\hat{C}'}{\hat{y}} \tag{35}$$

Equations 34 and 35 describe the variation of H_2 concentration in the sample cavity and the position of the moving adsorption front with time.

This set of simultaneous nonlinear ODEs (Eqs. 34 and 35) has been solved numerically, using an IMSL package, DGEAR, to obtain the gas-phase concentration of the adsorbate as a function of time in the sample cavity. Once the gas-phase concentration has been obtained, the transient heat-transfer coefficient in the sample cavity can be estimated from:

$$\frac{hd}{k}=1.86\left(Re\,Pr\frac{d}{l}\right)^{1/3}\left(\frac{\mu_b}{\mu_o}\right)^{0.14} \tag{36}$$

where μ_b is the viscosity of the H_2/inert gas mixture at T_s, and μ_o is the viscosity of the H_2/inert gas mixture at T_{hs} (Bird et al., 1960). The reference-side concentration of H_2 is given by:

$$C_r=I(1-e^{-t/\tau}) \tag{37}$$

By suitably evaluating the mixture physical properties, the heat-transfer coefficient in the gas phase for the reference side has been estimated.

Once these heat-transfer coefficients have been evaluated as a function of the time, the integral error associated with the energy trace has been determined from Eq. 5.

Results and Discussion

The effect of various physical parameters, such as total flow rate, inlet concentration of the adsorbate, sink temperature, amount of H_2 adsorbed by the catalyst, and the thermal conductivity of the carrier gas, Ar and He, on the magnitude of absolute error was studied.

Figure 2 shows the difference in concentration of H_2, which exists between the sample and reference cavity during the adsorption process. At the onset, this difference is small, but it appears to grow with time until the catalyst is saturated with the adsorbate. The sample- and reference-side concentrations converge to the same value after approximately 3τ. The concentration profile for the duration of the adsorption process has been shown in Figure 2: if the adsorption capacity of a 0.001-m bed of catalyst is 0.1 kmol/m^3 and the total inlet flow

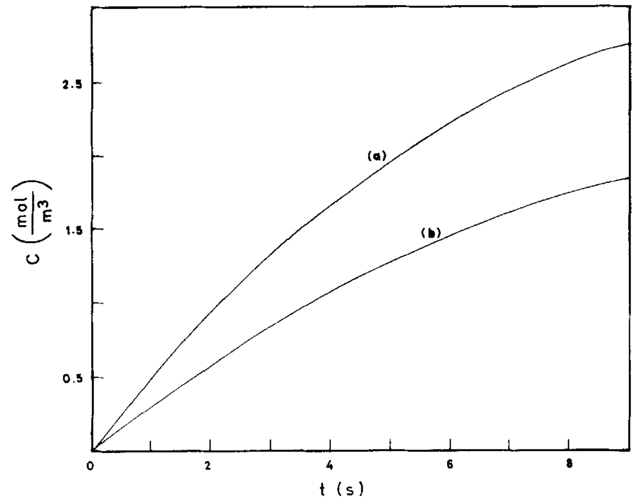

Figure 2. Variation of the gas-phase H_2 concentration with time accompanying adsorption in the DSC cavities.

(*a*) concentration of H_2 in the reference cavity
(*b*) concentration of H_2 in the sample cavity
$F = 3.33\times10^{-7}$ m³ (STP)/s; $I = 4.1$ mol/m³; $L = 0.001$ m; $\alpha = 0.1$ kmol/m³

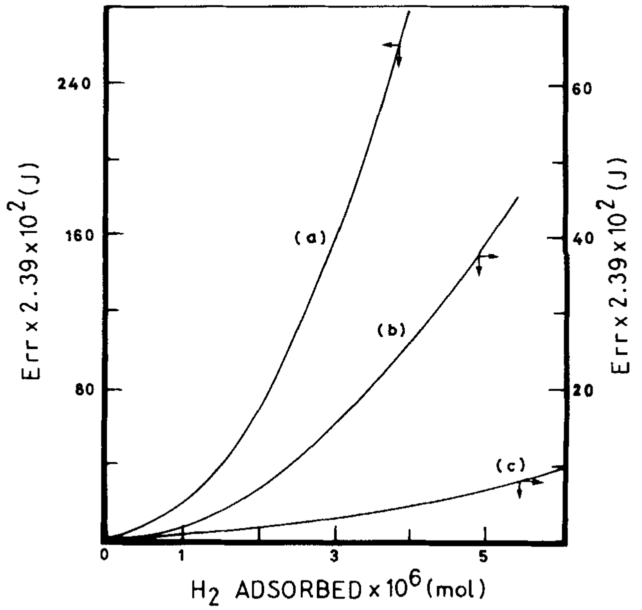

Figure 3. Effect of the amount of H_2 adsorbed on the magnitude of error in the DSC energy trace.

