Particle size effect in microwave-enhanced catalysis

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Heat transfer analysis is used to determine the potential for selective heating of metallic catalyst particles attached to a support through the use of microwaves. Important parameters are identified and estimated. Using these estimates, it is concluded that selective heating is possible with microwave fields of high frequency heating catalyst beds cooled by gases at low pressures. Selective heating is found to have a strong dependence on catalyst particle size, with optimum sizes in the 40–80 nm range. There is also strong dependence on microwave frequency. Areas of greatest uncertainty are discussed.

Keywords: catalyst, microwave, heat, selective

1. Introduction

Microwave heating offers several potential advantages over conventional heating for inducing or enhancing chemical reactions. These include direct microwave interaction with certain classes of molecules, volumetric heating rather than heat flow through the vessel wall, energy savings (less waste heat), increased control over heating rates, and the possibility of selective enhancement of desired reactions. The advantages of microwave heating are particularly attractive in the case of catalytic reactions, where it may be possible to selectively promote desirable reactions while suppressing undesirable ones. The state-of-the-art in this field has been summarized recently by Roussy and Pearce [1].

One of the principal limitations to wider employment of microwave heating in the chemical industry is a lack of fundamental understanding of microwave heat generation and transport at the microscopic level [2]. The work reported here is directed toward increasing understanding of heat production and transport when microwave energy is used to promote chemical reactions on supported metal catalysts. These materials consist of nanometer-size metallic particles distributed within a porous ceramic substrate. Microwave fields do not couple to the ceramic support at temperatures of interest in chemical reactions, but they may couple strongly to the metallic particles because of their high electrical conductivity. This offers the opportunity to selectively heat the catalyst particles to temperatures higher than the matrix if heat loss from the particles is not too rapid. Selective heating translates to greater control over the chemical reactions, and possibly greater selectivity of reaction pathways.

Several investigators have reported experimental results which appear to support assumptions of enhanced catalysis under microwave irradiation. In 1975, Bartley [3] reported selective heating of iron particles on a silica–alumina support using RF heating (4 MHz). The reported temperature difference of up to 94°C was inferred from observed chemical reactivities whose temperature dependencies are known. However, the experimental results are apparently open to other interpretations [4]. Wan et al. describe success in cracking methane to ethylene and hydrogen [5,6], the destruction of chlorinated hydrocarbons [7,8], and the hydrodesulfurization of hydrocracked pitch [9] using pulsed microwave heating. Seyfried et al. [10] studied the effects of microwave irradiation of an alumina-supported 0.2 wt% platinum catalyst. They report increased isomer selectivity when the catalyst is treated by microwaves; in addition, the selectivity remains high even when the catalyst is subsequently heated conventionally due to an apparent change in the size or shape of the catalyst particles. Bool et al. [11] applied microwave energy to the oxidative coupling of methane over rare-earth oxide catalysts. They found that the microwave heated reaction occurred at lower bulk temperatures than the conventionally-heated counterpart. They also report enhanced yields and selectivities at lower temperatures under microwave irradiation.

These enhancements are often explained in terms of locally higher temperatures at certain active centers within the catalyst bulk. This would certainly accord with the known rapid heating of metal particles in the presence of a microwave field. However, some investigators suggest that the tiny metallic particles typical of supported metal catalysts cannot achieve a temperature significantly higher than that of the support or the fluid medium because of the efficiency of energy transport at this small case. Holstein and Boudart [12], on the basis of an elementary energy balance, argue that the temperature of a catalyst particle cannot exceed the support temperature by more than 0.03% as a result of the heat released during an exothermic reaction. However, if a microwave field is used for the heat source, it is possible that the particle temperatures can significantly exceed those of the support. The arguments in ref. [12] are not directly applicable to nanometer-sized particles.

