A moment technique for adsorption rate on metal surfaces of supported catalysts CO adsorption on Pt–Al$_2$O$_3$ washcoated monolith

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Abstract

A moment technique was developed for the investigation of adsorption on metal surfaces of supported catalysts. The technique was applied to the evaluation of adsorption rate parameters of CO on a Pt–Al$_2$O$_3$ washcoated monolith. The adsorption rate constants evaluated in the temperature range 273–316 K showed significant decrease with an increase in surface coverage. Results of pulse response experiments corresponding to zero coverage gave the apparent activation energy for adsorption as 21 kJ/mol. This method allowed the evaluation of adsorption rate constant on metal surfaces at different coverages. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption rate; Bidisperse catalyst; Monolithic catalyst; Supported catalyst; Moment technique; CO adsorption

1. Introduction

Moment techniques have been frequently used for the investigation of diffusion, adsorption and reaction in porous solids. In these techniques, response peaks to concentration pulses of inert, adsorptive or reactive tracers were analyzed for the evaluation of diffusion, adsorption rate and equilibrium, and reaction rate parameters. Moment techniques were applied to packed beds [8,9,12], single catalyst pellets [3,5,11] and to monolithic catalysts [19]. More recently, Gleaves and coworkers [7,23] used a moment-based theoretical approach for the temporal analysis of the products (TAP) from pulse-response data. In the present study, a simple moment technique was presented for the investigation of adsorption on metal surfaces of supported catalysts. This technique allows the evaluation of adsorption rate constant at different surface coverages. In this work, the proposed technique was applied to the evaluation of adsorption characteristics of CO on a Pt–Al$_2$O$_3$ washcoated monolith.

Adsorption rate and equilibrium parameters on metal surfaces have always been a major area of interest in catalytic research. Transient experimental methods such as temperature programmed desorption (TPD), reduction (TPR), surface reaction (TPSR) [9,20] and step, frequency and pulse-response techniques [4,12–14,18] are powerful tools in the analysis of catalytic processes.

Due to its significance in automobile exhaust emission control and also in the purification of CO-contaminated hydrogen rich gas produced by steam reforming of organic fuels, selective oxidation of CO over Pt–Al$_2$O$_3$ catalysts and sorption of CO on transition metals attracted wide attention in the literature [1,10,15,17]. Carbon monoxide is generally considered to be adsorbed undissociatively and it is also quite mobile on the surface. In a number of studies, the presence of two distinct types of adsorbed CO species are reported [10,14,20,21]. Adsorption of CO on Pt is expected to change from linear to bridged structure with an increase of surface coverage [18]. Adsorption energetics and sticking probabilities are expected to change with surface coverage. Although CO–Pt interaction is one of the most extensively investigated adsorption systems, most of the results are for the equilibrium condition. Some desorption rate data are also available. Some experimental sticking probability results on Pt (III) surfaces are reported by McCabe and Schmidt [16], Campbell et al. [2], Steininger et al. [21].

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Nomenclature

a	cell dimension (cm) (Fig. 1)
b	wall thickness of the monolith (cm) (Fig. 1)
C	concentration in the channels of the monolith
$\overline{C}$	Laplacian of C
C_A	concentration in the macropores of Pt–Al$_2$O$_3$ catalyst layer
C_i	concentration in the micropores of Pt–Al$_2$O$_3$ particles
D_a	effective diffusivity in the macropores (cm^2/s)
D_i	effective diffusivity in the micropores (cm^2/s)
k_a	adsorption rate constant (cm^3/gs)
$k_{a,app}$	apparent value of k_a (cm^3/gs)
k_a^0	the value of k_a at zero coverage (cm^3/gs)
k_d^0	desorption rate constant at zero coverage (s)
k_m	mass transfer coefficient (cm/s)
L	length of monolith (cm)
L_n	moles of CO adsorbed per gram of catalyst (cumulative value in n pulses)
m	parameter defined by Eq. (13)
m_n	nth moment defined by Eq. (11)
M	strength of the input pulse (zeroth moment at the inlet $m_{oi} = M$)
n	adsorbed concentration (moles/g cat)
r	radial coordinate in the Pt–Al$_2$O$_3$ particle
r_0	radius of microporous Pt–Al$_2$O$_3$ particle
s	Laplace variable (s^{-1})
U_0	superficial velocity in the monolith
w_M	mass of the monolith
w_p	mass of the Pt–Al$_2$O$_3$ layer
y	diffusion coordinate in the Pt–Al$_2$O$_3$ layer
z	flow direction in the monolith

