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On the possibility of a significant temperature gradient in supported metal catalysts subjected to microwave heating

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A simple model is presented which estimates the temperature gradients in microwave-irradiated 1 and 100 nm metallic particles which are typically found in a supported metal catalyst structure. The two particle sizes allow limiting case calculations of the temperature rise over the range of typical particle sizes. The model, based on a simple steady-state energy balance, uses the assumption that the particles only lose heat to the gas-phase, and not the support matrix. This represents a best-case scenario for a temperature gradient relative to the surroundings. The model indicates that the temperature gradient is insignificant and this conclusion is supported by an experiment in which the microwave-driven carbon monoxide reaction acts as an in situ temperature probe.

Keywords: microwave catalysis, selective heating, temperature gradients

1. Introduction

The possibility of selectively heating small metal crystallites in supported media has important consequences in some catalytic reactions. Often, undesirable gas-phase reactions degrade the desired selectivity. If the small metal crystallites absorb microwave energy at a substantially higher rate than their surroundings, there is the possibility of establishing a temperature gradient from the reaction surface to the gas-phase. This may allow quenching of the undesirable gas-phase reactions. An important example is the oxidative coupling of methane to higher hydrocarbons where the gas-phase reactions of methyl radicals could yield economically unimportant products. It is because of these important possibilities that we investigate the possibility of a temperature rise in these supported metal crystallites. Figure 1 shows a sketch of a supported metal catalyst system where microwave energy is being absorbed and temperature differences may exist.

Previous work in the literature has suggested that a temperature gradient may exist from the surface to the gas-phase during microwave heating [1,2]. In this previous work, the surface temperature has not been directly measured. However, we have recently investigated CO oxidation kinetics under microwave heating [3]. Our results suggest that the reaction surface is not significantly hotter than the average bed temperature for the catalyst system studied. It will be shown in this paper that it is highly unlikely that a temperature gradient can be sustained from the particle surface to the surroundings.

2. Heat transfer model

The analysis begins by considering a metal crystallite in a supported metal catalyst subjected to microwave heating. A similar analysis was performed by Holstein and Boudart [4], where heat was provided to the catalyst via an exothermic chemical reaction. These authors refuted the possibility of any temperature rise due to exothermic reaction, but used a theory which is most

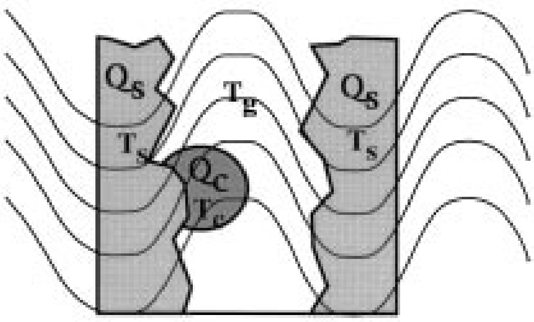

Figure 1. A representation of a supported metal crystallite in a pore. The sinusoids represent the presence of microwave energy. The Q terms represent the rate of energy absorption by the crystallites and the support. The different T subscripts represent gas, crystallite and support and in general $T_g \neq T_s \neq T_c$.

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appropriate when the Knudsen number is small (mean free path/characteristic dimension $= \lambda_g D_p \ll 1$). We will use the theory presented by Springer which [5] accounts for steady-state heat transfer when the Knudsen number is large, as is the case for nanometer-sized crystallites in a micropore. Figure 2 shows a schematic of the system where energy is absorbed by the metallic particle and subsequently dissipated into the gas-phase. First, we consider a steady-state energy balance where the heat dissipated in the crystallite equals the heat lost only into the gas-phase. As per Holstein and Boudart [4], this represents the best opportunity for a temperature gradient to be sustained; including the heat conduction into the support would lower the temperature gradient. Indeed, this is a reasonable approximation because typical Pd or Pt particles are spheroids and only make a small area contact with the support [6–9]. The steady-state energy balance is simply:

$$Q_\mathrm{d} = Q_\ell \,, \tag{1}$$

where the subscript d refers to dissipation via microwaves in the crystallite and ℓ refers to heat lost into the gas-phase. When the gas mean free path exceeds the particle size, the term on the right may be written [5] as

$$Q_\ell = A\left[\frac{1}{\alpha_1} + \left(\frac{R_1}{R_2}\right)^b \left(\frac{1}{\alpha_2} - 1\right)\right]^{-1} \left\{\frac{P}{(2\pi MRT)^{1/2}}\right\} \times (C_\mathrm{v} + \tfrac{1}{2}R)(T_1 - T_2)\,. \tag{2}$$

