A Dynamic Method for the Effective Thermal Conductivity of Porous Solids

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For many catalytic reactions, significant temperature gradients may develop within the porous catalysts. Especially for systems with high heat of reaction and low thermal conductivity of pellets, considerable variation of the observed rate from the rate evaluated at the surface temperature is to be expected. Excellent reviews of heat effects and heat conduction in porous catalysts were reported in the well known books of Satterfield (1970), Petersen (1965), and Carberry (1976).

Heat conduction through porous catalysts takes place during the solid and gas phases in parallel with interchange of heat between the two phases. A model was proposed by Butt (1965) for the prediction of effective thermal conductivities. The thermal conductivity of porous solids depends strongly upon geometrical factors and porosity. Most of the effective thermal conductivity values reported in the literature are in the range of 10^{-3} to 10^{-2} J/s · cm · °C (Doğu, 1986). Effective thermal conductivities of some catalysts were reported by Sehr (1958), and by Mischke and Smith (1962).

In this study, a new dynamic technique was introduced for the measurement of effective thermal conductivity and the Biot number for heat transfer, for porous solids. For this purpose, pulse-response experiments were conducted in a single-pellet reactor. Application of this technique is not limited to porous catalysts. The technique allows fast and precise determination of thermal conductivity of any porous solid.

Method and Theoretical Development

The diffusion cell used for the measurement of effective diffusion, adsorption and reaction rate parameters (Doğu and Smith, 1975; Doğu 1984; Doğu and Ercan, 1983; Doğu et al., 1986) was modified and used for the measurement of effective thermal conductivity of a porous solid (Mürtezaoğlu, 1988). As shown in Figure 1, a two-zone cylindrical pellet was prepared in a teflon mold and placed into the single-pellet cell. The lower pellet's effective thermal conductivity was to be measured. In this work, the lower zone was made from α-Alumina. The upper zone of the pellet was made from (Pt-Al_2O_3 containing 0.5% Pt—active catalyst), and it acts as the heat source. Hydrogen gas streams passed over both end faces of the pellet in the single-pellet reactor. A pulse of oxygen gas (6% O_2 in H_2) was injected into the hydrogen stream flowing over the upper face. Oxygen tracer reacted with hydrogen within the upper active zone, and the heat liberated due to reaction in this zone was conducted through the porous solid placed to the lower zone of the pellet. Bell-shaped temperature-time curves were measured at the interface of upper and lower zones, and at the lower end face of the pellet by using carefully placed thin thermocouples. It was shown that the ratio of zeroth moments and the difference of first absolute moments of the temperature-time curves, were functions of Biot number and the effective thermal diffusivity of the lower pellet.

The controlling differential equation for the conduction of heat through the lower pellet is expressed as

$$\frac{\partial \theta}{\partial t} = \alpha_e \frac{\partial^2 \theta}{\partial Z^2} \tag{1}$$

The initial and boundary conditions are as follows:

$$t = 0; \quad 0 < Z < L; \quad \theta = 0 \tag{2}$$

$$Z = 0; \quad \theta = \frac{F_1(t)}{T_o} - 1 \tag{3}$$

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$$Z = L; \quad -k_e \frac{\partial \theta}{\partial Z} = h\theta \tag{4}$$

The solution of Eqs. 1–4 in the Laplace domain gives

$$\bar{\theta}|_{Z=L} = \frac{\overline{F_1^*}}{\cosh\left((s/\alpha_e)^{1/2}L\right) + \dfrac{h}{k_e}\dfrac{\sinh\left((s/\alpha_e)^{1/2}L\right)}{(s/\alpha_e)^{1/2}}} \tag{5}$$

where $\overline{F_1^*}$ is the laplacian of $(F_1(t) - T_o)/T_o$.

The zeroth and first moment expressions for the temperature-time curves at the lower end face of the pellet were evaluated from

$$m_n = (-1)^n \lim_{s \to 0} \frac{d^n \bar{\theta}|_{Z=L}}{ds^n} \tag{6}$$

The ratio of zeroth moments and the difference of first absolute moments of the temperature-time curves (at $Z = 0$) were then expressed as

$$\left(\frac{m_{0_{bottom}}}{m_{0_{top}}}\right) = \frac{1}{1 + \dfrac{hL}{k_e}} \tag{7}$$

$$\Delta\mu_1 = \mu_{1_{bottom}} - \mu_{1_{top}} = \left(\frac{L^2}{2\alpha_e}\right) \frac{\left(1 + \dfrac{1}{3}\dfrac{hL}{k_e}\right)}{\left(1 + \dfrac{hL}{k_e}\right)} \tag{8}$$