Unfortunately, a direct experimental proof of this concept is extremely difficult. Measuring the temperature of individual particles in the nanometer size range is beyond current experimental capabilities. The philosophy of the work reported here is to postulate a plausible model for microwave interactions with the catalyst particle and for heat transport from the particles, and to investigate the resulting potential for particle heating. This modelling effort will thus focus attention on the areas of greatest uncertainty, perhaps generating further research which will help to reduce these uncertainties.

2. Mathematical model

We are primarily considering supported metal catalysts, which consist of a porous ceramic support, such as alumina or magnesia, containing a distribution of nanometer-size metallic particles such as platinum or iron. Typically, the ceramic support is in the form of spherical pellets a few millimeters in diameter arranged in a packed or fluidized bed (figure 1). These pellets have surface areas of 50–100 m^2/g, with densities of about 25% of the maximum theoretical density. The metallic particles are present to a concentration of 0.2–5 wt%, so individual particles are effectively isolated from each other (figure 2). Because of their tiny size (1–20 nm) and high thermal conductivity, no temperature gradients can exist within a particle. In their initial state, these particles are nearly spherical in shape, but can deform when heated [13]. The particles are partially attached to the ceramic matrix, and partially exposed to the fluid which carries the reactants. In the most common applications, the fluid is a hydrocarbon gas, such as methane or butane, in an inert carrier gas, such as helium.

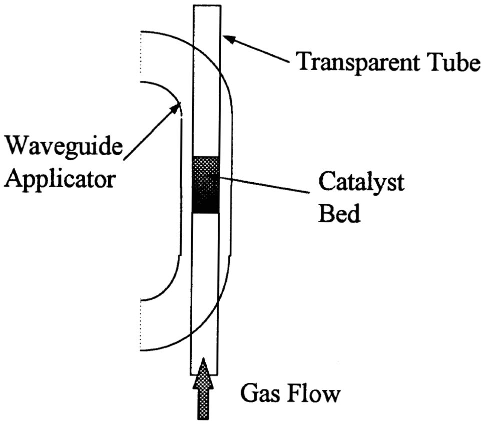

Figure 1. Typical catalyst bed experiment.

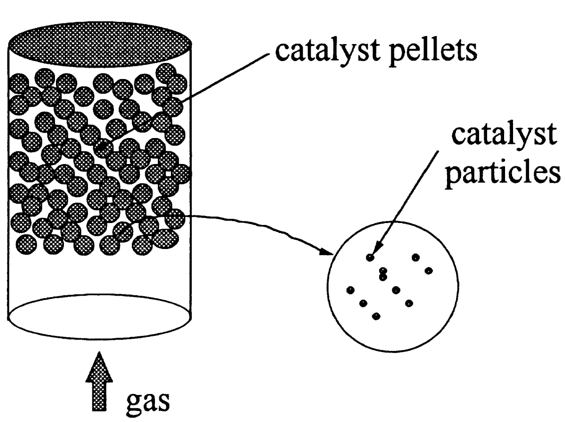

Figure 2. Detail of catalyst bed.

There are available in the literature a number of high-resolution electron microscopy studies of the microstructure of supported metal catalysts [13–16]. This work suggests that a fraction of the particle surface is in direct contact with the support material, and the remainder is exposed to convection and radiation heat loss. Thus an approximate model for the time-dependent temperature T_p of a catalyst particle may be based on a lumped-capacitance approach, and represented as

$$\rho_p C_p V_p \frac{dT_p}{dt} = \dot{q}_p V_p - h_s A_s (T_p - T_m) - h_{nc}(A - A_s)(T_p - T_m) \,, \qquad (1)$$

where h_s represents the contact conductance heat transfer coefficient between the particle and the matrix, and h_{nc} represents the non-contact heat transfer coefficient, composed of contributions from convection, h_{conv}, and radiation, h_{rad}. A_s represents the catalyst particle surface area which contacts the matrix. For purposes of this study, we assume that the gas and the support matrix are at the same temperature (T_m). $\dot{q}_p$ represents the volumetric heat generation in the particles from microwave absorption, V_p is the particle volume, and ρ_p and C_p are the particle density and specific heat capacity, respectively.