Greek letters

α	dimensionless parameter defined by Eq. (15)
δ	thickness of the Pt–Al$_2$O$_3$ layer
ε_a	macroporosity of the Pt–Al$_2$O$_3$ layer
ε_b	void fraction of the monolith
ε_i	microporosity of the Pt–Al$_2$O$_3$ particles
ρ_p	apparent density of the Pt–Al$_2$O$_3$ layer
ρ_{p_i}	apparent density of the Pt–Al$_2$O$_3$ particles
φ_a	adsorption Thiele modulus for the Pt–Al$_2$O$_3$ catalyst layer (Eq. (17))
φ_i	adsorption Thiele modulus for particles (Eq. (14))

2. Moment analysis of adsorption rate on a monolithic catalyst

In this work, a moment technique was developed for the analysis of adsorption rate parameters on the metal surface of supported catalysts. The technique was applied to investigate adsorption of CO on a monolithic catalyst which was washcoated by Pt–Al$_2$O$_3$. In this technique, successive pulses of CO tracer were injected into the carrier gas (helium) flowing through a monolithic catalyst and response peaks were analyzed for the moments to evaluate the adsorption rate parameters on the Pt-surface. The Pt–Al$_2$O$_3$ layer covering the surface of the channels of the monolith is expected to have bidisperse pore structure. This thin layer is composed of microporous Pt–Al$_2$O$_3$ particles and macropores between these particles. The mass conservation equation in the channels of the monolithic catalyst, in the porous Pt–Al$_2$O$_3$ layer covering the surface of channels and in the microporous Pt–Al$_2$O$_3$ particles are as follows:

Monolithic channels

$$-U_0 \frac{\partial C}{\partial z} - \left(\frac{2\varepsilon_b}{a}\right) D_a \left.\frac{\partial C_A}{\partial y}\right|_{y=\delta} = \varepsilon_b \frac{\partial C}{\partial t} \quad (1)$$

Active layer of thickness δ

$$D_a \frac{\partial^2 C_A}{\partial y^2} - (1 - \varepsilon_a)\frac{3}{r_0} D_i \left.\frac{\partial C_i}{\partial r}\right|_{r=r_0} = \varepsilon_a \frac{\partial C_A}{\partial t} \quad (2)$$

Pt–Al$_2$O$_3$ particles

$$\frac{D_i}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_i}{\partial r}\right) - \rho_{p_i} \frac{\partial n}{\partial t} = \varepsilon_i \frac{\partial C_i}{\partial t} \quad (3)$$

Adsorption isotherms are generally highly nonlinear and, in many cases, adsorption process is reversible. At any point within a microporous Pt–Al$_2$O$_3$ particle, the rate of change of adsorbed concentration "n" with respect to time can be expressed as

$$\frac{\partial n}{\partial t} = k_a^0 f(\theta) C_i - k_d^0 g(\theta) n \quad (4)$$

Here, k_a^0 and k_d^0 correspond to the adsorption and desorption rate constants at zero fractional coverage "θ" of the surface by the adsorbing molecules. The adsorption rate is expected to be a function of surface coverage. For a monolayer adsorption, the limiting values of the function $f(\theta)$ are 1 and 0 for $\theta = 0$ and $\theta = 1$, respectively. In the case of Langmuir adsorption isotherm $f(\theta) = (1 - \theta)$. However, in the case of nonuniform surfaces, the variation of activation energy of adsorption with surface coverage also contributes to the function $f(\theta)$. Similarly, possible variations of desorption rate constant with surface coverage are represented by the function $g(\theta)$.

Under certain conditions, such as at low temperatures, the desorption rate becomes very low and the second term on the right-hand side of Eq. (4) may be negligible within the time-scale of a pulse-response experiment. For instance, at room temperature adsorption of CO and H$_2$ on metal surfaces of supported catalysts is generally considered to be irreversible and this feature was generally used for the estimation of metal surface areas of supported catalysts.