R_1 is the radius of the crystallite, R_2 is the radius of the pore, A is the surface area of the crystallite, C_v is the molar heat capacity of the gas, M is the molecular weight of the gas, R is the molar gas constant, and P is the gas pressure. T is evaluated as the average of T_1 and T_2 at the respective surfaces. α_1 and α_2 are the accommodation coefficients of the two surfaces. A good discussion of the accommodation coefficient is given in ref. [5], but suffice it to say that the coefficient is an empirical factor which indicates the efficiency of molecular energy transfer to a surface; e.g. analogous to a sticking coefficient. Generally, engineering materials have accommodation coefficients in the range of 0.8–1 for common gases. Since we are examining the limiting case for poor heat transfer, we use both coefficients = 0.8. Finally, the exponent b is a geometrical term, equal to 2 for concentric spheres [5]. For this simplified analysis, we assume that the system consists of an isolated metal sphere in a spherical cavity as shown in figure 2.

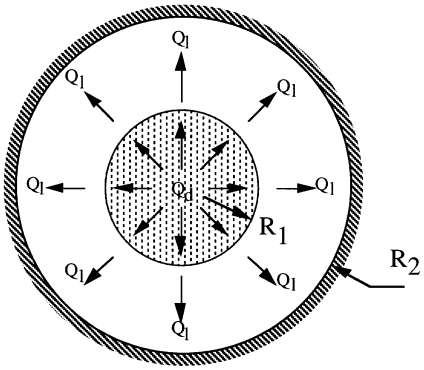

Figure 2. An illustration of a hypothetical metal crystallite which is suspended in air inside a spherical cavity. Q_d represents the microwave energy which is dissipated in the crystallite and Q_ℓ represents the heat loss into the gas by conduction.

Equation (2) can be loosely interpreted in a simple way. The term containing the accommodation coefficients indicates the efficiency with which gas molecules can gain energy from surface 1 and deposit energy on surface 2. The pressure term, in brackets, gives the collision frequency of molecules on the surface. Finally, the term containing the heat capacity indicates the amount of energy stored in each molecule for energy transport.

The LHS of eq. (1) was evaluated by using the expression for power dissipated in a dielectric, non-magnetic material which is exposed to an electromagnetic field [10]:

$$Q_\mathrm{d} = \pi V f E^2 \varepsilon_0 \varepsilon'' \,. \tag{3}$$

In this expression, V refers to the particle volume, f is the microwave frequency, E is the magnitude of the electric field, ε_0 is the permittivity of free space (8.8×10^{-12} F/m) and ε'' is the dielectric loss factor of the material. Substituting eqs. (2) and (3) into (1) and solving for the temperature rise yields:

$$(T_1 - T_2) = D_\mathrm{p}\pi f E^2 \left[\frac{1}{\alpha_1} + \left(\frac{R_1}{R_2}\right)^b \left(\frac{1}{\alpha_2} - 1\right)\right] \varepsilon_0\varepsilon'' \times \left[6\left\{\frac{P}{(2\pi MRT)^{1/2}}\right\}(C_\mathrm{v} + \tfrac{1}{2}R)\right]^{-1}. \tag{4}$$

All of the parameters on the RHS of eq. (4) are known, can be calculated, or limiting case assumptions can be made. Numerical values of the LHS terms for calculating temperature rise are reported in table 1.

