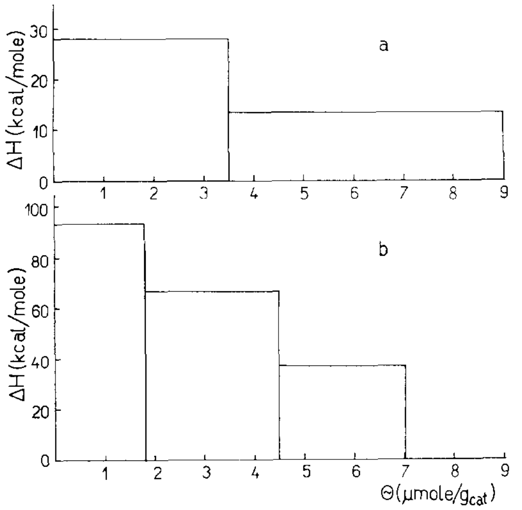

FIG. 1. Dependence of heat of adsorption of propylene (a) and oxygen; (b) on the occupation of the surface of Bi-Mo/SiO_2 oxide catalyst at 170°C.

surface of the catalyst is heterogeneous. The oxidation of propylene starts on the most active part of the surface and reduces it. In the presence of the gas-phase oxygen, this part of the surface is regenerated, but in the absence of the gas-phase oxygen the oxidation of propylene continues on parts of the surface, with more and more of a decrease in activity.

The heterogeneity of the surface was found also for the catalyst without a carrier [Fig. 5 of Ref. (*2*)]. In the range of 8% coverage of the surface the heat of adsorption of propylene at 35°C decreases from 12 to 7 kcal/mol.

From this point of view, the equations of the isotherm for a homogeneous surface cannot be used for the description of the adsorption of propylene on Bi–Mo/SiO_2 oxide catalysts.

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Relative Importance of Intraparticle and Interphase Heat Transport in Gas–Solid Catalysis

Two criteria have been developed to indicate the relative importance of intraparticle and interphase temperature gradients in catalytic reactors. We undertake in this note to evaluate these criteria, compare typical values for different types of catalytic reactors, and compare this result with actual experiments in which temperature differences associated with catalyst pellets have been measured.

Carberry (*1*) showed that in order for interphase heat transfer effects to predominate over intraparticle effects,

$$hd_p/\lambda < 1, \qquad (1)$$

where h is the gas–solid heat-transfer coefficient, d_p the particle diameter, and λ the effective thermal conductivity of the particle. For the same situation, Mears (*8*) developed the criterion,

$$hd_p/\lambda < 10. \qquad (2)$$

The Carberry criterion is based on maximum temperature gradients possible in the particle, using the Prater formula (*12*), plus the intuitive notion that the relative sizes of the internal and external temperature gradients should be approximately equal at the point of crossover from interphase to intraparticle control. However, the Mears criterion is based on a comparison of the same relative change (5%) in the reaction rate in the two phases. To discover a rate-controlling step implies, by definition, making a comparison of the relative rates of two or more steps under a given set of conditions. Thus, the Mears criterion follows the fundamental notion of this definition, and this is accepted as the better guide to the predominance of interphase vs intraparticle thermal effects.

We may rearrange Eq. (2) into the following form:

$$\mathrm{Nu}\, k/\lambda < 10, \tag{3}$$

where Nu is the Nusselt number ($= hd_p/k$) and k is the thermal conductivity of the fluid. Also Nu k/λ may be rearranged to show that for small departures from the crossover value 10,

$$\mathrm{Nu}\, k/\lambda = \Delta T_i/\Delta T_e = \frac{(\partial T/\partial r)_{\text{intraparticle}}}{(\partial T/\partial r)_{\text{interphase}}}, \tag{4}$$

where ΔT_i represents the internal temperature difference between surface and center of a particle, and ΔT_e the difference between particle surface and bulk stream temperatures. The factor Nu k/λ will be examined in order to decide the most frequent forms of heat transfer control in fixed-bed catalyst particles.