The cell size ($2a$), wall thickness ($2b$) and Pt–Al$_2$O$_3$ catalytic layer thickness (δ) are illustrated in the schematic cross-sectional view of a single channel of a monolith
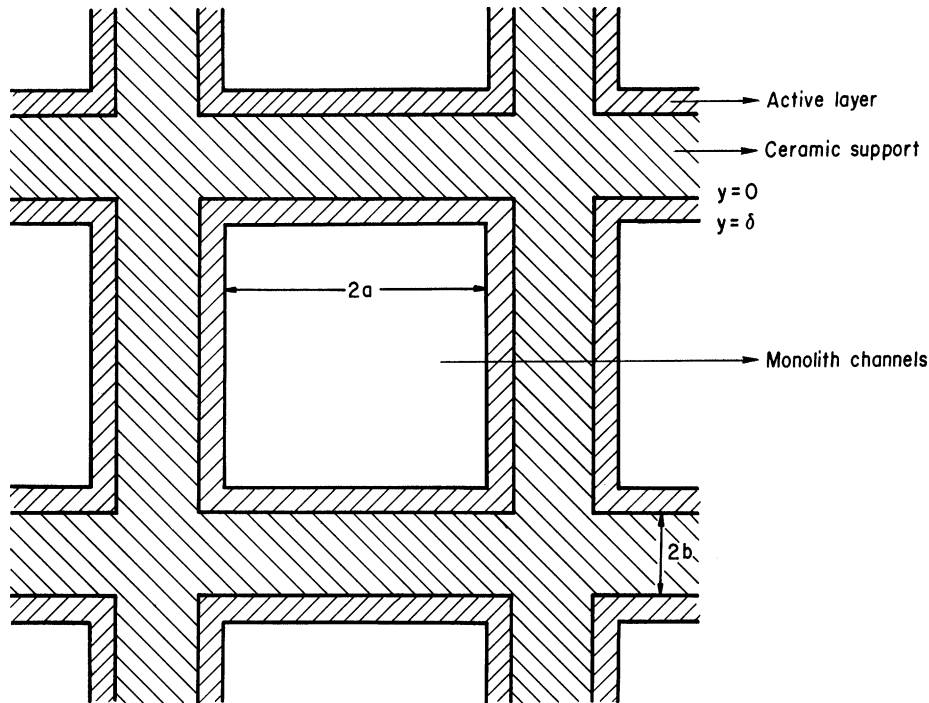
Fig. 1. Schematic cross-sectional view of the monolith.

(Fig. 1). The void fraction of the monolith (ε_b) can be expressed in terms of monolith characteristic dimensions as

$$\varepsilon_b = \frac{a^2}{(a+b+\delta)^2} \tag{5}$$

For a pulse injection experiment, the boundary conditions for Eqs. (1)–(3) are

$$C|_{z=0} = M\delta(t) \tag{6}$$

$$\left.\frac{\partial C_A}{\partial y}\right|_{y=0} = 0 \tag{7}$$

$$k_m(C - C_A|_{y=\delta}) = D_a \left.\frac{\partial C_A}{\partial y}\right|_{y=\delta} \tag{8}$$

$$C_A = C_i \quad \text{at } r = r_0 \tag{9}$$

$$\left.\frac{\partial C_i}{\partial r}\right|_{r=0} = 0 \tag{10}$$

The nth moment of the response peak is defined as

$$m_n = \int_0^\infty C t^n \, dt = (-1)^n \lim_{s\to 0} \frac{d^n(\overline{C})}{ds} \tag{11}$$

Here s and $\bar{C}$ correspond to the Laplace variable and the Laplacian of C, respectively. The major limitation of the moment technique is its applicability to linear systems.