The preceding analysis assumes that the mean free path of the gas is larger than the particle size. We now consider the case where the gas mean free is the same order of magnitude as the particle size, such that $\lambda \sim Dp$. We choose a particle size of 100 nm because this represents a practical upper limit in a typical supported metal catalyst. In the transition regime, the heat loss in eq. (2) is modified using [5]:

$$\frac{Q_{\ell,\mathrm{tr}}}{Q_\ell} = 1 + \left(\frac{4}{15}\right)\left(\frac{R_1}{\lambda}\right)\alpha_1\left[1 - \left(\frac{R_1}{R_2}\right)\right]^{-1}, \tag{5}$$

where the subscript tr indicates the transition regime. For $R_1 = 100$ nm, $R_2 = 200$ nm, $\alpha_1 = 0.8$ and $\lambda = 100$ nm, the above expression is evaluated as 1.43. This value scales the temperature rise, given by eq. (4), such that $\Delta T_\mathrm{tr} = 0.7\Delta T$.

Table 1
Numerical values for the parameters in eqs. (4) and (5)

Variable	Definition	Value	Units	Justification
E	electric field	10^6	V/m	breakdown of air
α_1	accommodation coefficient	0.8	none	optimized heating
α_2	accommodation coefficient	0.8	none	optimized heating
R_1	particle radius	0.5×10^{-9}	m	typical particle size
R_2	pore radius	10×10^{-9}	m	typical pore size
P	pressure	1.01×10^5	kg/(m s^2)	typical pressure
M	molecular weight	28.97	kg/kg-mol	MW of air
R	gas constant	8314.4	J/(kg-mol K)	gas constant
T	average temperature	500	K	typical reaction temperature
C_v	heat capacity	21000	J/(kg-mol K)	approximate value for air at STP
D_p	particle diameter	10^{-9}	m	particle diameter
f	electric field frequency	independent variable	Hz	typical microwave frequency

Table 1 provides numerical values for the parameters in eqs. (4) and (5). Using these parameters, eq. (4) becomes

$$\Delta T = (6.2 \times 10^{-5}) D_p f \varepsilon'' \tag{6}$$

for the case where the particle size is smaller than the mean free path, and

$$\Delta T_{tr} = (4.4 \times 10^{-5}) D_p f \varepsilon'' \tag{7}$$

for the case where the particle size is approximately equal to the mean free path. The crux of this analysis now lies in the determination of ε''.

3. Dielectric loss in metallic particles

The preceding analysis yielded a relationship between commonly known or determinable quantities, dielectric loss of the metallic crystallites and their effect on a temperature rise from the small metallic crystallites to the surroundings. The Drude [12] theory of metals provides an estimate for the conductive loss of a metal:

$$\varepsilon''(\omega) = \frac{\sigma/\omega\varepsilon_0}{1+\omega^2\tau^2} \approx \frac{\sigma}{\omega\varepsilon_0} . \tag{8}$$

For metals, the room-temperature relaxation time τ is (5–25)$\times 10^{-15}$ s and $\omega\tau$ may be neglected at frequencies up to the far infrared.

Wagner [10,13] and Hamon [10,14] have examined a situation comparable to our own study. In 1914 Wagner proposed a model for loss due to interfacial polarization effects, the loss in a system composed of a small volume-fraction of a conducting phase dispersed in a loss-free dielectric medium. The macroscopic dielectric loss is:

$$\varepsilon''(\sigma,\omega) = \frac{9\upsilon\varepsilon_m^2(\sigma/\omega\varepsilon_0)}{[\varepsilon(\infty)+2\varepsilon_m]^2+(\sigma/\omega\varepsilon_0)^2} \approx 9\upsilon\varepsilon_m^2\frac{\omega\varepsilon_0}{\sigma} . \tag{9}$$

Here υ is the volume fraction of the conducting phase, ε_m is the permittivity of the medium and is some fraction of 9.34, the permittivity of bulk alumina. The quantity σ is the low-frequency conductivity and $\varepsilon(\infty)$ is the high-frequency permittivity of the metallic particles. The full expression in eq. (9) increases at first linearly with σ as in eq. (8), goes through a maximum for $\sigma \approx \omega\varepsilon_0$, and decreases as $1/\sigma$ at higher conductivity. At an operating frequency of 915 MHz, the conductivity at the maximum is 0.051 $(\Omega\ \mathrm{m})^{-1}$, far below metallic conductivities and allowing us to make the indicated approximation. In 1953 Hamon [10,14] verified an equation similar to eq. (9) by measuring the dielectric loss of copper phthalocyanine particles dispersed in a paraffin matrix.