Experimental

Details of the single pellet conduction cell, and the schematic diagram of the experimental system are shown in Figures 2 and 3 respectively. The lower pellet was prepared from α-Al_2O_3 powder dried at 300°C for 18 hours. In order to minimize radial temperature variations, the pellet was made by pressing this powder into a teflon mold. The teflon mold was placed into a stainless-steel mold, to prevent any deformation during pellet preparation. After the preparation of the lower pellet, active catalyst powder (0.5% Pt on Al_2O_3) was pressed into the mold over the inert lower pellet. This active powder was prepared by the impregnation of α-Al_2O_3 powder by chloroplatinic acid solution. After the impregnation, the powder was heated up to 550°C for 5 hours, dried in a vacuum oven at 120°C, and reduced in a hydrogen atmosphere at 350°C. After the pulse response experiments, the two-zone pellet was taken out of the mold. The two zones of the pellet were easily separated and the physical properties of the lower pellet were determined using the mercury intrusion porosimeter. The porosity and the apparent density of the pellet were determined as 0.72 and 0.7 g/cm^3 respectively. The length of the lower zone of the pellet was 0.24 cm.

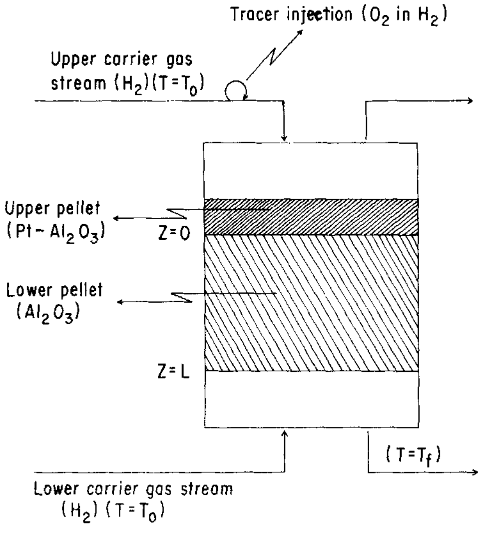

Figure 1. Single-pellet system.

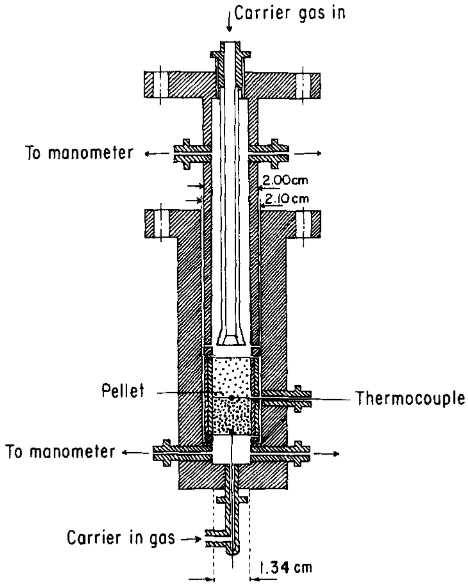

Figure 2. Single-pellet conduction cell.

The pulse-response experiments were conducted in the single-pellet conduction cell which was placed in a constant temperature oven at different temperatures (Mürtezaoğlu, 1988). A pulse of oxygen in hydrogen was injected into the upper H_2 carrier gas stream (6% O_2 in H_2). The highly exothermic reaction of H_2 with O_2 takes place within the upper, active zone of the pellet. The experimental values of the zeroth and first moments were then determined from

$$m_0 = \int_0^\infty \left(\frac{T - T_o}{T_o}\right) dt \tag{9}$$

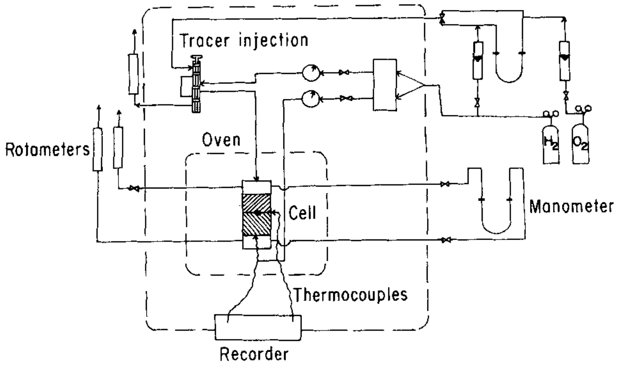

Figure 3. Experimental system.