Since the mean-free-path of the gas molecules is much larger than the catalyst particles, the convection component is computed from the kinetic-theory result appropriate to free-molecular flow, given by [17]

$$h_{conv} = \alpha P \left(\frac{2k}{\pi M T} \right)^{1/2} , \qquad (2)$$

where α is the thermal accommodation coefficient, P is the gas pressure, k is Boltzmann's constant, T is the gas temperature, and M is the molecular weight of the gas. The radiation coefficient, h_{rad}, is given by

$$h_{rad} = \epsilon_r \sigma (T_p^3 + T_p^2 T_m + T_p T_m^2 + T_m^3) \,, \qquad (3)$$

where ϵ_r is the emissivity of the particle and σ is the

Stefan–Boltzmann constant. Using $\alpha = 0.1$ [18,19], $\epsilon_r = 0.8$, $T_p = 500$ K, $T_m = 300$ K, and assuming an 80%/20% mixture of helium and butane at normal atmospheric pressure, eqs. (2) and (3) yield $h_{\mathrm{conv}} \approx 12{,}000\ \mathrm{W/(m^2\,K)}$ and $h_{\mathrm{rad}} \approx 12\ \mathrm{W/(m^2\,K)}$.

The heat conductance h_s to the solid at areas of contact is more difficult to estimate. The phonon mean free path in the solid matrix is likely to be of the same order of magnitude as the particle size, leading to a temperature discontinuity at the particle surface [20,21], analogous to the temperature-jump regime of heat conduction in a low-density gas [17]. The magnitude of this temperature jump is determined by the size of the particle relative to the phonon mean free path, and the effective phonon emissivity of the particle. Since we are interested here in the maximum potential temperature difference between particle and matrix, and the contact area is likely to be small [14,15], heat conduction to the matrix is neglected in the calculations.

The volumetric heat generation rate, $\dot{q}_p$, is computed from

$$\dot{q}_p = \sigma_e |E|^2 , \tag{4}$$

where σ_e is the DC electrical conductivity and E is the rms electrical field strength in the particle. The field interior to the particle can be determined from [1]

$$E = \frac{3\epsilon_1^*}{2\epsilon_1^* + \epsilon_2^*} E_0 , \tag{5}$$

where E_0 is the exterior field, and ϵ_1^* and ϵ_2^* are the complex permittivities of the matrix and the metallic particle, respectively. The complex relative permittivity of the metal particles is [1] $\epsilon_2^* = 1 - j\sigma/\omega\epsilon_0$, where σ is the electrical conductivity. Nimtz et al. [22] have shown both experimentally and theoretically that the electrical conductivity of metal particles smaller than about 5 μm decreases proportional to the third power of the particle diameter because of 3D quantum size effects. Thus we take

$$\sigma_e = \left(\frac{D_p}{5 \times 10^{-6}} \right)^3 \sigma_0 , \tag{6}$$

with $\sigma_0 = 10^7\ (\Omega\ \mathrm{m})^{-1}$, the bulk conductivity. For a field strength of 6×10^5 V/m, a frequency of 10^9 Hz, and $\epsilon_1^* = 10 - j0$ (appropriate for alumina), eqs. (4)–(6) yield $\dot{q} \approx 5 \times 10^{11}\ \mathrm{W/m^3}$. At equilibrium we have

$$(h_{\mathrm{conv}} + h_{\mathrm{rad}}) A \Delta T = \dot{q}_p V , \tag{7}$$

where ΔT represents $T_p - T_m$. Also ignoring radiation heat loss, which is likely to be small at temperatures of interest in catalyst bed applications, gives

$$\Delta T_{\max} = \frac{\dot{q}_p r_0}{3 h_{\mathrm{conv}}} . \tag{8}$$

For a 10 nm particle and the parameter values described above, eq. (8) predicts a temperature difference of about 0.1 K. This is clearly too small to be of interest. However, there are several parameters in the calculation which can be controlled to increase this temperature difference dramatically. These include the gas pressure, the microwave frequency, and the catalyst particle size.