In the case of negligible desorption rate term (irreversible adsorption) within the time-scale of a pulse-response experiment, model equations are solved in the Laplace domain and the moment expressions are derived following the procedure reported in the literature for other systems [3,8,19]. In this derivation, the adsorption rate constant corresponding to a certain surface coverage $k_a = k_a^0 f(\theta)$ was assumed to be constant within a single pulse-response experiment. The change of surface coverage during a single pulse-response experiment may be kept small by injecting small amounts of adsorbing tracer into the system in each pulse. In this case an average value of k_a may be considered for each pulse-response experiment. Of course, the value of k_a changes from one pulse-response experiment to another. With these assumptions, the following expression was derived for the ratio of zeroth moments of response and injection peaks (ratio of peak areas).

$$\frac{m_0}{M} = \exp\left[-\left(\frac{2\varepsilon_b L}{aU_0}\right)\left(\frac{1}{(1/k_m) + (\delta/D_a m \tanh(m))}\right)\right] \tag{12}$$

$$m = \left[\alpha\left(\frac{\varphi_i}{\tanh \varphi_i} - 1\right)\right]^{1/2} \tag{13}$$

Here, φ_i and α are the adsorption Thiele modulus and the dimensionless parameters showing the ratio of macropore and micropore diffusion resistances, respectively.

$$\varphi_i = r_0 \left(\frac{\rho_{pi} k_a}{D_i}\right)^{1/2} \tag{14}$$

$$\alpha = 3(1 - \varepsilon_{a})\frac{\delta^2}{r_0^2}\frac{D_i}{D_a} \qquad (15)$$

In the case of negligible film mass transfer resistance, Eq. (12) reduces to

$$\frac{m_0}{M} = \exp\left[-\left(\frac{2\varepsilon_b L D_a}{a U_0 \delta}\right) m \tanh(m)\right] \qquad (16)$$

For negligible micropore diffusion resistance, the parameter m should be replaced by φ_a.

$$\varphi_a = \delta \left(\frac{\rho_p k_a}{D_a}\right)^{1/2} \qquad (17)$$

where,

$$\rho_p = \rho_{p_i}(1 - \varepsilon_a) \qquad (18)$$

is the apparent density of the active layer. In a monolithic catalyst, the active catalytic layer is usually very thin (in the order of magnitude of a few particle diameters) and the macropore sizes are relatively large. The ratio of macro- to micropore diffusion coefficients is generally expected to be the much higher than 10^3 [6]. In this case, value of parameter α (Eq. (15)) is expected to be less than 10^{-2} and if diffusion plays a significant role on the sorption rate, diffusion resistance within the microporous particles is expected to be more significant than the diffusion resistance in the macropores of the catalyst layer. If macropore diffusion resistance is negligible, Eq. (16) reduces to

$$\frac{m_0}{M} = \exp\left[-\left(\frac{L}{U_0}\right)\left(\frac{2\varepsilon_b \delta}{a}\right) \rho_p k_{a,app}\right] \quad \text{(monolith)} \quad (19)$$

where, the apparent adsorption rate constant can be expressed as

$$k_{a,app} = k_a \left(\frac{3}{\varphi_i \tanh \varphi_i} - \frac{3}{\varphi_i^2}\right) \qquad (20)$$

For the case of negligible micro and macropore diffusion resistances the apparent adsorption rate constant $\rho_p k_{a,app}$ is equal to the actual adsorption rate constant $\rho_p k_a$.

In many cases the thickness of the catalyst layer δ may not be uniform and information may be absent for the value of δ. In this case Eq. (19) may be approximated as

$$\frac{m_0}{M} = \exp\left[-\left(\frac{L}{U_0}\right)\left(\frac{w_p}{w_M}\right) \rho_M k_{a,app}\right] \qquad (21)$$

Here, w_p/w_M is the weight ratio of Pt/Al$_2$O$_3$layer to the monolithic catalyst. This analysis indicated that irreversible adsorption rate constant may in principle be evaluated at different surface coverages from the ratio of peak areas of response and injection peaks obtained from successive pulse response experiments. Zeroth moments of the injection peaks may be determined from pulse-response calibration experiments which may be carried out with an empty reactor (without catalyst). The equations derived here for the monolithic system may easily be modified and used in a