(*a*) H_2/Ar mixture, $T_{hs} = 200$ K
(*b*) H_2/Ar mixture, $T_{hs} = 290$ K
(*c*) H_2/He mixture, $T_{hs} = 290$ K
$F = 3.33\times10^{-7}$ m³ (STP)/s; $I = 4.1$ mol/m³; $\alpha = 0.1$ kmol/m³

rate is 3.33×10^{-7} m³ (STP)/s with $I = 4.1$ mol/m³, the catalyst is completely saturated in approximately 9 s.

The amount of H_2 adsorbed by the catalyst is listed in Table 3. This was estimated from the concentration-time profile in Figure 2. The amount of H_2 adsorbed by the sample was obtained by discretizing Eq. 6, and the adsorption term was evaluated by using linear interpolation over a time interval of 1 s. The data in Table 3 show that the uptake of H_2 from the gas phase increases linearly with time. This is a consequence of the diffusion-limited adsorption.

The effect on the amount of H_2 adsorbed by the catalyst on the magnitude of error has been shown in Figure 3. Errors clearly occur most, if Ar is used as the carrier gas and the sink temperature is low. This error is reduced by a factor of four for the Ar/H_2 system, if the difference between the preset temperature and sink temperature is reduced from 90 K to 10K (note the change in scale). The benefit of using a carrier gas, whose thermal conductivity is similar to the adsorbate, such as He/H_2, is evident from Figure 3. If the difference between the preset temperature and the sink temperature is kept at 10 K, using a He/H_2 mixture for adsorption, instead of Ar/H_2, reduces the error approximately by a factor of six.

Figure 4 shows the effect of flow rate on the magnitude of the error. There appears to be a very weak dependence of the error on the flow rate, for $F \geq 3.33\times10^{-7}$ m³ (STP)/s. However, operating at flow rates less than 1.67×10^{-7} m³ (STP)/s

Table 3. Amount Adsorbed as a Function of Time
$F = 3.33\times10^{-7}$ m³ (STP)/s
$I = 4.1$ mol/m³
$L = 0.001$ m
$\alpha = 0.1$ kmol/m³

Time (s)	Moles Adsorbed (mol × 10^6)
0	0
0.5	0.5
1.5	1.0
2.5	1.4
3.5	1.9
4.5	2.4
5.5	2.8
6.5	3.3
7.5	3.8

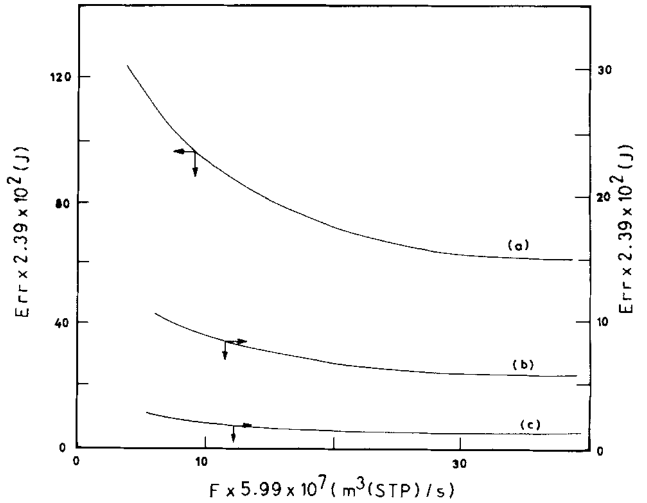

Figure 4. Effect of flow rate on the magnitude of error in the DSC energy trace.

(*a*) H_2/Ar mixture, $T_{hs} = 200$ K
(*b*) H_2/Ar mixture, $T_{hs} = 290$ K
(*c*) H_2/He mixture, $T_{hs} = 290$ K
$I = 4.1$ mol/m³; $L = 0.0005$ m; $\alpha = 0.1$ kmol/m³