The most obvious way to increase the ΔT is to decrease the gas pressure, as eq. (2) shows that the heat loss is directly proportional to gas pressure. Thus the ΔT increases by an order-of-magnitude for each order-of-magnitude decrease in pressure. The downside of this approach is that it also decreases the collision rate of gas molecules with catalyst sites, thus decreasing the chemical reaction rate.

The effect of microwave frequency is not so obvious since this parameter appears in the complex permittivities of eq. (5). The heat generation, in general, increases with microwave frequency; however the effect is strongly dependent on the catalyst particle size. For a 10 nm particle, increasing the frequency has negligible effect, whereas for a 50 nm particle, the effect of increasing frequency is quite significant. These effects are illustrated in figure 3 for a gas pressure of 0.1 atm.

Eq. (8) suggests that the temperature difference decreases with particle size. However, the electrical conductivity σ_e also decreases with particle size as discussed above. Decreasing conductivity leads to a more dielectric-like behavior, with consequent increase in the strength of the field interior to the particle, but decrease in ohmic heating. This leads to an optimum particle size for selective heating, which depends on the particular catalyst/support system. For platinum on alumina, the size dependence is displayed in figure 4, again for 0.1 atm gas pressure. It is clear that there is an optimum particle size for each frequency.

3. Conclusions and future work

The results reported here are not very optimistic for achieving selective heating of supported metal catalysts by microwaves under conventional conditions. It does appear that tiny metallic catalyst particles of the type considered here can be heated to temperatures significantly higher than those of the support matrix and the catalyst bed under ideal conditions. These results lend credibility to published experimental studies where enhanced chemical reactions under microwave heating were attributed to a small number of sites with temperatures significantly in excess of the measured catalyst bed temperature [11]. Since catalyst systems necessarily include particles with a range of sizes and exposures, it is possible that some small number do achieve the right conditions for selective heating. This would clearly be enhanced by heating with higher-frequency microwave fields, and using catalysts with larger catalyst particle size.