Table 1
Physical constants of the monolithic catalyst

Weight of the monolith, w_M (g)	18.16
Weight of the Pt–Al$_2$O$_3$ layer, w_p (g)	1.44
Open frontal area fraction, ε_b	0.73
Number of cells (cm^{-2})	60
Cell size, $2a$ (cm)	0.1092
Wall thickness, $2b$ (cm)	0.018
Length of monolith (cm)	7.37
Diameter of the monolith (cm)	2.5
Apparent density of monolith, ρ_m (g/cm^3)	0.5
Platinum amount[a] (mg Pt/g monolith)	0.44
Average radius of Pt–Al$_2$O$_3$ particles, r_0[b] (cm)	23×10^{-4}
Apparent density of Pt–Al$_2$O$_3$ particles, ρ_{p_i} (g/cm^3)	1.08

[a] Determined by atomic adsorption spectrometry.
[b] Estimated from SEM photographs.

packed bed adsorber. In a packed bed system, the $(2\epsilon_b \delta/a)$ term which appear in Eq. (19) should be replaced by $(1 - \varepsilon_b)$.

$$\frac{m_0}{M} = \exp\left[-\left(\frac{L}{U_0}\right)(1 - \varepsilon_b) \rho_p k_{a,app}\right] \quad \text{(fixed bed)} \quad (22)$$

3. Experimental work

Pulse response experiments were carried out with cylindrical monolithic catalysts which are washcoated by Pt–Al$_2$O$_3$. The catalyst was placed into a specially designed reactor which is placed into a temperature controlled oven. Details of the reactor are reported elsewhere [19].

In the preparation of the catalyst, the ceramic monolith was first treated with 1% HF solution before the washcoating procedure. The monolith was then coated with alumina by successive treatments with an Al$_2$O$_3$ slurry [19]. The alumina coated monolith was then treated with chloroplatinic acid solution. After the impregnation procedure, this catalyst was calcined at 500°C and reduced in hydrogen atmosphere. Physical properties and the dimensions of the monolithic catalyst are given in Table 1. Pulses of CO (0.25 ml each) were injected into the helium carrier gas flowing at a flow rate of 68 ml/min (measured at 25°C), through the monolith and the concentration response peaks were measured by a TC detector connected to the reactor outlet.

4. Results and discussions

Results of CO pulse-response experiments conducted at different temperatures are illustrated in Fig. 2. In this figure, fraction of CO irreversibly adsorbed, $[(M - m_0)/M]$, in each pulse is plotted as a function of pulse number. Here M corresponds to the strength of the inlet pulse (zeroth moment of the inlet pulse). In the temperature range 273–316 K, most of the irreversible adsorption was completed within eight pulses. Zeroth moments of CO response curves approach to the zeroth moment of the injection pulse (M) in less than eight pulses.
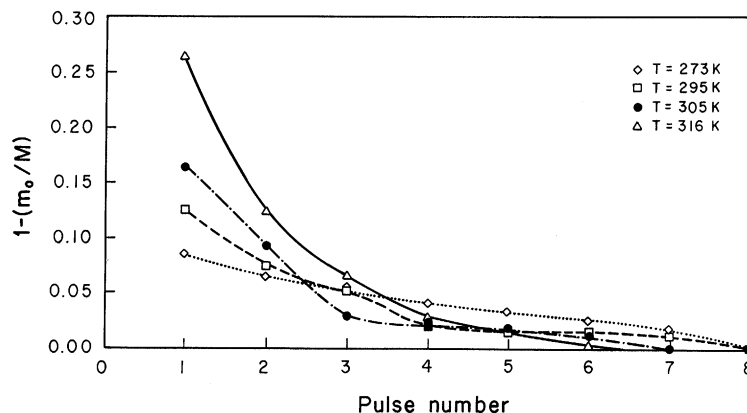
Fig. 2. Zeroth moment data for CO adsorption on Pt–Al$_2$O$_3$ ($F = 68\,\text{cm}^3/\text{min}$; pulse volume $=0.25\,\text{cm}^3$).