4. Estimating the temperature rise

We estimate the specific loss factor:

$$\frac{\varepsilon''}{\upsilon} = 9\varepsilon_m^2 \frac{\omega\varepsilon_0}{\sigma(D_p)} , \tag{10}$$

where σ is a function of particle diameter D_p, the result of internal surface scattering [15,16]:

$$\sigma(D_p) = \frac{\sigma(\infty)}{1+\lambda_e/D_p} . \tag{11}$$

The bulk conductivity $\sigma(\infty)$ is taken as 10^7 $(\mathrm{Q\ m})^{-1}$ and the electron mean free path λ_e as 7.5 nm, representative of either Pd or Pt.

For particles 1 nm in diameter, the particle specific loss factor is 2.05×10^{-6}. The upper limit of the temperature rise is:

$$\Delta T = (6.2 \times 10^{-5}) D_p f \varepsilon''/\upsilon = 1.6 \times 10^{-10}\ \mathrm{K} \tag{12}$$

and for particles 100 nm in diameter, the particle specific loss factor is 2.4×10^{-7}. The upper limit of the temperature rise is:

$$\Delta T = (4.3 \times 10^{-5}) D_p f \varepsilon''/\upsilon = 1.1 \times 10^{-10}\ \mathrm{K} . \tag{13}$$

This limiting case (optimal heating) analysis indicates that the particles are in thermal equilibrium with their surroundings.

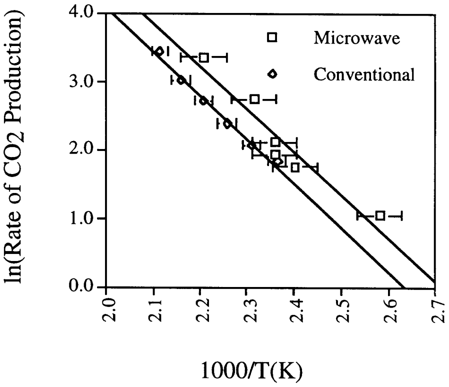

Fig. 3. Arrhenius plot from ref. [3] which compares the rate of the CO oxidation reaction under microwave versus conventional heating. A stoichiometric mixture of CO and O_2 was used with a 5 wt% Pd/alumina catalyst. The reaction rate was insensitive to the mode of heating, and therefore provides indirect evidence that the surface temperature of the metal crystallites is not significantly hotter than their surrounding support.

5. Supporting evidence

The kinetics of the carbon monoxide oxidation reaction over 5% Pd/Al_2O_3 was studied under conventional versus microwave heating [3]. The reaction temperature was measured using a thermocouple which was inserted into the reaction zone after the microwave energy was turned off. A temperature decay curve was recorded and extrapolated back to the true reaction temperature. The process was calibrated and an error analysis was performed [3]. This method only allows observation of the bulk support temperature. The metal particle temperature was not observable due to the low mass fraction and rapid transient behavior of such small objects. However, the rate of reaction provides an indirect measure of the metal surface temperature. We would have expected that the microwave-heated reaction rate would be higher than that for conventional heating at a given temperature if a significant temperature gradient existed between the metallic particles and their surroundings. The Arrhenius plot is shown in figure 3, and the rates of reaction are found to be nearly identical within experimental error at any given observed temperature [3]. This indicates that the temperature of the microwave-heated metallic particles is not significantly higher than the surrounding support material.

6. Conclusion

A best-case analysis has been presented for the largest possible temperature gradient, relative to the surroundings, of small metallic particles which are exposed to microwave energy. The analysis assumes that the metal particles are embedded in a loss-free dielectric support, hence the model is not intended for calculating the total power consumption. The temperature difference between the metal particle and the surroundings was calculated for two limiting cases: (1) gas mean free path greater than the particle size and (2) particle size comparable to the mean free path. In both cases, the temperature rise was determined to be insignificant. We do not believe it is possible to cause a temperature gradient between metallic particles (1–100 nm) and their surroundings in a typical supported metal catalyst structure (metal particles deposited on a ceramic support) by using microwave energy. This conclusion was supported by the observed reaction rates of the microwave-heated CO oxidation reaction.

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