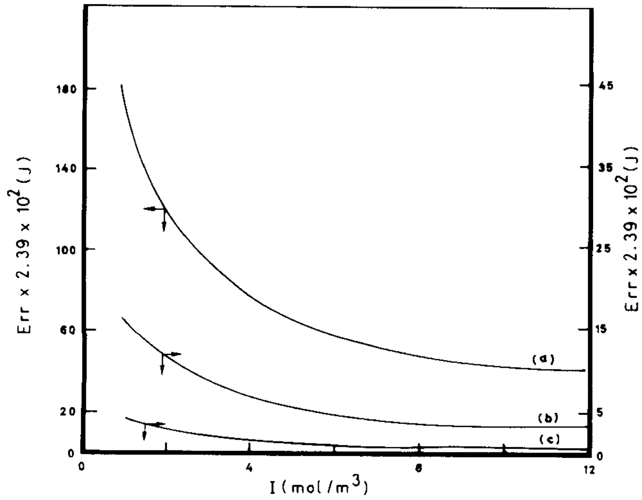

Figure 5. Effect of inlet concentration of H_2 on the magnitude of error in the DSC energy trace.

(a) H_2/Ar mixture, $T_{hs} = 200$ K
(b) H_2/Ar mixture, $T_{hs} = 290$ K
(c) H_2/He mixture, $T_{hs} = 290$ K
$F = 3.33 \times 10^{-7}$ m^3 (STP)/s; $L = 0.0005$ m; $\alpha = 0.1$ kmol/m^3

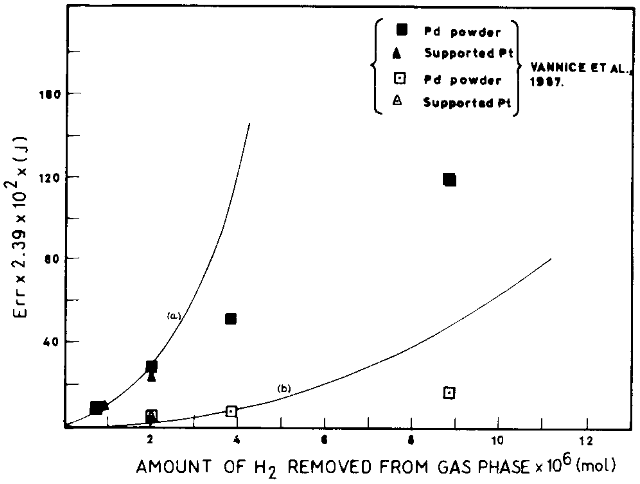

Figure 6. Comparison of the simulated error with experimentally measured values in H_2/Ar mixture.

(a) H_2/Ar mixture, $T_{hs} = 200$ K
(b) H_2/Ar mixture, $T_{hs} = 290$ K

leads to substantial enhancement in the magnitude of the error for the Ar/H_2 system.

The inlet concentration of H_2 also affects the magnitude of the error associated with the energy trace recorded by the DSC. The error decreases with increasing inlet concentration of H_2, all other variables remaining constant. From the predicted trends in Figure 5, the error is expected to increase significantly if $I \leq 2.0$ mol/m^3.

From the results in Figures 4 and 5, it is apparent that the error increases with a decrease in the total flow rate of the carrier gas/H_2 mixture and with a decrease in the inlet H_2 concentration. Since the error is directly proportional to the time integral of the difference in the sample- and reference-side heat-transfer coefficients (Eq. 5), this increase in the H_2 adsorption-induced error at low total flow rates and low inlet concentrations can be attributed to the greater lengths of time required to replenish the pool of H_2 in the gas phase.

These model simulations are in good agreement with the experimental results reported earlier for unsupported Pd samples and supported Pt catalysts (Vannice et al., 1987; Sen et al., 1986). A comparison of the model calculations with the experimental results obtained by Vannice et al. (1987) using high-purity palladium samples and supported platinum catalysts is presented in Figure 6. The adsorption of H_2 on bulk palladium at 300 K leads to the formation of a beta-hydride phase. Since the heat of formation of Pd beta-hydride is known (Kuji et al., 1983), a comparison of the measured energy change to the expected energy change allowed an estimation of the error. For the supported Pt catalysts, the error was determined by measuring the energy change on H_2 adsorption on a Pt catalyst sample in a H_2/Ar mixture at $T_{hs} = 200$ or 290 K and comparing this to the energy change measured in a H_2/He mixture at $T_{hs} = 290$ K (Sen et al., 1986; Vannice et al., 1987).