The apparent adsorption rate constant of CO on the metal surface of Pt–Al$_2$O$_3$ catalyst was evaluated at different surface coverages, from the zeroth moment data, using Eq. (21). Before evaluating the adsorption rate constant it was necessary to check the significance of film mass transfer resistance on the adsorption rate data. Film mass transfer resistance which appear in the general zeroth moment expression (given by Eq. (12)) was estimated from the correlation proposed by Votruba et al. [22], for the monolithic catalyst. The value of k_m was estimated to be in the order of magnitude of $1 \times 10^{-3}\,\text{m/s}$. As it is shown in Fig. 2, the experimental values of m_0/M vary between 0.75 and 1.0 in all the pulse-response experiments conducted within the temperature range 273–316 K. Using the geometric parameters reported in Table 1 and the film mass transfer coefficient estimated from the Votruba correlation, the values of the term $\delta/D_a m \tanh(m)$ which appear in Eq. (12) were calculated from the experimental values of m_0/M. This analysis showed that the order of magnitude of $1/k_m$ is at least 200 times smaller than the order of magnitude of the second term ($\delta/D_a m \tanh(m)$) which appear in the denominator of Eq. (12) and film mass transfer resistance may safely be neglected in the analysis of zeroth moment data. Consequently, Eq. (19) or Eq. (21) may be used for the evaluation of apparent adsorption rate constants on the Pt surface, from the zeroth moment data.

The adsorption rate constants were then evaluated at different surface coverages in the temperature range 273–316 K using data reported in Fig. 2. Results are shown in Fig. 3. The effect of diffusion resistance in the micropores of Pt–Al$_2$O$_3$ particles is expected to have some contribution on the values of apparent adsorption rate constants found from this analysis. The effect of diffusion resistance on the observed adsorption rate constant is expressed by Eq. (20). The order of magnitude of micropore diffusion coefficient is expected to be 10^{-12}–$10^{-14}\,\text{m}^2/\text{s}$ [6]. For D_i values of 10^{-14} and $10^{-12}\,\text{m}^2/\text{s}$, the adsorption Thiele modulus (φ_i) values which satisfy Eq. (20) are about 70 and 1.5, respectively (at zero coverage and at $T = 316\,\text{K}$). These results indicate that micropore diffusion resistance might have a significant role

on the adsorption rate. Exact analysis requires independent information about the value of micropore diffusion coefficient in this system. In principle, the micropore diffusion coefficients can be obtained from the analysis of second moment data in the same system. Since the experimental errors involved in the tail region of the response curves have a big influence on the second moment data, such data are usually rather scattered. Due to this, no attempt was made for the analysis of second moment data in this work.

The adsorption rate constants reported in Fig. 3 should be considered as the apparent values on the Pt surface. Carbon monoxide molecules adsorbed on the external surface of Pt–Al$_2$O$_3$ particles are expected to diffuse into these particles by a mechanism involving Knudsen and surface diffusion. A strong interaction between the diffusing molecules and the surface sites is expected in the micropores.

As it is expected, a significant decrease of adsorption rate constant was observed with an increase in surface coverage (Fig. 3). Also the initial value of adsorption rate constant (at zero coverage) showed an increasing tendency with an increase in temperature in the range 273–316 K. To illustrate the temperature dependence of adsorption rate constant, Arhenius plot corresponding to zero coverage (fresh
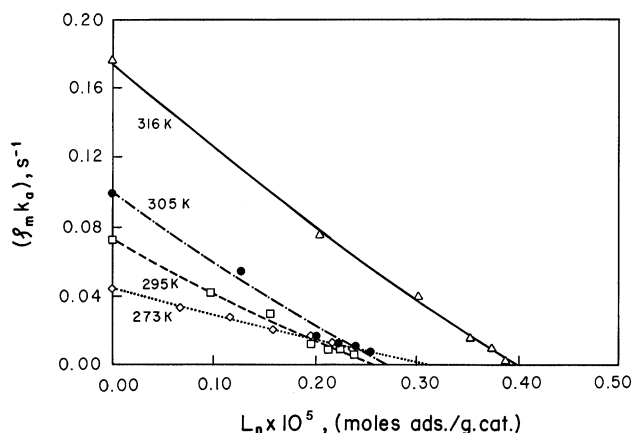