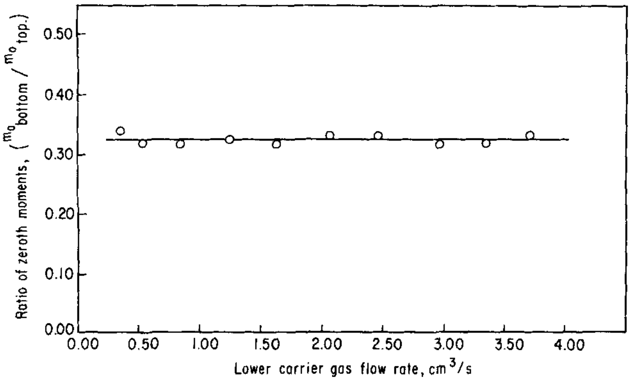

Figure 4. Zeroth-moment data (T_o = 110°C).

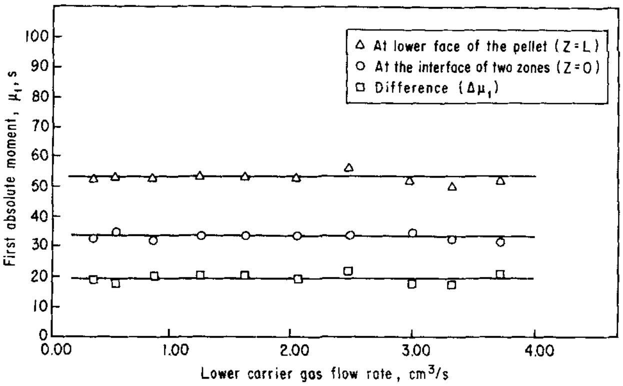

Figure 5. First-moment data (T_o = 110°C).

$$m_1 = \int_0^\infty \left(\frac{T - T_o}{T_o}\right) t\,dt \qquad (10)$$

The ratio of zeroth moments of the bell-shaped temperature-time curves obtained at the bottom and top of the lower pellet, obtained at 110°C oven temperature (T_o), are shown in Figure 4. One can see that, the dependence of this ratio on the lower carrier gas stream is negligible, showing that (hL/k_e) is essentially constant in this system. The first absolute moment data corresponding to the same set of experiments are given in Figure 5. Equations 7 and 8 were rearranged as

$$\left(\frac{hL}{k_e}\right) = \frac{1}{(m_{0_{bottom}}/m_{0_{top}})} - 1 \qquad (14)$$

$$\alpha_e = \frac{L^2}{6\Delta\mu_1}\left(\frac{m_{0_{bottom}}}{m_{0_{top}}}\right)\left(2 + \frac{m_{0_{top}}}{m_{0_{bottom}}}\right) \qquad (15)$$

and the data reported in Figures 4 and 5 were analyzed to determine the Biot number (hL/k_e) and α_e.

$$\frac{hL}{k_e} = 2.08$$

$$\alpha_e = 8.02 \quad 10^{-4}\,\mathrm{cm^2/s}$$

Neglecting the heat capacity of the gas in the pores as compared to the heat capacity of the solid, effective thermal conductivity of the Al_2O_3 pellet ($\epsilon = 0.72$) was determined as: $k_e = \alpha_e \rho_p C_{p_s} = 5.06 \times 10^{-4}$ J/cm · S · K at 110°C. The thermal conductivity value reported here corresponds to the effective conductivity of the alumina pellet used with H_2 as the carrier gas. Some difference of k_e was expected if the pores were filled with some other gas (Mischke and Smith, 1962).

The data in Figures 4 and 5 show that $m_{0_{bottom}}/m_{0_{top}}$ and $\Delta\mu_1$ values are essentially constant. Consequently, even a single pulse-response experiment is sufficient to determine k_e. The upper zone of the pellet is used essentially as the heat generation zone. The lower zone of the pellet can be prepared from any material of which the effective thermal conductivity is to be measured.

Notation

C_{p_s} = heat capacity of solid
$F_1(t)$ = temperature function at $Z = 0$
$\bar{F}_1^*$ = laplacian of $[F_1(t) - T_o]/T_o$
h = heat transfer coefficient
k_e = effective thermal conductivity
L = pellet length
m_n = nth moment
p = defined by Eq. 8
s = Laplace variable
t = time
T = temperature
T_o = oven temperature

Greek letters

α_e = effective thermal diffusivity
μ_1 = first absolute moment
ρ_p = apparent pellet density
θ = temperature, $=(T - T_o)/T_o$

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