The experimental results clearly indicate that the absolute error is directly proportional to the amount of H_2 removed from the gas phase. The model predictions agree well with the experimental data, if the amount of H_2 removed from the gas phase is small. The difference between the predicted and experimental error is negligible, if the amount of H_2 removed from the gas phase is $\leq 2 \times 10^{-6}$ mol, when the energy change is measured in a H_2/Ar mixture with $T_{hs} = 200$ K (Figure 6a). The predicted and experimental errors are in excellent agreement until $\sim 4 \times 10^{-6}$ mol H_2 adsorbed, when the heat sink temperature is 290 K (Figure 6b). However, the predicted functional relationship between the error and the amount of H_2 removed from the gas phase is different from the experimental results. The functionality of the predicted error can be explained thus. Referring to Eq. 36, the heat-transfer coefficient is directly proportional to the composition of the gas in the cavity volumes:

$$(h_s - h_r)\alpha(C' - C_r)$$

Since this difference increases in a nonlinear manner with time (Figure 2), the predicted error will exhibit a nonlinear time dependence. Again, since the amount adsorbed is directly proportional to time (Table 3), the predicted error shows a nonlinear dependence on the amount adsorbed.

The discrepancy between the experimental and predicted values of error at higher H_2 uptakes suggests that the isothermality in the catalyst bed and the well-mixed assumption in the cavity volumes may not be strictly valid when larger amounts of H_2 are adsorbed. However, the proposed model does incorporate all the physical features of the process at low H_2 uptakes.

Conclusions

A moving adsorption front model has been developed to predict transient gas-phase concentration of the adsorbate in the sample cavity of the DSC. Based on the difference in the concentration of H_2 between the sample and the reference cavity, the magnitude of the absolute error associated with the energy trace when Ar is used as the carrier gas has been predicted and compared with the experimental results of Vannice et al. (1987).

For supported Pt catalysts (1.5% $Pt/SiO_2-Al_2O_3$, 2.1% Pt/SiO_2, and 2.1% $Pt/\eta-Al_2O_3$) the mean value of the measured heat of adsorption of H_2 in Ar/H_2 mixture with $T_{hs}=200$ K is 108 kJ/mol H_2 (Vannice et al., 1985). Predicted values under identical conditions would be off by about 12%.

It has also been shown in accordance with the experimental findings (Vannice et al., 1987) that the errors are negligible, if helium is used as the carrier gas for H_2 adsorption.

Acknowledgment

I would like to thank Dr. Ajay Chatterjee for many fruitful discussions and providing useful insights.

Notation

A = heat-transfer area, m^2
B = total geometric surface area of the catalyst exposed to the gas, m^2
C = gas-phase concentration of H_2, mol/m^3
d = diameter of sample and reference cavity, m
D = effective diffusivity of H_2 in the porous catalyst sample, m^2/s
$\dot{E}$ = instantaneous DSC output, J/s
E = integral DSC output, J
E = desorption activation energy for H_2, kJ/mol
Err = integral error associated with the energy trace, J
F = total gas flow rate through each cavity, m^3 (STP)/s
h = instantaneous heat-transfer coefficient between the cavity and the heat sink, $J/s \cdot m^2 \cdot K$
I = inlet concentration of H_2 into the sample and reference cavity, mol/m^3
k = thermal conductivity, $J/s \cdot m \cdot K$
l = length of the sample and reference cavity, m
L = depth of the catalyst bed, m
M = molecular weight, kg/kmol
P = instantaneous power supplied to the holder, J/s
Pr = Prandtl number
Q = heat released due to adsorption, J/s
r = rate of adsorption or desorption, 1/s
R = ideal gas constant, 8.3144×10^3 $kg \cdot m^2/s^2 \cdot kmol \cdot K$
Re = Reynolds number
S = initial sticking coefficient
t = time, s
T = temperature, K
V = volume of cavity, m^3
x = space coordinate, m
y = position of the moving adsorption front, m
z = fraction of the metal atoms that are exposed to the gas phase

Greek letters

α = adsorptive capacity of the catalyst, $kmol/m^3$
β = ratio of the catalyst volume to the volume of cavity
γ = ratio of the adsorptive capacity of the catalyst to the inlet concentration of H_2
η = diffusion time constant, s
θ = fractional coverage of adsorbate
κ = pre-exponential factor in the desorption rate expression, 1/s
μ = viscosity, $N \cdot s/m^2$
ν = stoichiometry of adsorption, 1 for H_2
ρ = catalyst density, kg/m^3
σ = specific area of adsorption sites, $m^2/kmol$
τ = time constant, s
ω = molar loading of the metal of catalyst sample, kmol/kg

Subscripts

a = adsorption
d = desorption
hs = heat sink
r = reference side
s = sample side

Superscripts

$'$ = gas phase in the sample cavity
$''$ = porous catalyst sample
$\hat{}$ = dimensionless variable

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