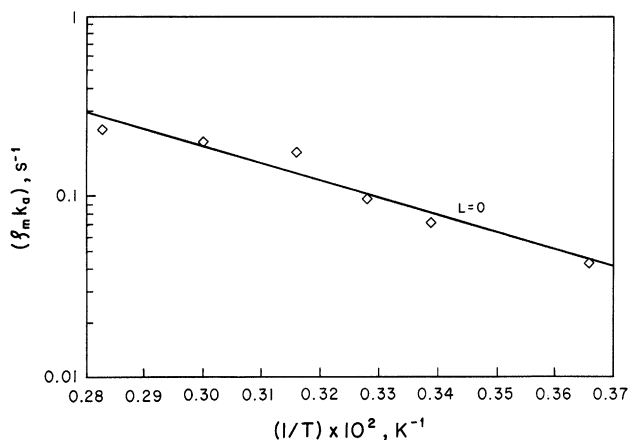Fig. 3. Variation of adsorption rate constant of CO with surface coverage.

Fig. 4. Temperature dependence of adsorption rate constants at zero coverage.

catalyst) is given in Fig. 4. The apparent adsorption rate constant was found to be slightly temperature dependent. The adsorption process is not totally nonactivated. The activation energy of adsorption was found as 21 kJ/mole at zero coverage. As expected, the activation energy of adsorption is rather small. This is of course an apparent activation energy value. Possible effect of pore diffusion resistance might have some influence on this value.

In order to see the high temperature behavior, CO pulse-adsorption experiments corresponding to zero coverage were carried out at temperatures up to 618 K. At temperatures above 320 K desorption rate may also become measurable and the assumptions involved in the derivation of Eq. (19) may not be justified. Experimental results obtained with a fresh catalyst indicated that irreversibly adsorbed fraction of a single CO pulse increased up to a temperature of about 350 K (Fig. 5). At higher temperatures, desorption process becomes more significant and at temperatures above 580 K the adsorption process becomes
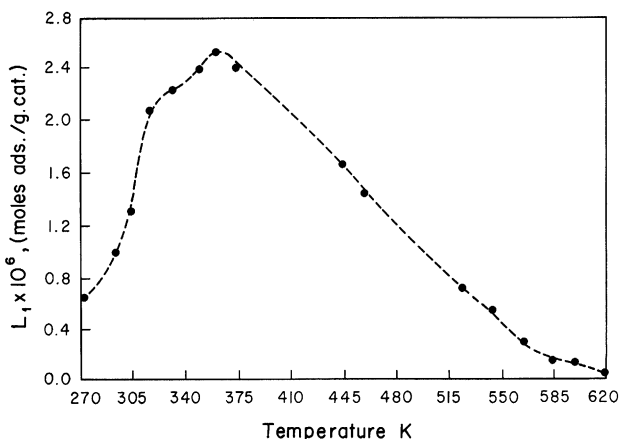
almost completely reversible within the time scale of a single pulse-response experiment. At such high temperatures instantaneous equilibration between gas phase and adsorbed concentrations may be assumed. At such high temperatures contribution of the support to the adsorption process [19] and spillover from metal to support may also be important.

The zeroth moment data obtained from the pulse-response experiments may also be used for the evaluation of metal surface area. Total amount of CO irreversibly adsorbed on the catalyst was calculated by the summation of moles of CO adsorbed in each pulse. The cumulative value of CO adsorbed was found to be about the same (2.6×10^{-6} mol CO adsorbed per g cat) within the 273–305 K temperature range. Using an adsorption stoichiometry of CO/Pt = 0.7 [10] the metal surface area was estimated to be as $0.37\,\text{m}^2/\text{g}$ of Pt–Al$_2$O$_3$, which corresponds to $147\,\text{cm}^2$ Pt/cm^3 of monolith.

5. Concluding remarks

In this work, the moment analysis was applied for the evaluation of adsorption rate constant on the metal surface of washcoated monolithic catalyst. It was illustrated that, by this technique adsorption rate parameters on the metal surfaces of supported catalysts may be evaluated at different surface coverages. It is a simple and fast technique and it gives significant information about the surface coverage dependence of adsorption rate constants and activation energy of adsorption rate.

Fig. 5. Temperature dependence of moles CO adsorbed per gram of fresh Pt–Al$_2$O$_3$ catalyst (obtained from first pulse-response adsorption experiments).

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