First, we examine the range of the variables k and λ. The thermal conductivity k of gases, including a wide range of polar and nonpolar organic vapors, is of the order of from 2×10^{-5} to 6×10^{-5} cal/sec cm °C, except for helium and hydrogen, whose thermal conductivities are of the order of 10 times greater than other gases (*3*). Effective thermal conductivities λ at approximately 1 atm pressure have been compiled over a wide variety of porous and powdered materials by Satterfield (*14*). These values generally range from 0.3×10^{-3} to 1×10^{-3} cal/sec cm °C, taking into account that the dependence of λ on k of the gas filling the pores is very weak (*10*). Thus, for ordinary gases, the ratio k/λ ranges from 0.02 as a minimum to 0.2 as a maximum. For hydrogen, k/λ will be of order 1, having a range of approximately 0.5–1.5.

We now examine several common fixed-bed reactor situations where the above conditions apply.

ESTIMATES OF NU k/λ *in Fixed Beds*

In single-pass laboratory reactors, values of the Reynolds number Re ($= d_pv/\nu$, where v is the superficial velocity, and ν the kinematic viscosity) will be low, since small diameters are used to avoid internal concentration gradients, while small flows are used to achieve measurable conversions. At low flows, the value of Nu approaches 2 or less (*5*). Thus, for systems using ordinary gases, Nu k/λ will be $2 \times 0.2 = 0.4$ as a maximum, indicating that interphase heat transfer will predominate.

In industrial reactors, large particle diameters (commonly 1/16–1/2 in.) and larger superficial velocities (of the order of several feet per second) give rise to typical Re values of 100–200. Kunii and Levenspiel (*5*) recently summarized existing data on heat and mass transfer coefficients. For these values of Re, values of Nu are typically from 20 to 30. Thus, Nu k/λ for ordinary gases will range from 0.3 to 5 in industrial reactors. This result indicates that interphase heat transfer will usually predominate, although at the upper end of this range, Eq. (4) shows that intrapellet temperature gradients may be significant.

In hydrogenation reactions, ammonia synthesis, etc., where hydrogen is in large excess, the situation is different. The ratio k/λ is substantially larger, while Nu is smaller. Even with similar superficial velocities, the value of Re decreases, because the kinematic viscosity of hydrogen is of the order of 10 times larger than for other gases at the same pressure (*15*). Thus typical values of Re at atmospheric pressure will be of the order of 30. Kunii and Levenspiel (*5*) have summarized fixed-bed heat transfer data from particles where $\mathrm{Re} < 100$. These data can be adequately represented in the range $1 < \mathrm{Re} < 100$ by their corresponding correlation for fluidized beds (correcting their erroneous coefficient 0.3 to read 0.03) as: $\mathrm{Nu} = 0.03\ \mathrm{Re}^{1.3}$. Thus, for $\mathrm{Re} = 30$, this correlation predicts Nu of the order of 3. Hence, Nu k/λ will also be of order 3, a value which corresponds to some of the higher values of Nu k/λ of ordinary gases. Although a value of 3 is less than that required for intraparticle control in Eq. (3), it is large enough that significant intraparticle thermal effects may sometimes be present. This conclusion is contrary to that of Carberry (*1*) and McGreavy and Cresswell (*7*), who state without proof that for hydrogen-rich gases the parameter $hd_p/\lambda (= \mathrm{Nu}\ k/\lambda)$, termed Nu′ by the latter, would be of the order of 0.1, indicating that intraparticle temperature effects would be insignificant in such reactions. However, it will now be demonstrated that for hydrogen-rich gases, significant intraparticle thermal effects may exist in laboratory reactors at values of Nu k/λ which are possible in industrial reactors.

Discussion of Measured ΔT's

Table 1 shows that the majority of measurements of thermal effects in pellets have been with hydrogenation reactions. Evidently these systems were chosen for their exothermicity; in retrospect, however, a somewhat less obvious reason can be ascribed by noting the large excess of hydrogen in all cases. As the fraction of H_2 increases, the ratio k/λ increases, permitting Nu k/λ to approach 10, where intraparticle thermal effects start to control.