Several aspects of the model described here are rather

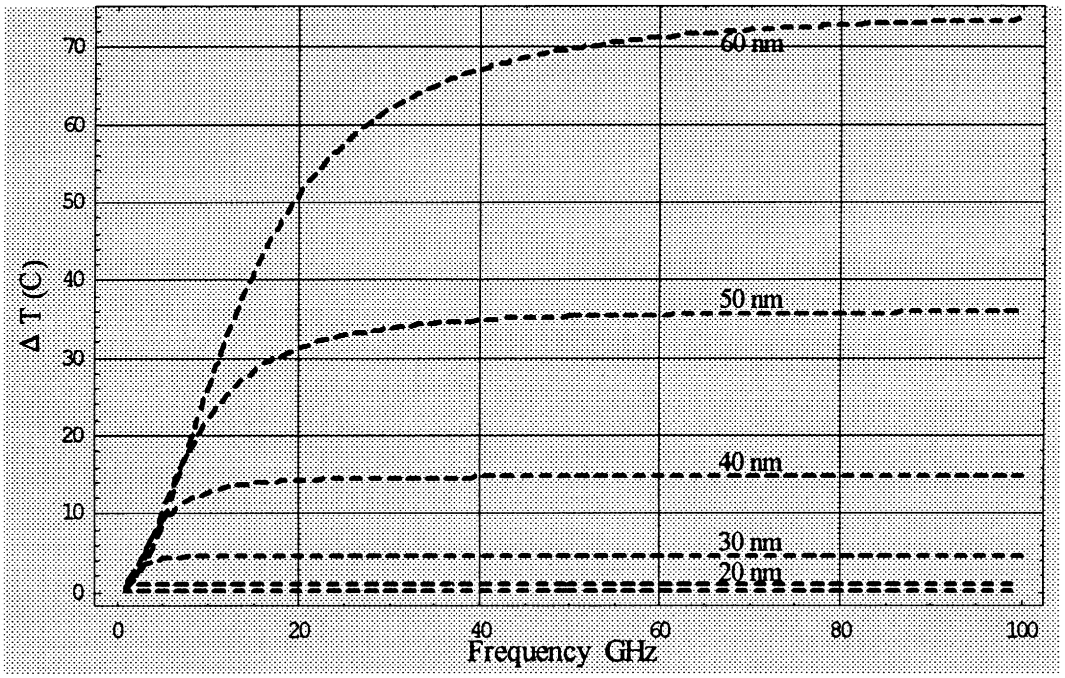

Figure 3. Effect of microwave frequency and particle size on temperature rise.

speculative and could significantly alter these conclusions. The extent of contact between the catalyst particles and the support matrix can only be guessed at from the TEM photographs [13–16]. The heat transfer coefficient at the areas of contact is unknown. The heat transfer to the gas was treated as free-molecule heat transfer from an isolated spherical particle. If particles are partially embedded in the solid matrix, then this approach is not valid and the heat transfer to the gas would be much smaller.

The heat generation rate predicted for a catalyst particle is rather large, and when distributed over a reactor of industrial size, even at 1% metal loading, would consume considerable power. One approach to minimizing

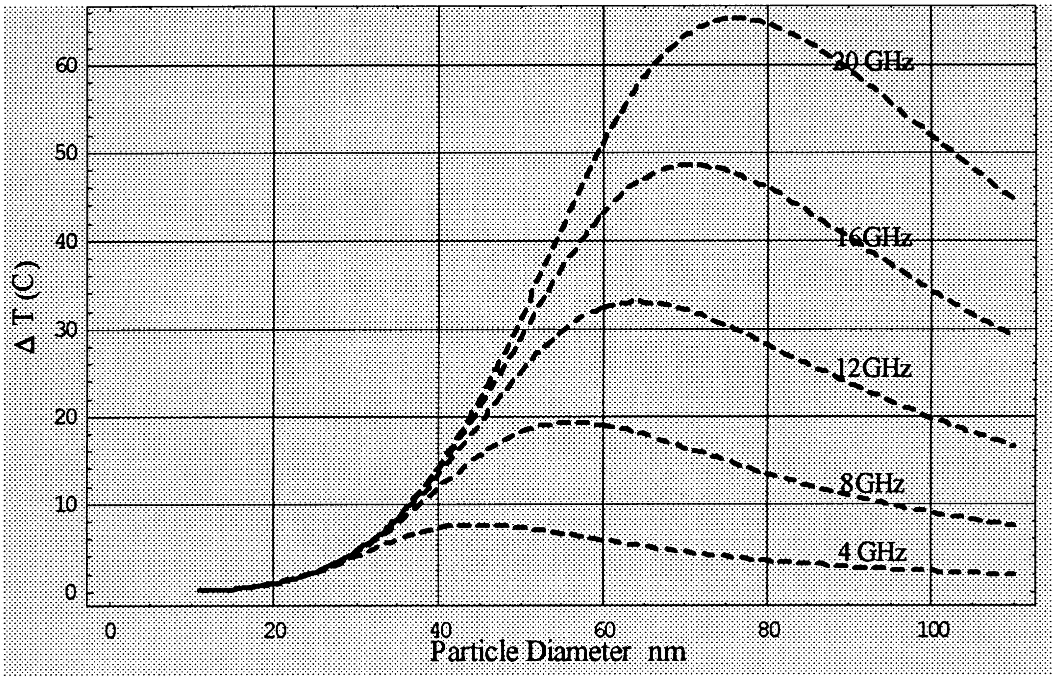

Figure 4. Effect of particle size and microwave frequency on temperature rise.

this would be to operate the system in a pulsed manner as described by Wan in ref. [2]. A more detailed model, to compute the temperatures of the catalyst bed and the gas as well as the particle, is in progress. In addition, a novel experimental technique for the measurement of catalyst particle temperatures is under development.

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