Table 1 also shows that most studies have been performed in single-particle reactors with recirculation (to increase Re and Nu values). For these reactors, one can use 2 as a minimum value of Nu, the limit for an isolated sphere in a stagnant medium. For the case of Maymo and Smith (*6*), Re is estimated as 5, and from the correlation of Ranz and Marshall (*12*) for single spheres, the equivalent Nu is 3. Thus, the product Nu $k/\lambda = 3 \times 0.7 = 2$. However, using $\Delta T_i/\Delta T_e$ from Eq. (4), a better estimate would be 3.5. Although this value is less than the criterion value 10, the table shows that significant temperature gradi-

TABLE 1

Summary of Studies of Measured ΔT in Catalyst Particles

Authors	System	Composition	Reactor type[a]	k/λ	$\Delta T_i/\Delta T_e$[b] (°C/°C)	$\Delta T_{\max}$ (total) = $\Delta T_i + \Delta T_e$ (°C)
Cunningham, Carberry, and Smith (*2*)	$H_2 + C_2H_4 \rightarrow$ Cat: Cu/MgO	85% H_2	SP	1.4	—	20
Maymo and Smith (*6*)	$H_2 + \frac{1}{2}O_2 \rightarrow$ Cat: Pt/Al_2O_3	95% H_2	SP, R	0.7	320/90 = 3.5	410
Otani and Smith (*1*)	$CO + \frac{1}{2}O_2 \rightarrow$ Cat: Cu/MgO	94% O_2	SP, R	0.16	—	6.5
Wurzbacher (*16*)	$H_2 + \frac{1}{2}O_2 \rightarrow$ Cat.1: Ag/ porcelain wall	92% H_2	SP using "artificial" particle	1	38/19 = 2	57
	Cat.2: Pt/ porcelain wall			0.28	51/92 = 0.6	143
Miller and Deans (*9*)	$H_2 + \frac{1}{2}O_2 \rightarrow$ Cat: Pt/Al_2O_3	95% H_2	SP, R	1.4	—	33
Irving and Butt (*4*)	$H_2 + C_6H_6 \rightarrow$ Cat: Ni/ kieselguhr	83% H_2	SP	7	20/120 = 0.17	140

[a] SP = single particle; R = recirculating.

[b] Using corresponding maximum reported ΔT values.

ents occurred within the catalyst particles.

With the other hydrogen-rich systems of Table 1, it is expected that Nu k/λ will be of the same order as for Maymo and Smith. However, there are apparent exceptions. The value $k/\lambda = 7$ of Irving and Butt (*4*) seems unusually high, and would require that Nu k/λ be at least 14, whereas $\Delta T_i/\Delta T_e$ is of the order of 100 times lower. This suggests that their attempt at modelling *a priori* the value of $\lambda = 0.7 \times 10^{-4}$ was unsuccessful, λ being severely underestimated.

Also, k/λ seems inexplicably low with the Pt catalyst in Wurzbacher's study (*16*). However, in five cases in Table 1, Nu k/λ appears to lie above at least 2, which suggests that internal temperature gradients cannot be neglected.

By contrast, in the hydrogen-free system of Otani and Smith (*11*), Nu k/λ appears to be of the order of 0.3, and the measured overall temperature difference may be mainly an interphase effect, though no surface temperatures were taken to support this view.

The values of Nu k/λ of Table 1, associated with significant intraparticle temperature gradients, are also possible in hydrogen-rich systems in industrial reactors. For example, suppose in a hydrogenation system of 90% H_2 we have an ambient temperature of 100°C, $v = 2.5$ ft/sec, and $d_p = \frac{1}{4}$ in. Taking $\nu_{H_2} = 0.0015$ ft^2/sec (*15*), we find Re = 35. From the Kunii and Levenspiel correlation cited earlier, we calculate Nu = 3. If $k/\lambda = 1$, then Nu $k/\lambda = 3$, which indicates that an appreciable temperature gradient may be present within the catalyst particles.

Conclusions

For the majority of laboratory and industrial fixed-bed reactors, interphase heat transfer will predominate over intraparticle heat transfer. However, in hydrogen-rich atmospheres especially, intraparticle heat effects may not always be negligible.

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